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STRUCTURAL DETERMINATIONS OF SOME TRANSITION METAL HYDRIDO, AND *TRIS*(BENZENE-1,2-DITHIOLATO) COMPLEXES

by

© MARTIN COWIE

A THESIS

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EDMONTON, ALBERTA

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled STRUCTURAL DETERMINATIONS OF SOME TRANSITION METAL HYDRIDO, AND *TRIS*(BENZENE-1,2-DITHIOLATO) COMPLEXES submitted by MARTIN COWIE in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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TO MY PARENTS

ABSTRACT

The crystal and molecular structures of $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ have been determined. The central Re_2Si_2 clusters are similar in both molecules and form a rhombus with a Re-Re bond across the shorter diagonal. The Re-Si bond lengths in both compounds are all similar, and are therefore consistent with the hydrogen ligands being terminally bound to the rhenium atoms rather than bridging the rhenium-silicon bonds. The mode of bonding of the hydride ligands is discussed in relation to other similar systems.

The crystal and molecular structures of three *tris* (benzene-1,2-dithiolato) complexes, $Mo(S_2C_6H_4)_3$, $[As(C_6H_5)_4][Nb(S_2C_6H_4)_3]$ and $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$ have been determined in an attempt to explain the stability of the trigonal prism with respect to the octahedron. In the molybdenum and niobium complexes the metals are surrounded by six sulfur atoms in trigonal prismatic coordination. The zirconium complex, however, has a coordination which is best described as a distorted octahedron. The increase in S-C distances, observed through this series, indicates an increasing tendency of the ligands towards the reduced $S_2C_6H_4^{2-}$ formulation. This ten-

dency is discussed in relation to a molecular orbital scheme for trigonal prismatic dithiolenes (by Gray *et. al.*) and is correlated to the destabilization of the prism which is observed progressing through this series.

A disorder in $Re_2(CO)_8[Si(C_6H_5)_2]_2$, involving a small translation of the complete molecule along the crystallographic *b* axis, was investigated in order to ascertain the effect on molecular geometry and thermal parameters.

PREFACE

This thesis presents the results of two independent problems. The first section deals with a structural study of a particular class of transition metal hydrides. The second section is concerned with the structures of transition metal complexes of ligands coordinated through sulfur atoms. The same techniqu , namely single crystal -ray diffraction, was used for both problems. The theoretical and experimental details of X-ray diffraction are described in several standard reference texts.[1,2,3,4]

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CHAPTER I: TRANSITION METAL HYDRIDE

INTRODUCTION

The discovery of the first transition metal hydride complexes,[5,6] $FeH_2(CO)_4$ and $CoH(CO)_4$, in the 1930's marked the beginning of approximately twenty years of controversy concerning the structures of hydride complexes and the mode of bonding of the hydrogen atoms in these complexes.

The first electron diffraction study[7] on gaseous $CoH(CO)_4$ and $FeH_2(CO)_4$ led to the conclusion that the metals were surrounded tetrahedrally by the carbonyl groups. The hydrogen atoms were assumed to be bound to the oxygen atoms of the carbonyl groups. Hieber later suggested[8] that the hydrogens were actually bonded to the metals, but were buried in the electron density of the metal and thus had no stereochemical influence.

The infrared spectrum of $CoH(CO)_4$ was initially interpreted[9] as being consistent with the hydrogen atom being primarily bonded to the carbon p_π orbitals at approximately 2.0 Å from the cobalt atom. In this model the hydrogen was believed to be bridging three carbonyl groups. However the findings of Cotton and Wilkinson,[10] based on nuclear magnetic

resonance and acid dissociation constants for $CoH(CO)_4$ and $FeH_2(CO)_4$, agreed with Hieber,[8] suggesting that the hydrogens were close to and primarily bonded to the metal atoms. Subsequent L.C.A.O. calculations[11] on $CoH(CO)_4$ yielded the greatest total overlap integral of Co-H and C-H for a Co-H distance of 1.2 Å. This distance was again consistent with the hydrogen being buried in the Co orbitals, since a covalent distance of 1.593 Å had been obtained[12] in CoH.

Since $HMn(CO)_5$ had physical properties[13] similar to $Fe(CO)_5$, its infrared spectrum was interpreted assuming it, like $Fe(CO)_5$, had trigonal bipyramidal coordination,[14,15] with the hydrogen buried in the manganese orbitals and exerting no stereochemical influence. In addition the identification[16] of the Co-H stretching frequency at 1934 cm^{-1} added further proof that the hydrogen was bound to the metal. The large shifts to high field of the proton resonance that were observed in transition metal hydrides were also initially interpreted as evidence for "buried" hydrogens. However subsequent studies[17,18] showed that these shifts were due to more subtle electronic effects and could be explained assuming normal metal-hydrogen covalent distances.

In addition it was shown[19] that the neglect of quadrupole effects which resulted[20,21] in short M-H distances, was not justified.

Thus until 1959 the experimental evidence was interpreted as indicating that the hydrogen atom exerted no stereochemical influence and was buried in the transition metal orbitals.

Discovery of the true coordination in the metal hydride complexes had to await the availability of good quality X-ray and neutron diffraction data and also the discovery of stable crystals of these hydrides [$CoH(CO)_4$ and $FeH_2(CO)_4$ were unstable gases]. In X-ray diffraction studies, since the X-rays are scattered by electrons, hydrogen atoms contribute little to the total scattering. Therefore location of the hydrogen atom requires extremely high quality data, and the difficulty of direct observation of hydrogen atoms increases with increasing atomic number of the atoms present. However, even when the hydrogen atom is not located, its approximate position can be deduced from the coordination of the other ligands. In neutron diffraction the scattering of thermal neutrons is by the nucleus and varies[22] approximately as $A^{1/3}$ (where A is the atomic mass number). Thus the scattering amplitudes

of all atoms are of the same order of magnitude, allowing the hydrogen atoms to be located with a precision comparable to that of heavier atoms.

The X-ray structural determinations[23,24] of $PtHBr[P(C_2H_5)_3]_2$ and $OsHBr(CO)[P(C_6H_5)_3]_3$ and later[25] of α-$HMn(CO)_5$ failed to locate the hydrogen atoms but showed the empty coordination sites where the hydrogens were probably located. In the X-ray crystallographic study[26] of $RhH(CO)[P(C_6H_5)_3]_3$, however, the hydrogen atom *was* located, at 1.72(15) Å from the rhodium atom, a distance consistent with the sum of the rhodium and hydrogen covalent radii.[27] (The reliability of this hydrogen identification has recently been challenged.[28] However the original paper[26] clearly outlined the conditions that would favour the direct observation of hydrogen atoms in heavy atom structures and provided the impetus for crystallographers to attempt hydrogen atom location.)

Neutron diffraction experiments[29,30] on K_2ReH_9 and also β-$HMn(CO)_5$ proved unequivocally that the hydrogens acted as typical ligands and were not buried in the metal orbitals. The Re-H distances average 1.68(1) Å and the Mn-H distance is 1.601(16) Å in these compounds.

It was a fortunate sequence of events that the molecular structure[31] of $RhH[P(C_6H_5)_3]_4$ was not determined prior to those mentioned above. Otherwise the hypothesis that the hydrogen was buried in the metal orbitals might have had a longer lifetime. In this compound the phosphorus atoms form, within experimental error, a regular tetrahedron about the Rh atom. Although it seems that the hydrogen is exerting no stereochemical influence, its influence is just minimized by the bulky $P(C_6H_5)_3$ groups. Comparing for example the volume[32,33,34] of a $P(C_6H_5)_3$ group at ~ 370 $\mathring{A}^3$ to that of CO (~ 45 $\mathring{A}^3$)[35] and H (~ 7 $\mathring{A}^3$)[36] it becomes obvious that this distortion is reasonable.

Of the many subsequent transition metal hydride complexes to be studied[35,37,38] some of the most interesting involved bridging hydrogens, where the hydrogen ligands were simultaneously bonded to two atoms. Two main categories of bridging hydrogens exist, the most common being between two transition metals, and the second involving bridging between a transition metal and a non-transition metal. In the former category two types have been observed, involving either a bent or a linear M-H-M bond.

A linear M-H-M bond[39,40] was deduced in the

structure of $Cr_2H(CO)_{10}^-$. Although the hydrogen atom position was not located, stereochemical and bonding arguments suggest that it is collinear with the two chromium atoms and equidistant from each. [It is to be noted, however, that the X-ray data cannot differentiate between two possibilities: either the hydrogen is bonded symmetrically to both chromium atoms (single-minimum potential well), or it is preferentially bonded to one chromium atom (double-minimum potential well) and is "tunnelling" between the two sites.] The observed Cr···Cr distance of 3.41(1) Å is considerably longer than the Cr-Cr bond length[39] of 2.97(1) Å in $Cr_2(CO)_{10}^{2-}$ and yields a Cr-H distance of 1.70 Å which is in good agreement with the other known metal-hydrogen distances. The hydrogen ligand then occupies the sixth coordination site of each $Cr(CO)_5$ fragment giving the anion D_{4h} symmetry. The insertion of the hydrogen ligand causing the two $Cr(CO)_5$ moieties to be further apart also results in the carbonyl groups being eclipsed, compared with the staggered carbonyls in $Cr_2(CO)_{10}^{2-}$. More recently a linear Re-H-Cr bond has also been inferred[41] in $(OC)_5ReHCr(CO)_5$. Although the hydrogen was not located it was considered to be collinear with the Re and Cr atoms, since again the two metal-

pentacarbonyl groups are eclipsed and since the least squares planes containing the equatorial CO groups are within 2.5° of being parallel. The Re-Cr distance is 3.435(1) Å, which is again consistent with hydrogen insertion between the two metals.

Bent M-H-M bonds have been deduced in several complexes. In $Re_3H(CO)_{12}^{2-}$ and $Re_3H_2(CO)_{12}^{-}$ the triangular species[42,43] contain an isosceles triangle of rhenium atoms with Re-Re distances of ~ 3.04 Å and 3.17 Å, with the longer distances presumably being bridged by the hydrogen ligands. These bent hydrogen bridges were confirmed recently[44] in the analogous $H_3Mn_3(CO)_{12}$ complex, in which the hydrogen atoms were located. The manganese atoms form an equilateral triangle with the hydrogen ligands symmetrically bridging the triangle edges. The average Mn-Mn distance is 3.111 Å compared with 2.923 Å in $Mn_2(CO)_{10}$[45] and thus again shows the lengthening of the bridged metal-metal bond, a feature which has been used as evidence for hydrogen bridging in ~~ne~~ rhenium clusters.[42,43] The average Mn-H distance is 1.72 Å.

In $Re_2MnH(CO)_{14}$[46,47] and $Re_3H(CO)_{14}$[48] the hydrogen ligands are located between the rhenium atoms in a position which is almost collinear with

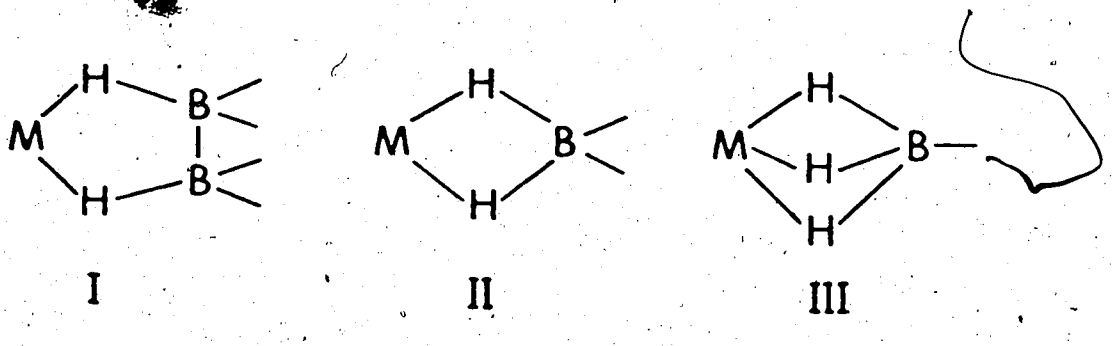
these atoms. However the estimated Re-H-Re angles, calculated assuming octahedral coordinations, are 164° in $Re_2MnH(CO)_{14}$ and 159° in $Re_3H(CO)_{14}$.

The structure[49] of $Mo_2H(CO)_4(\pi\text{-}C_5H_5)_2[P(CH_3)_2]$ consists of two $(\pi\text{-}C_5H_5)Mo(CO)_2$ fragments joined at the Mo atoms by a symmetrically bridged $P(CH_3)_2$ group and presumably by a hydrogen atom. The structure[50] of $Mn_2H(CO)_8[P(C_6H_5)_2]$ closely resembles that of $Mo_2H(CO)_4(\pi\text{-}C_5H_5)_2[P(CH_3)_2]$ with two carbonyl groups on each metal replacing a $(\pi\text{-}C_5H_5)$ group. However, in the manganese compound the hydrogen atom *was* located, in the position equivalent to that postulated in the molybdenum complex, with a Mn-H distance of 1.86(6) Å and a Mn-H-Mn angle of 104(5)°.

Hydrogen bridging three metal atoms has been postulated in $Ru_6H_2(CO)_{18}$[51] and $Rh_3H(\pi\text{-}C_5H_5)_4$.[52,53] The ruthenium structure consists of an octahedron of Ru atoms each bound to three terminal carbonyl groups. The hydrogen ligands appear to occupy two opposite faces of the octahedron. In $Rh_3H(\pi\text{-}C_5H_5)_4$ the equilateral triangle of Rh atoms has one cyclopentadienyl ring bonded to each Rh with the fourth ring parallel to the rhodium triangle. The hydrogen ligand is then postulated as being equidistant from each Rh on the opposite side of the triangle from

the fourth C_5H_5 group.

Hydrogen bridging between a transition metal and a non-transition metal has been observed in boron complexes with the hydrogen bridging the boron and the transition metal. Three basic types exist:



Structures of type I were observed in $Mn_3H(BH_3)_2(CO)_{10}$,[54] $Cu(B_3H_8)[P(C_6H_5)_3]_2$[55] and $Cr(B_3H_8)(CO)_4^-$.[56,57,58] In the manganese compound all hydrogen atoms of the BH_3 group are coordinated to a Mn atom and in addition a bent Mn-H-Mn bond exists between the two $Mn(CO)_3$ moeities. In $Cu(B_3H_8)[P(C_6H_5)_3]_2$ the coordination of the copper atom is a distorted tetrahedron with two of the coordination sites occupied by bridging hydrogens. The P-Cu-P and H-Cu-H angles of 120° and 103° respectively, reflect this distortion. $Cr(B_3H_8)(CO)_4^-$ has an octahedrally hybridized chromium atom with two sites again being occupied by bridging hydrogens.

Coordination of type I is exhibited[59,60] by $Cu(BH_4)[P(C_6H_5)_3]_2$. The copper geometry again is distorted tetrahedral with two hydrogen atoms of the borohydride group bridging the copper and boron atoms. The short Cu-B distance of 2.184(9) Å and long Cu-H distance of 2.02(5) Å suggests delocalized bonding between the copper atom and the borohydride group in which direct Cu-B overlap might be significant.

In $Zr(BH_4)_4$[61] the molecule is crystallographically required to possess T_d symmetry. The zirconium atom is tetrahedrally surrounded by the four boron atoms, and one terminal hydrogen atom is located on each C_3 axis. So it appears that M-H-B bonding of type III is present with the Zr atom surrounded by twelve H atoms.

The reactions of disubstituted silanes with dirhenium decacarbonyl and with both tungsten and molybdenum hexacarbonyls produced an interesting series of silicon-bridged, metal-metal bonded species which were also postulated as containing hydrogen-bridged metal-silicon bonds.[62,63] Since this was only the second class of compounds in which hydrogen was postulated as bridging a transition metal-non-transition metal bond, a systematic study of the representative molecules from this series was therefore

undertaken to elucidate the major structural characteristics of the systems.

Viewing only the central cluster and ignoring the carbonyl groups, the molecules fall into five major classes:

I. no hydrogen ligands,[64] e.g. $Re_2(CO)_8[Si(C_6H_5)_2]_2$,

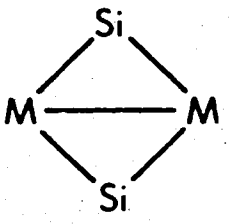
II. two hydrogens, each on different transition metals but adjacent to the same silicon atom[62,65] e.g. $Re_2(CO)_8H_2Si(C_6H_5)_2$,

III. two hydrogens, each on different transition metals and adjacent to two different silicon atoms,[66] e.g. $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$,

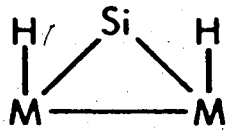
IV. two hydrogens, both on the same transition metal but adjacent to different silicons, e.g. $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, and

V. four hydrogens, two attached to each transition metal, each silicon having two adjacent hydrogens, e.g. $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$.

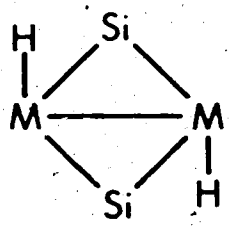
The structural fragments are shown in Fig. 1 using valence bond description and normal terminal transition metal hydride formulation, with the exceptions of III(b) where bridging hydrogens are indicated and III(c) where the terminal hydrogens interact weakly with the silicon atoms. The main interest in this series centred around the central cluster of transition



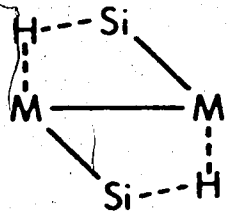
I



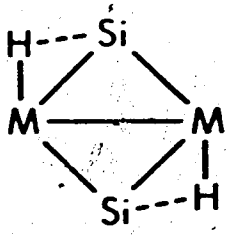
II



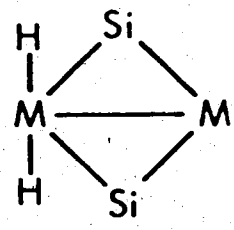
III(a)



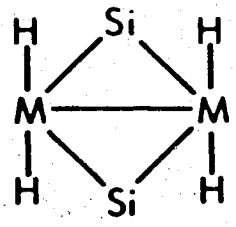
III(b)



III(c)



IV



V

Fig. 1: CENTRAL FRAMEWORKS OF THE SILICON-BRIDGED TRANSITION METAL SERIES.

metal and silicon atoms, especially when hydrogen ligands were present, to obtain information concerning the nature of the bonding of the hydrogen ligands.

It had been suggested on the basis of spectroscopic evidence that in these compounds the hydrogen ligands bridged the metal-silicon bonds rather than being bonded terminally to the metals.[62,63] The basis of this argument was the spectroscopic studies by Kaesz and coworkers[67,68] on the trimeric rhenium hydride $[HRe(CO)_4]_3$ and its deuteride $[DRe(CO)_4]_3$, in which the absence of a distinct metal-hydrogen stretching frequency in the infrared was interpreted as evidence that the hydrogens were bridging. Since the terminal metal-hydrogen stretch should be visible in the infrared, its silence was postulated as a characteristic feature of M-H-M bridges. This was extended to the series of transition metal silicon hydrides where the metal-hydrogen stretch was again absent in the infrared,[63] and consequently a Si-H-M bridge was postulated. In addition, in $Re_2(CO)_8H_2Si(CH_3)_2$, the methyl resonance appeared as a 1:2:1 triplet at $\tau = 8.87$ with a coupling constant $J = 1.5$ Hz.[63] The magnitude of this coupling constant also suggested that the high field protons, which are splitting the methyl resonance, were close to the dimethylsilicon moiety since $J(CH_3\text{-}Si\text{-}H) = 4.2$ Hz for dimethyl-

silane alone.

The first member of this series to have its molecular structure solved by X-ray techniques was $Re_2(CO)_8H_2Si(C_6H_5)_2$.[62,65] Unfortunately, due to the dominance of the rhenium scattering, location of the hydrogen ligands was not possible. However, the coordination sites adjacent to the metal-silicon bonds were conspicuously vacant so the approximate locations of the hydrogens were apparent. Elder postulated[65] that the hydrogens were located in the Re_2Si plane such that the Re-Re-H angle was 90°. Thus for a rhenium-hydrogen bond length[29] of 1.68 Å, a silicon-hydrogen bond length of 1.59 Å would result. This position he said would give the proper orientation for a three centre Si-H-Re bond.

However, the subsequent structure determination of the non-hydridic species $Re_2(CO)_8[Si(C_6H_5)_2]_2$[64] showed a remarkable similarity in Re-Si bond lengths [2.542(3) Å] with $Re_2(CO)_8H_2Si(C_6H_5)_2$, [2.544(9) Å], which was not expected if a three centre two electron Si-H-Re bond is involved in the latter. An unambiguous comparison of the two structures was hindered, however, by the realization that a disorder problem was present in $Re_2(CO)_8[Si(C_6H_5)_2]_2$ (see Appendix 1). Although it was not believed that this

would affect the bond lengths in the central Re_2Si_2 cluster, it did cast some doubt on accurate comparisons of the two compounds.

Further evidence favouring the three centre Si-H-M bond arose from the structural determination of $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$,[66] [type III(b) in Fig. 1] in which two differing tungsten-silicon bonds were found [2.586(5) Å and 2.703(4) Å]. This was interpreted as being due to hydrogen insertion in the tungsten-silicon bond, thus forming a three centre W-H-Si bond. Therefore the crystal and molecular structure determinations of members IV and V ($Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ and $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$) were undertaken to obtain further information concerning the bonding of the hydrogen ligand in this series. These structure determinations are described in Chapters II and III.

CHAPTER II: THE CRYSTAL AND MOLECULAR STRUCTURE OF DIHYDRIDO TRICARBONYL RHENIUM *BIS* (μ-DIETHYLSILICON) DIHYDRIDO TRICARBONYL RHENIUM, $[Re_2(CO)_6H_4(Si(C_2H_5)_2)_2]$.

EXPERIMENTAL

The sample of $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ which was kindly supplied by Dr. Graham and Mr. Hoyano[63] was recrystallized from normal hexane, yielding colourless crystals with the shape of a general parallelepiped. Preliminary photography indicated only Laué symmetry $\bar{1}$ indicative of a triclinic space group. The systematic absences for the working cell, as determined by Weissenberg (0kℓ, 1kℓ, 2kℓ: CuK_α X-radiation), and Precession methods (h0ℓ, h1ℓ, h2ℓ, hk0, hk1, Hk2: MoK_α X-radiation), are hkℓ: $h + k = 2n + 1$, $h + \ell = 2n + 1$, $k + \ell = 2n + 1$, and are consistent with the non-standard space groups F1 and $F\bar{1}$. The non-standard cell was retained as the working cell for its convenience with respect to the crystal morphology and unit cell angles. Precise lattice parameters were obtained at 23°C from an analysis of the setting angles for 18 reflections which had been carefully centred on a Picker manual four circle diffractometer using CuK_{α_1} radiation of wavelength 1.54051 Å.

A Delaunay reduction was performed[69] and failed to show the presence of higher symmetry. The F centred cell parameters are : a = 8.357(3) Å, b = 16.228(6) Å, c = 18.184(6) Å, α = 118.98(2)°, β = 92.62(3)° and γ = 95.44(3)°, and the reduced primitive cell parameters are: a = 8.357(3) Å, b = 8.767(3) Å, c = 8.776(3) Å, α = 109.07(3)°, β = 97.76(3)°, and γ = 112.88(3)°. The reduced primitive cell is related to the F centred cell by: $\underset{\sim}{a}_P = -\underset{\sim}{a}_F$, $\underset{\sim}{b}_P = 1/2(\underset{\sim}{b}_F + \underset{\sim}{a}_F)$, $\underset{\sim}{c}_P = -1/2(\underset{\sim}{b}_F + \underset{\sim}{c}_F)$. The observed density [2.23(2) g cm^{-3}] obtained by floatation in aqueous Clerici's solution (Thallous formate-malonate, ρ_{max} = 4.3 g ml^{-1}), is in satisfactory agreement with that calculated on the basis of four molecules in the F centred cell (2.25 g cm^{-3}). For space group $F\bar{1}$ the imposed symmetry on the molecule is $\bar{1}$, while no restrictions are possible for space group F 1. Since $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ can have $\bar{1}$ symmetry, $F\bar{1}$ was chosen and was later verified by successful refinement of the model. The General Equivalent Positions for the space group $F\bar{1}$ are : $\pm$(x, y, z; 1/2 + x, 1/2 + y, z; 1/2 + x, y, 1/2 + z; x, 1/2 + y, 1/2 + z).

Intensity data were collected on the Picker manual diffractometer using CuK_α radiation monochromated by the (002) reflecting plane of an oriented graphite

crystal using a take-off angle of 2°. Two crystals were used during data collection and in each case they were aligned with their a* axis coincident with the ϕ axis of the diffractometer. The crystal faces were identified and the perpendicular distances between parallel faces of the same form were measured as: crystal 1 - {1,0,0}, 0.095 mm; {0,1,0}, 0.065 mm; {0,$\bar{1}$,1}, 0.084 mm; and crystal 2 - {1,0,0}, 0.077 mm; {0,0,1}, 0.065 mm; and {0,$\bar{1}$,1}, 0.036 mm. Data were collected for reflections with 2θ values between 0° and 125° using the coupled $\omega/2\theta$ scanning technique with a 2θ scan speed of 2°/min and scan width of three degrees (to allow for increase in mosaic spread as crystal decomposition occurred). Stationary background counts were measured at the limits of each scan for 20 seconds. Assuming approximate linearity of background, the intensity of the peak (I) is given by:

$$I = P - t(B_1 + B_2) \qquad (1)$$

where P = peak count, $t = t_p/t_B$ or the ratio of peak scan time to the sum of the background times, and B_1 and B_2 are the background counts. Standard deviations of the intensities were computed from the relationship:

$$\sigma(I) = (P + t^2B + p^2I^2)^{1/2} \qquad (2)$$

where $B = B_1 + B_2$. An ignorance factor (p) of 0.03 was used to account for machine errors and to prevent unreasonably high weighting being applied to reflections of high intensity.[70] The detector was a scintillation counter and was used in conjunction with a pulse height analyzer which was tuned to accept 95% of the CuK_α peak.

Eight well distributed standard reflections were monitored at approximately 10 hour intervals to investigate possible decomposition. The decomposition was found to be approximately linear with time and was essentially free of $\sin\theta/\lambda$ dependence. The total decomposition for the data collection was about 10%. The 1690 unique reflections collected were reduced to 1510 using the criterion that a peak is significantly above background when $I/\sigma(I) \geq 3.0$. The significant data were reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. Standard deviations in the structure factors, $\sigma(F)$, were obtained from the expression:[71]

$$\sigma(F) = \frac{1}{2}\sqrt{\frac{D}{ALp'}} \cdot \frac{\sigma(I)}{I^{1/2}} \qquad (3)$$

where D, A, L, and p' are the decomposition, absorption,[72] Lorentz, and polarization correction factors res-

pectively. The high linear absorption coefficient[86] for $Re_2(CO)_6H_6[Si(C_2H_5)_2]_2$ using CuK_α X-radiation (226.07 cm^{-1}) gave rise to a wide range of transmission factors (0.138 to 0.382) which made an absorption correction imperative. The absorption correction was verified by observation of the variation in I_{h00} ($\chi = 90°$) as ϕ was varied. The final corrected intensities of this ϕ scan data showed variation from the mean of less than 10% and thus were judged to be internally consistent.

STRUCTURE SOLUTION AND REFINEMENT

A Patterson map[73,74] was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, and $0 \leq w \leq 0.5$. The Re-Re, Re-Si, and Si-Si vectors are derived for space group $P\bar{1}$ in Table 1. The vectors for space group $F\bar{1}$ are generated by adding (0,0,0), (1/2,1/2,0), (1/2,0,1/2) and (0,1/2,1/2) to those derived for $P\bar{1}$. In addition all vector multiplicities increase by a factor of 4. The origin peak is due to the sum of the vectors between every atom and itself, thus the magnitude of the origin vector is roughly given by: $(2 \times 75^2 + 2 \times 14^2 + 6 \times 8^2 + 14 \times 6^2 + 24 \times 1^2) = 12554$. In the Fourier

program used to calculate the vector map, however, the origin peak is normalized to 1000. Therefore taking account of the largest negative peak (~ -40), and assuming the temperature factors are comparable, one expects the Re-Re vectors to have approximate magnitude 466, the Re-Si vectors ~ 174 and the Si-Si vectors 17 above background. Viewing the Patterson map (summarized in Table 2) it is obvious that the first two vectors correspond to Re-Re vectors. On inspection of the map the first vector is identified as associated with the 0, 1/2, 1/2 origin therefore is attributed as $(2x_R, 1/2 + 2y_R, 1/2 + 2z_R)$. The coordinates of the rhenium atom are then calculated as (0.120, -0.010, -0.061). The second peak then corresponds to the edge of the vector (1/2,1/2,0) - $(2x_R, 2y_R, 2z_R)$.

The next most intense peak, having a magnitude approximately comparable to that expected for a Re-Si vector, was situated at approximately 2.44 Å from the origin (a distance which is similar to the Re-Si distance in $Re_2(CO)_8H_2Si(C_6H_5)_2$[62,65]). For this reason it was chosen as the $(x_R - x_S, y_R - y_S, z_R - z_S)$ vector and from this the silicon coordinates were calculated as (-0.08, -0.13, -0.61). The next two vectors were then identified as (1/2,1/2,0) - $(x_R - x_S,$

TABLE 1: DERIVATION OF Re-Re, Re-Si, AND Si-Si VECTORS FOR SPACE GROUP $P\bar{1}$

	x_R, y_R, z_R [a]	$-x_R, -y_R, -z_R$	x_S, y_S, z_S	$-x_S, -y_S, -z_S$
x_R, y_R, z_R	0, 0, 0	$-2x_R, -2y_R, -2z_R$	$-(x_R - x_S)$, $-(y_R - y_S)$, $-(z_R - z_S)$	$-(x_R + x_S)$, $-(y_R + y_S)$, $-(z_R + z_S)$
$-x_R, -y_R, -z_R$	$2x_R, 2y_R, 2z_R$	0, 0, 0	$x_R + x_S$, $y_R + y_S$, $z_R + z_S$	$x_R - x_S$, $y_R - y_S$, $z_R - z_S$
x_S, y_S, z_S	$x_R - x_S$, $y_R - y_S$, $z_R - z_S$	$-(x_R + x_S)$, $-(y_R + y_S)$, $-(z_R + z_S)$	0, 0, 0	$-2x_S, -2y_S, -2z_S$
$-x_S, -y_S, -z_S$	$x_R + x_S$, $y_R + y_S$, $z_R + z_S$	$-(x_R - x_S)$, $-(y_R - y_S)$, $-(z_R - z_S)$	$2x_S, 2y_S, 2z_S$	0, 0, 0

[a] (x_R, y_R, z_R) and (x_S, y_S, z_S) are the coordinates for the rhenium and silicon atoms respectively.

TABLE 2: ASSIGNMENT OF MOST INTENSE PATTERSON VECTORS

u	v	w	RELATIVE PEAK HEIGHT	ASSIGNMENT
0.240	0.480	0.378	487	$(0,1/2,1/2) + (2x_R, 2y_R, 2z_R)$
0.240	-0.500	0.126	370	$(1/2,1/2,0) - (2x_R, 2y_R, 2z_R)$ [b]
0.200	0.120	0.0	131	$(x_R-x_S, y_R-y_S, z_R-z_S)$
0.280	0.380	0.0	123	$(1/2,1/2,0) - (x_R-x_S, y_R-y_S, z_R-z_S)$
0.040	0.360	0.360	119	$(0,1/2,1/2) + (x_R+x_S, y_R+y_S, z_R+z_S)$
0.240	0.040	0.396	98	Re-C and Re-O vector build-up.
0.480	0.460	0.234	91	
0.0	0.140	0.126	90	$-(x_R+x_S, y_R+y_S, z_R+z_S)$ [b]

[b] shoulder of the peak.

$y_R - y_S$, $z_R - z_S$) and (0,1/2,1/2) + ($x_R + x_S$, $y_R + y_S$, $z_R + z_S$). Image seeking around the Re-Re vectors then identified three of the next four vectors as being due to build-ups of Re-C and Re-O vectors from the molecules at (1/2,1/2,0) and (0,1/2,1/2). The peak observed at (0.00, 0.140, 0.126) was identified as the edge of the vector - ($x_R + x_S$, $y_R + y_S$, $z_R + z_S$).

At this point it was obvious that the Re_2Si_2 core had an inversion centre or at least was very close to having one, otherwise a more complex vector pattern would have been expected corresponding to independent Re(1), Re(2), Si(1), and Si(2) positions.

A least squares refinement phased on the rhenium and silicon positions converged in two cycles yielding a discrepancy index, $R_1 = 0.132$, and a weighted residual, $R_2 = 0.186$. These "R factors" as calculated in the least squares program are defined as:

$$R_1 = \sum \left| |F_o| - |F_c| \right| / \sum |F_o| \qquad (4)$$

$$R_2 = \left\{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \right\}^{1/2} \qquad (5)$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes respectively, and w the weighting factor is defined by $w = 1/\sigma^2(F)$.

Structure factors were calculated using the atomic scattering factors [75] for rhenium and silicon atoms to which the anomalous dispersion corrections,[76] both real and imaginary were applied [77] ($^{\Delta}f'_{Re} = -5.58$, $^{\Delta}f''_{Re} = 5.37$, $^{\Delta}f'_{Si} = 0.23$, $^{\Delta}f''_{Si} = 0.36$). The function which was minimized during the least squares refinement was $\Sigma w(|F_o| - |F_c|)^2$.

An electron density difference map, phased on the rhenium and silicon atom positions, yielded the location of all other non-hydrogen atoms. A least squares calculation performed on all non-hydrogen atoms converged in two cycles to $R_1 = 0.061$ and $R_2 = 0.074$. Decomposition and absorption corrections were applied to the data and one further cycle of refinement gave $R_1 = 0.055$ and $R_2 = 0.073$. Comparison of $|F_o|$ and $|F_c|$ showed no indication of extinction problems so no correction was applied. This was reasonable considering the width of the peaks ($\sim 2°$) indicating high mosaicy of the crystals.

Refinement of the model with rhenium and silicon atoms having anisotropic temperature factors gave $R_1 = 0.039$ and $R_2 = 0.053$ after two cycles. An electron density difference map phased on this model showed features in the regions of the other atoms which suggested that they too be given anisotropic temperature

factors. This gave $R_1 = 0.034$ and $R_2 = 0.045$ after a further two cycles of refinement. The form of the temperature factors used was:

$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)\right].$$

The validity of the anisotropic refinement was verified by a Hamilton's R test[79] at the 0.005 significance level.

An electron density difference map was calculated in an attempt to locate the hydrogen atoms in the structure, especially those attached to the rhenium atoms. It was encouraging that the highest peaks in the electron density difference map (1.75 - 1.14 e Å^{-3}) were located in the space between the rhenium and silicon atoms in the approximate position expected for a hydrogen bound to rhenium. For this reason the method of La Placa and Ibers[33] was used in an attempt to discern whether these peaks were hydrogen atoms or just artifacts arising from the improper treatment of the rhenium scattering or vibrations. Ibers reasoned that if the peak is not due to hydrogen scattering, then as the number of terms in the Fourier series is varied, the peak should disappear or shift markedly. A peak due to a hydrogen atom, however, should remain approximately in the same position and the peak height would be expected to vary in accordance

with the equation

$$\rho_H = \frac{1}{2\pi^2} \int_0^{s_o} (1 + a^2 s^2/4)^{-2} \exp(-Bs^2/16\pi^2) s^2 ds \quad (6)$$

where ρ_H is the electron density of the hydrogen atom, a is the Bohr radius = 0.5292 Å, $s = 4\pi\lambda^{-1}\sin\vartheta$, and B is the hydrogen temperature factor. Using a temperature factor of 3.6, electron density difference maps were calculated for sin θ/λ cut-offs of 0.2, 0.25, 0.3, 0.35, 0.4, 0.58 (Complete Data). The results are summarized in Table 3.

TABLE 3: OBSERVED AND CALCULATED ELECTRON DENSITIES FOR VARYING SIN θ/λ CUT-OFFS

SIN θ/λ LIMIT	NUMBER OF TERMS	$\rho_{CAL.}$ ($e\text{Å}^{-3}$)	$\rho_{OBS.}$ ($e\text{Å}^{-3}$)
0.20	74	0.16	0.49 - 0.42
0.25	143	0.25	0.78 - 0.6
0.30	243	0.33	1.07 - 0.87
0.35	371	0.41	1.25 - 0.97
0.40	556	0.47	1.44 - 1.02
0.58 (Complete Data)	1509	0.63	1.75 - 1.14

The electron density observed is in all cases much greater than that calculated by Ibers' formula. A representation of the electron density difference

factors. This gave $R_1 = 0.034$ and $R_2 = 0.045$ after a further two cycles of refinement. The form of the temperature factors used was:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)].$$

The validity of the anisotropic refinement was verified by a Hamilton's R test[79] at the 0.005 significance level.

An electron density difference map was calculated in an attempt to locate the hydrogen atoms in the structure, especially those attached to the rhenium atoms. It was encouraging that the highest peaks in the electron density difference map (1.75 - 1.14 e Å^{-3}) were located in the space between the rhenium and silicon atoms in the approximate position expected for a hydrogen bound to rhenium. For this reason the method of La Placa and Ibers[33] was used in an attempt to discern whether these peaks were hydrogen atoms or just artifacts arising from the improper treatment of the rhenium scattering or vibrations. Ibers reasoned that if the peak is not due to hydrogen scattering, then as the number of terms in the Fourier series is varied, the peak should disappear or shift markedly. A peak due to a hydrogen atom, however, should remain approximately in the same position and the peak height would be expected to vary in accordance

with the equation

$$\rho_H = \frac{1}{2\pi^2} \int_0^{s_o} (1 + a^2 s^2/4)^{-2} \exp(-Bs^2/16\pi^2) s^2 ds \quad (6)$$

where ρ_H is the electron density of the hydrogen atom, a is the Bohr radius = 0.5292 Å, $s = 4\pi\lambda^{-1}\sin\vartheta$, and B is the hydrogen temperature factor. Using a temperature factor of 3.6, electron density difference maps were calculated for sin θ/λ cut-offs of 0.2, 0.25, 0.3, 0.35, 0.4, 0.58 (Complete Data). The results are summarized in Table 3.

TABLE 3: OBSERVED AND CALCULATED ELECTRON DENSITIES FOR VARYING SIN θ/λ CUT-OFFS

SIN θ/λ LIMIT	NUMBER OF TERMS	$\rho_{CAL.}$ ($e\text{Å}^{-3}$)	$\rho_{OBS.}$ ($e\text{Å}^{-3}$)
0.20	74	0.16	0.49 - 0.42
0.25	143	0.25	0.78 - 0.69
0.30	243	0.33	1.07 - 0.87
0.35	371	0.41	1.25 - 0.97
0.40	556	0.47	1.44 - 1.02
0.58 (Complete Data)	1509	0.63	1.75 - 1.14

The electron density observed is in all cases much greater than that calculated by Ibers' formula. A representation of the electron density difference

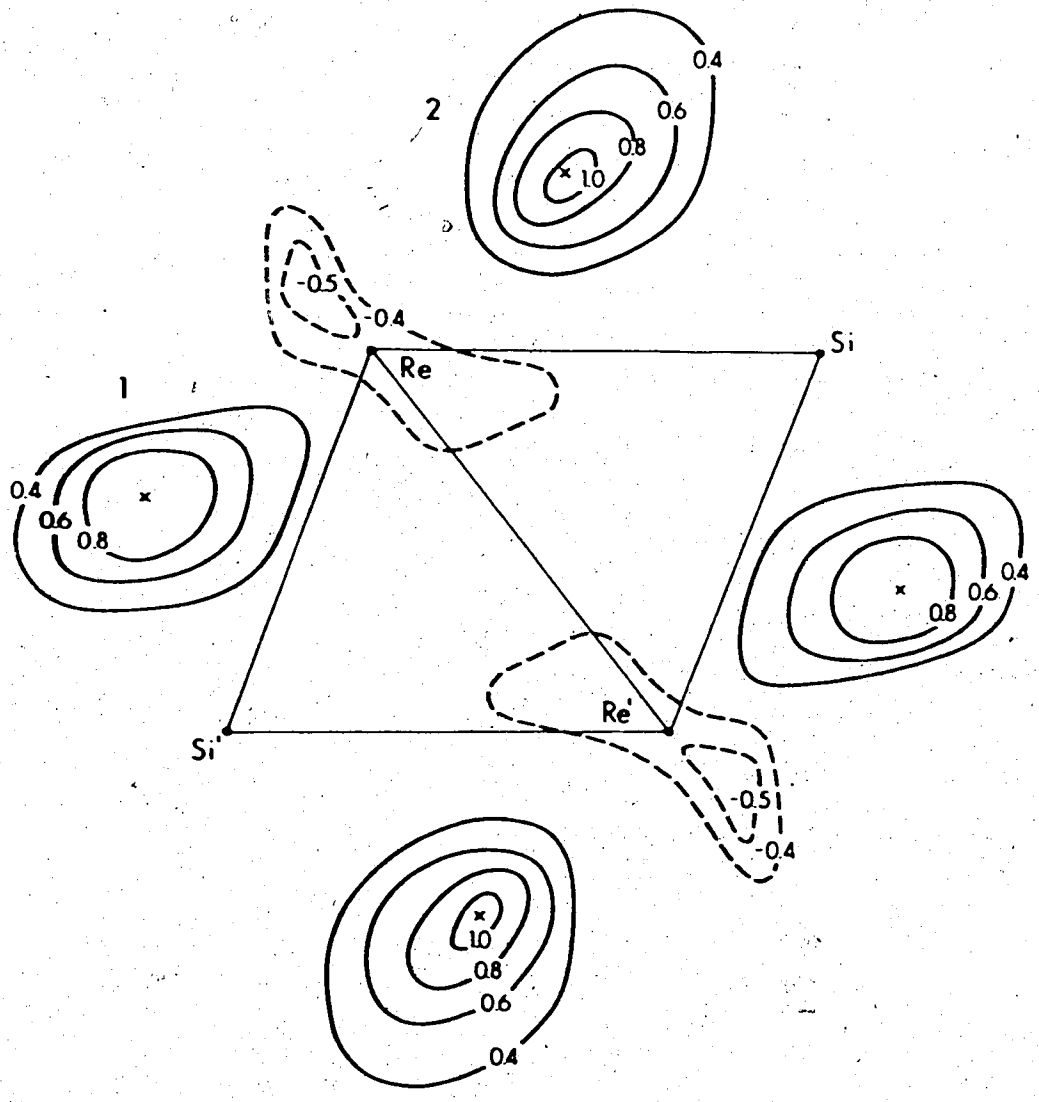


Fig. 2: ELECTRON DENSITY DIFFERENCE MAP THROUGH THE Re_2Si_2 PLANE [$(SIN\ \theta/\lambda)_{MAX} = 0.35$].

map calculated through the plane of the rhenium and silicon atoms for a sin θ/λ limit of 0.35 is shown in Figure 2. The hydrogen, which could be situated anywhere within the 0.4e Å^{-3} contour on this diagram, therefore cannot be located with certainty. This implied that the peak height, although being contributed to by the hydrogen, could be receiving a strong contribution due to the inadequacy in description of the rhenium scattering. For this reason several least squares refinements and corresponding electron density difference maps were calculated making changes of ± 0.5 e to each of the real and imaginary parts of the anomalous dispersion corrections in turn. This produced no changes in the refinements or in the difference maps. It was therefore concluded that the peaks, although possibly containing contributions due to the hydrogen atoms, are due mainly to inadequacies of the model or systematic errors in the data. Among these are inadequate description of the scattering due to the rhenium atoms and residual absorption effects. In addition, doubt concerning the degree of contribution of the hydrogen ligands to these peaks existed because of the failure to locate the methylene hydrogen atoms of the ethyl groups.

The computer programmes used in solution and

refinement of structure and presentation of Data are listed and briefly described in Appendix 2.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 4. The final fractional coordinates of all atoms except hydrogens are shown in Table 5, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic U's[80] and the equivalent isotropic B's[81] of all atoms are shown in Table 6. Relevant bond lengths and bond angles are shown in Table 7. The bond lengths and angles along with their standard deviations were obtained from ORFFE. A packing diagram for the face centred cell, viewed onto the 0kℓ plane is shown in Figure 4. The open bonds indicate molecules in the 0kℓ plane whereas solid bonds indicate molecules in the 1/2 kℓ plane.

TABLE 4: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
*** H = -*****				10	-6	1726	1780	-5	-5	3097	3806	7	1	6726	6657	-17	18	967	936
3	15	670	660	10	-2	2559	2624	-5	-3	1870	1991	7	3	1579	1527	-19	20	1315	1332
5	11	1151	1111	10	0	1572	1649	-5	1	1088	1220	7	5	788	777	-8	-12	757	870
5	13	1194	1156	10	2	276	318	-5	3	4308	4419	7	7	1838	1735	-8	-10	1243	1360
7	11	1138	1069	10	4	1658	1594	-5	5	3258	2929	7	9	1717	1672	-8	-8	732	725
7	13	1085	1118	10	6	1636	1587	-5	7	865	816	7	11	699	616	-8	-6	677	729
9	7	1165	1135	10	8	658	698	-5	9	2566	2487	9	-17	1322	1341	-8	-4	1858	1828
9	9	671	620	12	-16	1190	1253	-5	11	2706	2623	9	-15	2029	2061	-8	-2	1795	1826
9	11	1159	1195	12	-14	573	576	-5	13	1355	1366	9	-13	1395	1395	-8	0	575	559
11	3	1715	1606	12	-12	1046	988	-5	15	526	506	9	-11	565	667	-8	2	1092	1095
11	5	1439	1351	12	-10	2062	1939	-5	17	1560	1500	9	-9	2892	2872	-8	4	2642	2725
13	1	562	490	12	-8	1597	1678	-5	19	1137	1133	9	-7	2953	2946	-8	6	2290	2344
13	3	1100	998	12	-6	503	608	-3	-13	1818	1747	9	-5	677	651	-8	10	1598	1591
13	5	850	840	12	-4	1105	1070	-3	-11	1690	1617	9	-3	583	631	-8	12	2210	2085
15	-3	1376	1315	12	-2	1766	1750	-3	-7	2212	2242	9	-1	2349	2413	-8	14	1295	1230
15	-1	360	365	12	0	1086	1038	-3	-5	6397	6512	9	1	2858	2750	-8	16	327	395
15	1	360	396	12	4	816	796	-3	-3	3350	3423	9	3	665	639	-8	18	780	786
17	-5	1291	1326	12	6	1110	1149	-3	-1	616	566	9	5	899	850	-8	20	1070	1095
17	-3	1017	1015	14	-18	982	1038	-3	1	3449	3517	9	7	1289	1256	-6	-12	870	886
*** H = 0*****				14	-16	1214	1265	-3	3	5258	4857	9	9	936	942	-6	-10	1764	1781
-12	18	967	994	14	-14	618	359	-3	5	1253	1378	11	-17	878	928	-6	-8	1339	1346
-12	20	429	425	14	-12	1078	1055	-3	7	1078	1080	11	-15	1872	1877	-6	-6	728	693
-10	16	1881	1840	14	-10	1805	1750	-3	9	3026	2978	11	-13	1147	1137	-6	-4	2294	2342
-10	18	1477	1476	14	-8	1562	1463	-3	11	3178	3212	11	-9	1561	1503	-6	-2	2190	2225
-10	20	474	501	14	-6	452	395	-3	13	1085	1112	11	-7	2249	2117	-6	0	1367	1474
-8	12	829	822	14	-4	1298	1218	-3	15	1161	1189	11	-5	1338	1368	-6	2	573	648
-8	14	1676	1595	14	-2	1698	1719	-3	17	1809	1763	11	-1	1704	1683	-6	4	3986	4112
-8	16	2740	2586	14	0	926	906	-3	19	992	1030	11	1	1852	1795	-6	6	3443	3288
-8	18	1366	1363	14	4	777	820	-1	-15	1407	1382	11	3	815	718	-6	8	796	721
-6	10	2705	2562	16	-16	903	932	-1	-13	2821	2659	11	5	307	332	-6	10	1409	1375
-6	14	1782	1659	16	-12	1078	1118	-1	-11	1657	1660	11	7	950	950	-6	12	2937	2789
-6	16	2131	2002	16	-10	1862	1751	-1	-9	902	812	13	-17	1137	1150	-6	14	2020	1907
-6	18	962	909	16	-8	1070	1033	-1	-7	3556	3521	13	-15	1851	1891	-6	16	353	353
-4	6	1811	1646	16	-6	1157	1181	-1	-5	5726	5777	13	-13	1176	1250	-6	18	815	803
-4	8	3954	3857	16	-2	1224	1249	-1	-3	3190	3193	13	-9	2105	2011	-4	-14	438	269
-4	10	2529	2467	16	0	481	536	-1	-1	2206	2152	13	-7	2308	2227	-4	-12	1660	1633
-4	12	267	260	18	-14	365	328	-1	1	6243	5578	13	-5	989	940	-4	-10	2618	2344
-4	14	1393	1370	18	-12	949	1017	-1	3	4097	4268	13	-3	527	508	-4	-8	1041	1080
-4	16	2076	1959	18	-10	975	995	-1	5	1026	958	13	-1	1679	1689	-4	-6	1321	1309
-4	18	963	962	18	-8	369	403	-1	7	2231	2362	13	1	1655	1678	-4	-4	3828	3621
-2	4	1506	1456	18	-6	327	367	-1	9	3968	4123	13	3	639	657	-4	-2	3058	3398
-2	6	1799	1736	*** H = 1*****				-1	11	2428	2469	13	5	640	694	-4	0	763	825
-2	8	6109	6301	-17	7	755	611	-1	15	1389	1380	15	-17	1116	1152	-4	2	2966	3015
-2	10	2956	2673	-17	9	728	576	-1	17	1666	1671	15	-15	1572	1548	-4	4	5707	5470
-2	18	1580	1547	-17	11	1397	1226	1	-17	585	533	15	-13	693	677	-4	6	3145	2956
-2	16	1068	1985	-17	13	955	1060	1	-15	1884	1728	15	-11	799	850	-4	8	277	278
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Table 4 (continued)

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4	6	927	929
4	8	1383	1342
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6	-16	451	472
6	-14	2214	2080
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6	-10	1377	1430
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6	-4	3485	3658
6	-2	1115	1202
6	0	1736	1692
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6	10	1622	1611
6	12	891	926
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8	-18	470	470
8	-16	644	682
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8	10	1049	1100
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10	-16	672	658
10	-14	1659	1643
10	-12	1843	1881
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10	-8	744	694
10	-6	2081	2076
10	-4	1926	1916
10	-2	623	642
10	0	1222	1207
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12	4	845	878
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14	-8	1484	1411
14	-6	1636	1600
14	-4	754	788
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6	-4	1053	1051
6	-2	1956	2008
6	0	1802	1830
6	2	981	922
6	4	840	843
6	6	1957	1879
6	8	1234	1207
8	-18	1328	1200
8	-16	1547	1557
8	-14	781	830
8	-12	673	698
8	-10	2320	2312
8	-8	2670	2625
8	-6	811	852
8	-4	1176	1230
8	-2	2395	2457
8	0	1934	1940
8	2	892	864
8	4	1224	1222
8	6	1679	1700
8	8	986	1005
10	-19	1483	1506
10	-16	1575	1607
10	-12	1103	1076
10	-10	2233	2178
10	-8	2065	2029
10	-6	1909	1947
10	-2	2328	2372
10	0	1052	1053
10	8	1178	1165
10	6	1329	1356
12	-16	1196	1263
12	-14	846	877
12	-12	1116	1060
12	-10	1603	1618
12	-8	980	960
12	-6	683	678
12	-4	1619	1671
12	-2	1325	1369
12	0	655	577
12	2	291	270

Table 4 (continued)

K	L	FOBS	FCAL
***	4	*****	
14	-16	704	721
14	-12	699	675
14	-10	1189	1123
14	-8	818	817
14	-6	901	950
14	-2	1097	1112
14	-10	1108	1150
14	-8	593	676
***	5	*****	
-15	1	553	562
-15	3	1118	1078
-15	5	846	837
-15	7	355	329
-15	9	852	803
-15	11	1218	1298
-15	13	695	767
-13	-3	777	793
-13	-1	818	787
-13	1	588	667
-13	3	1092	1104
-13	5	860	790
-13	9	910	842
-13	11	1230	1294
-13	13	724	739
-11	-5	932	943
-11	-3	1110	1128
-11	-1	383	376
-11	1	1029	990
-11	3	1666	1655
-11	5	1025	997
-11	9	796	853
-11	11	1783	1797
-11	13	1033	1065
-9	-9	291	298
-9	-7	669	624
-9	-5	1643	1632
-9	-3	1882	1853
-9	1	1400	1412
-9	3	2393	2676
-9	5	1669	1646
-9	9	1662	1516
-9	11	1996	1969
-9	13	962	948
-9	15	403	353
-9	17	961	995
-7	-11	725	786
-7	-7	1219	1239
-7	-5	2256	2252
-7	-3	1377	1421
-7	-1	718	668
-7	1	2404	2516
-7	3	2813	2960
-7	5	1155	1088
-7	7	783	786
-7	9	1768	1784
-7	11	1874	1844
-7	13	888	515
-7	15	934	913
-7	17	1126	1140
-5	-13	1025	1125
-5	-11	638	653
-5	-9	846	823
-5	-7	1320	1381
-5	-5	1903	1965
-5	-3	893	933
-5	-1	737	770
-5	1	2155	2177
-5	3	2371	2395
-5	5	777	771
-5	7	756	778
-5	9	1579	1881
-5	11	1261	1224
-5	15	726	693
-3	-13	1460	1409
-3	-11	697	762
-3	-7	1407	1345
-3	-5	2699	2661
-3	-3	1499	1512
-3	-1	751	783
-3	1	2306	2328
-3	3	2727	2620
-3	5	1230	1292
-3	7	852	797
-3	9	1932	1902
-3	11	1472	1459
-3	13	842	823
-3	15	653	665
-1	-15	1063	1137
-1	-13	1793	1812
-1	-11	1031	1025
-1	-9	525	479
-1	-7	2260	2182
-1	-5	2984	2856
-1	-3	1230	1174
-1	-1	1334	1302
-1	1	3446	3362
-1	3	2701	2708
-1	5	594	586
-1	7	1563	1611
-1	9	2392	2330
-1	11	1375	1360
-1	15	918	956
1	-15	1637	1586
1	-13	2104	2077
1	-11	720	670
1	-9	1401	1329
1	-7	2832	2666
1	-5	2452	2366
1	-3	807	829
1	-1	2267	2246
1	1	3461	3653
1	3	1793	1816
1	7	1939	1868
1	9	2118	2129
1	11	831	809
1	13	323	338
3	-17	628	630
3	-15	1610	1590
3	-13	1360	1357
3	-9	1220	1206
3	-7	2294	2282
3	-5	1575	1601
3	-3	447	430
3	-1	2080	2158
3	1	2281	2260
3	3	1080	1060
3	7	1480	1492
3	9	1596	1527
3	11	458	450
5	-17	455	487
5	-15	1409	1332
5	-13	1464	1473
5	-11	520	551
5	-9	1434	1388
5	-7	2871	2890
5	-5	1447	1440
5	-3	377	295
5	-1	1385	1378
5	1	2619	2548
5	3	1528	1486
5	7	1290	1265
5	9	1357	1365
7	-17	771	796
7	-15	1708	1747
7	-13	1293	1307
7	-9	1784	1789
7	-7	2837	2834
7	-5	1719	1736
7	-3	399	403
7	-1	2232	2248
7	1	2213	2178
7	3	996	872
7	5	431	418
7	7	1861	1873
9	-17	1031	1049
9	-15	1667	1598
9	-13	830	881
9	-11	376	466
9	-9	2069	2084
9	-7	2812	2866
9	-5	789	738
9	-3	901	895
9	-1	1707	1652
9	1	1456	1444
9	3	656	614
9	5	790	757
11	-17	1072	1053
11	-15	1130	1123
11	-13	370	332
11	-11	628	582
11	-9	1559	1551
11	-7	1577	1558
11	-5	909	882
11	-3	726	719
11	-1	1151	1184
1	1	856	834
13	-15	981	986
13	-13	482	502
13	-11	318	281
13	-9	1148	1145
13	-7	1335	1359
13	-5	534	500
13	-3	468	507
13	-1	883	931
***	6	*****	
-14	4	657	677
-14	6	905	831
-14	8	587	695
-14	12	617	703
-12	-2	1056	1096
-12	0	636	770
-12	4	973	969
-12	6	1327	1265
-12	8	749	729
-12	10	399	416
-12	12	1038	1080
-12	14	692	917
-10	-6	1097	1199
-10	-2	1520	1550
-10	0	691	711
-10	2	627	617
-10	4	1421	1475
-10	6	1496	1617
-10	8	370	418
-10	10	893	948
-10	12	1501	1520
-10	14	931	965
-8	-8	332	328
-8	-6	687	697
-8	-4	1516	1524
-8	-2	1637	1657
-8	2	1292	1307
-8	4	1813	1835
-8	6	967	1011
-8	10	1216	1210
-8	12	1776	1678
-8	14	761	767
-6	-10	808	868
-6	-8	691	739
-6	-4	1490	1534
-6	-2	1366	1348
-6	2	1242	1226
-6	4	1768	1704
-6	6	987	951
-6	10	1125	1092
-6	12	1653	1630
-6	14	720	680
-4	-12	1015	1016
-4	-10	1082	1099
-4	-8	665	516
-4	-6	725	720
-4	-4	2123	2134
-4	-2	1903	1876
-4	2	1524	1545
-4	4	2670	2633
-4	6	1523	1472
-4	10	1231	1175
-4	12	1826	1725
-4	14	861	862
-2	-14	565	610
-2	-12	1561	1563
-2	-10	1391	1354
-2	-8	1625	1613
-2	-4	2787	2626
-2	-2	1895	1766
-2	2	2676	2561
-2	4	2926	2919
-2	6	1075	1070
-2	8	507	499
-2	10	1572	1516
-2	12	1569	1565
-2	14	801	826
0	-14	1080	1130
0	-12	1803	1747
0	-10	853	811
0	-8	805	338
0	-6	1926	1781
0	-4	3099	2903
0	-2	1235	1158
0	0	1153	1171
0	2	2353	2296
0	4	2145	2090
0	6	711	715
0	8	669	684
0	10	1360	1364
0	12	968	975
2	-14	1131	1116
2	-12	1656	1618
2	-10	672	683
2	-8	563	555
2	-6	1817	1773
2	-4	2115	2081
2	-2	788	752
2	0	655	626
2	2	1949	1886
2	4	1856	1830
2	6	829	818
2	8	656	627
2	10	931	958
4	-14	1202	1207
4	-12	1972	1888
4	-10	898	936
4	-6	1563	1555
4	-4	2631	2377
4	-2	1132	1229
4	0	814	800
4	2	2065	1959
4	4	1636	1602
4	8	660	601
4	8	506	585
6	-16	334	373
6	-14	1640	1728
6	-12	1985	2027
6	-10	693	718
6	-8	736	830
6	-6	2216	2236
6	-4	2153	2122
6	0	1370	1356
6	2	2015	1985
6	4	1665	1601
8	-16	616	643
8	-14	1577	1579
8	-12	1861	1859
8	-8	1165	1149
8	-6	1767	1732
8	-4	1078	1112
8	0	1215	1261
8	2	1512	1426
8	4	865	837
10	-14	1232	1219
10	-12	1066	1001
10	-8	963	903
10	-6	1108	1352
10	-4	894	861
10	0	868	882
10	2	892	943
12	-12	876	903
12	-8	867	820
12	-6	1275	1286
12	-4	799	840
***	7	*****	
-13	3	398	282
-13	5	600	612
-13	7	1223	1186
-13	9	793	785
-11	-3	646	657
-11	-1	1053	1150
-11	1	891	797
-11	5	1075	1107
-11	7	1513	1409
-9	-9	668	728
-9	-3	978	901
-9	-1	1270	1287
-9	1	638	685
-9	3	410	378
-9	5	1280	1195
-9	7	1289	1378
-7	-7	1087	1083
-7	-1	1423	1475
-7	1	730	679
-7	5	1091	1045
-7	7	1361	1353
-7	9	576	617
-7	11	628	386
-7	13	827	841
-5	-9	1292	1320
-5	-7	831	830
-5	-3	1288	1329
-5	-1	2075	2052
-5	1	1207	1207
-5	3	835	866
-5	5	1877	1886
-5	7	1526	1895
-5	9	599	621
-5	11	609	583
-3	-11	1132	1176
-3	-7	1118	1159
-3	-9	1560	1538
-3	-7	639	627
-3	-5	740	748
-3	-3	2148	2080
-3	-1	2248	2218
-3	1	469	489
-3	3	1251	1206
-3	5	1733	1700
-3	7	1261	1252
-1	-13	609	678
-1	-11	1338	1210
-1	-9	1295	1304
-1	-5	1069	1012
-1	-3	2046	1904
-1	-1	1527	1472
-1	3	1175	1153
-1	5	1522	1506
-1	7	820	782
-1	9	256	161
-1	11	847	846
1	-13	660	631
1	-11	1285	1255
1	-9	1213	1213
1	-5	853	847
1	-3	1808	1466
1	-1	1533	1516
1	3	1288	1262
1	5	1639	1605
1	7	695	730
3	-13	574	572
3	-11	1376	1413
3	-9	1282	1262
3	-7	515	418
3	-5	989	1038
3	-3	2211	2191
3	-1	1464	1441
3	3	1329	1262
3	5	1632	1576
3	7	930	910
5	-13	988	1060
5	-11	1797	1788
5	-9	1063	1066
5	-5	1600	1619
5	-3	2015	2050
5	1	531	516
5	3	1703	1650
5	5	1597	1601
7	-13	1062	1106
7	-11	1625	1363
7	-9	516	584
7	-7	380	670
7	-5	1301	1388
7	-7	1425	1425
7	-1	430	428
7	1	696	675
7	3	1091	1098
9	-13	996	1039
9	-11	1275	1259
9	-9	399	481
9	-5	980	967
9	-3	1160	1170
9	-1	690	686
11	-9	512	568
11	-7	350	326
11	-5	1072	1084
***	8	*****	
-10	0	695	756
-10	2	790	743
-10	6	675	579
-10	8	816	888
-8	-2	366	395
-8	0	969	888
-8	2	921	903
-8	6	703	738
-8	8	1089	1086
-8	10	715	686
-6	-6	1059	1032
-6	-4	527	315
-6	-2	605	636
-6	0	1313	1346
-6	2	1102	1083
-6	6	1071	1073
-6	8	1381	1408
-6	10	810	786
-4	-8	1227	1286
-4	-6	1099	1017
-4	-2	1301	1315
-4	0	1593	1586
-4	2	730	712
-4	4	328	369
-4	6	1359	1331
-4	8	1463	1425
-4	10	678	666
-2	-8	1285	1257
-2	-6	625	590
-2	-2	1138	1097
-2	0	1426	1406
-2	2	627	666
-2	4	665	671
-2	6	1092	1093
-2	8	944	937
0	-10	833	811
0	-8	1375	1342
0	-6	803	786
0	-2	1417	1326
0	0	1658	1638
0	2	690	678
0	4	936	939
0	8	1055	1080
2	-10	1085	1102
2	-8	1599	1553
2	-6	751	737
2	-4	457	501
2	-2	1570	1560
2	0	1626	1664
2	2	683	634
2	4	604	604
2	6	1194	1218
4	-12	661	665
4	-10	1324	1352
4	-8	1453	1421
4	-6	820	864
4	-2	1556	1631
4	0	1313	1322
4	4	849	879
6	-10	1038	1122
6	-8	827	879
6	-6	729	735
6	-2	1116	1178
6	0	740	797
8	-6	833	866
8	-4	565	595
***	9	*****	
-7	1	862	969
-7	3	1103	1118
-7	5	560	567
-5	-3	303	272
-5	-1	520	510
-5	1	1018	1023
-5	3	1063	1038
-3	-5	893	879
-3	-1	629	640
-3	1	910	895
-3	3	727	767
-1	-7	1019	1058
-1	-5	1160	1118
-1	-1	552	537
-1	1	1008	1017
-1	3	841	892
1	-7	1107	1226
1	-5	1026	1069
1	1	1223	1253
1	3	694	746
3	-7	1166	1259
3	-5	637	667
3	-1	917	991

TABLE 5: ATOMIC POSITIONAL PARAMETERS[a]

ATOM	x	y	z
Re	0.11870(5)	-0.01029(3)	-0.06551(2)
Si	-0.0875(3)	-0.1386(2)	-0.0709(2)
C1	0.271(1)	-0.0259(7)	-0.1477(7)
C2	-0.041(1)	0.0202(7)	-0.1282(7)
C3	0.278(1)	-0.0428(8)	-0.0045(7)
C4	-0.409(2)	-0.240(1)	-0.1392(8)
C5	-0.261(1)	-0.1901(8)	-0.1570(6)
C6	-0.006(1)	-0.2389(8)	-0.0638(6)
C7	0.075(2)	-0.3048(9)	-0.1401(8)
O1	0.364(1)	-0.0351(7)	-0.1945(6)
O2	-0.129(1)	0.0377(7)	-0.1691(6)
O3	0.377(1)	-0.0623(8)	0.0298(6)

[a]Standard deviations in parentheses refer to last digit quoted.

TABLE 6: THERMAL PARAMETERS ($\AA^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B^a ($\AA^2$)
Re	0.0380(3)	0.0406(3)	0.0331(3)	0.0010(2)	0.0037(2)	0.0175(2)	2.98
Si	0.0471(14)	0.0394(13)	0.0379(13)	-0.0013(10)	0.0018(10)	0.0176(11)	3.37
C1	0.062(7)	0.048(6)	0.048(6)	-0.006(5)	-0.001(5)	0.021(5)	4.36
C2	0.064(7)	0.043(6)	0.054(6)	0.000(5)	0.013(5)	0.020(5)	4.39
C3	0.052(6)	0.058(6)	0.054(6)	-0.004(5)	0.016(5)	0.026(5)	4.35
C4	0.060(8)	0.098(11)	0.068(8)	-0.028(7)	-0.004(6)	0.037(7)	6.38
C5	0.055(6)	0.060(6)	0.045(6)	-0.008(5)	-0.005(5)	0.020(5)	4.53
C6	0.076(8)	0.052(6)	0.046(6)	0.008(5)	0.013(5)	0.027(5)	4.49
C7	0.116(11)	(8)	0.068(8)	0.043(8)	0.028(7)	0.030(7)	6.50
O1	0.086(7)	0.103(8)	0.076(6)	0.004(5)	0.034(5)	0.036(6)	7.19
O2	0.082(6)	0.097(7)	0.063(5)	0.026(5)	-0.003(4)	0.049(5)	5.99
O3	0.054(5)	0.129(8)	0.095(7)	0.024(5)	0.006(4)	0.076(6)	6.53

[a]Equivalent isotopic thermal parameter.

TABLE 7: INTRAMOLECULAR DISTANCES AND ANGLES

INTRAMOLECULAR DISTANCES[a] (Å)

Re-Re'[b]	3.084(1)	Si-C6	1.88(1)
Re-Si	2.533(2)	C1-O1	1.14(2)
Re-Si'	2.535(3)	C2-O2	1.17(1)
Re-C1	1.94(1)	C3-O3	1.17(1)
Re-C2	1.96(1)	C4-C5	1.54(1)
Re-C3	1.97(1)	C6-C7	1.52(2)
Si-C4	1.885(8)		

INTRAMOLECULAR ANGLES[a] (DEGREES)

Re-Re'-C1[b]	178.5(3)	C3-Re-C2	179.1(5)
Re-Re'-C2	91.0(3)	C4-Si-C6	108.5(5)
Re-Re'-C3	89.3(3)	Re-Si-Re'	74.9(1)
Re-Re'-Si	52.6(1)	Re-C1-O1	178.0(9)
Re-Re'-Si'	52.5(1)	Re-C2-O2	175.7(9)
Cl-Re-C3	89.4(4)	Re-C3-O3	177.5(9)
Cl-Re-C2	90.3(4)	Si-C4-C5	114.5(8)
Cl-Re-Si	126.6(3)	Si-C6-C7	115.0(10)
Cl-Re-Si'	128.3(3)		

[a]Standard deviations in parentheses refer to last digit quoted.

[b]Primed atoms related by an inversion centre.

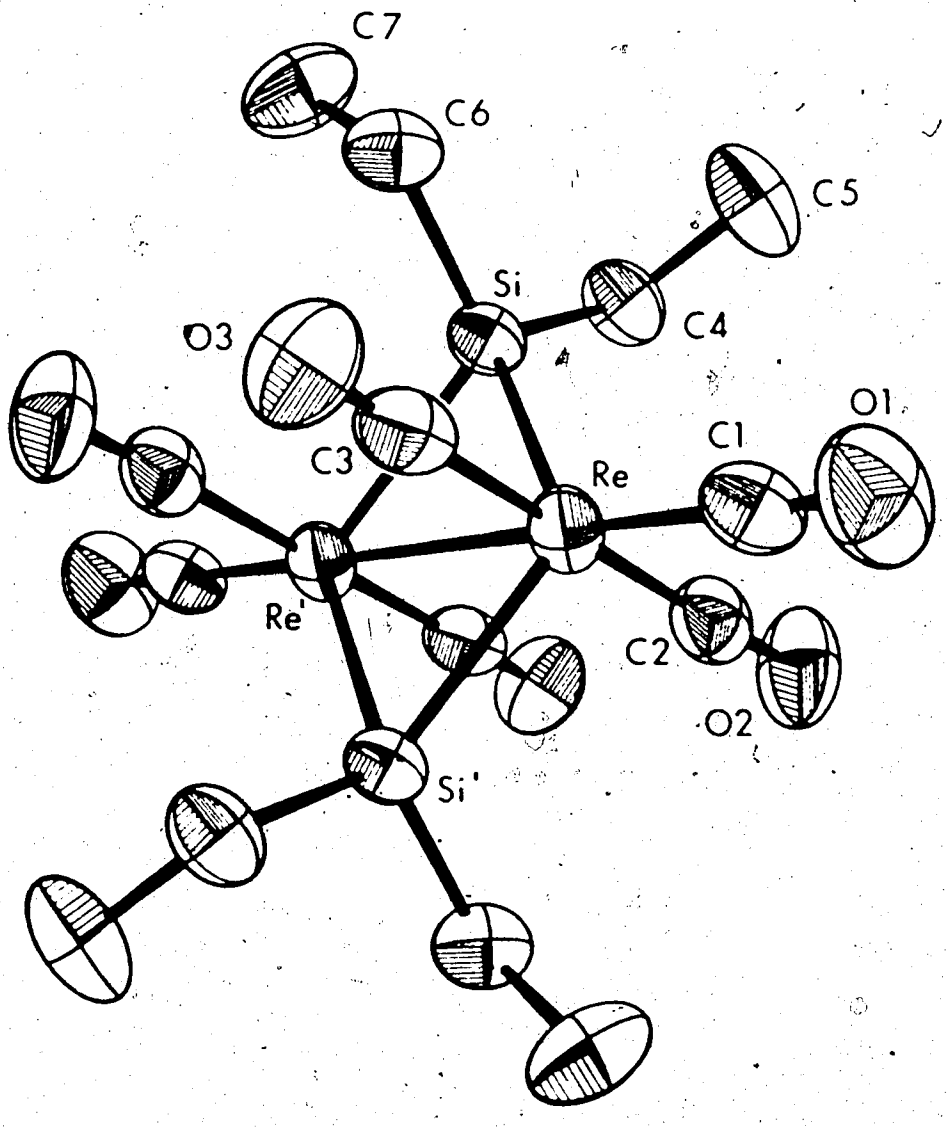


Fig. 3: A PERSPECTIVE VIEW OF $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$.

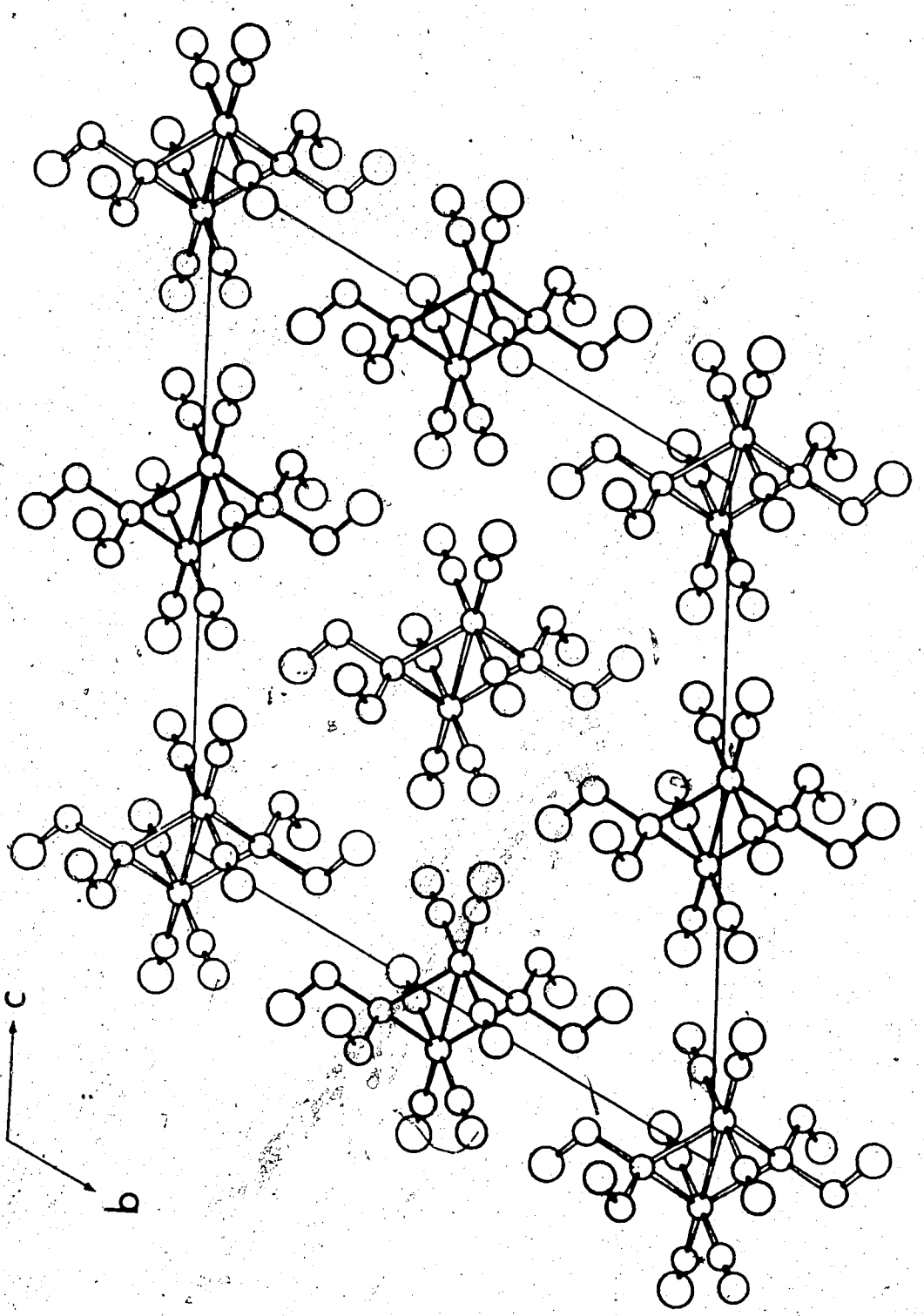


Fig. 4: PACKING DIAGRAM FOR $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$, PROJECTED ON *bc* PLANE.

DESCRIPTION OF STRUCTURE

$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ has approximate C_{2h} molecular symmetry. Its molecular structure is shown in Figure 3. The molecule is composed of a central cluster of two rhenium and two silicon atoms in the shape of a rhombus, with like atoms at opposing corners, and a bond joining the two rheniums across the shorter diagonal. One carbonyl group on each rhenium lies approximately along the Re-Re axis, while the other four lie above and below the plane of the rhombus, two on each rhenium. The ethyl groups are bonded two to each silicon, one above and one below the rhombus plane, giving the silicon atoms a distorted tetrahedral environment.

The Re-Re distance is 3.084(1) Å, compared with 3.121(2) Å in $Re_2(CO)_8H_2Si(C_6H_5)_2$,[62,65] 3.001(1) Å in $Re_2(CO)_8[Si(C_6H_5)_2]_2$,[64] and 3.02 Å in $Re_2(CO)_{10}$,[45,82,83] and thus is again consistent with a Re-Re single bond. This is further substantiated by the acute Re-Si-Re angle [74.9(1)°]. The average Re-C (carbonyl) distance is 1.96 Å and the average C-O distance is 1.16 Å. These agree well with the carbonyl distances in other rhenium carbonyl derivatives.[62,64,65] The Re-C and C-O bonds along the Re-Re bond are not significantly different from the two *trans* carbonyl

groups perpendicular to the Re_2Si_2 plane. In addition the average Si-C (ethyl) distance (1.88 Å) and C-C distance (1.53 Å) both agree with the sums of the Si-C (sp^3) and C(sp^3)-C(sp^3) covalent radii[27,84] (1.91 Å and 1.54 Å respectively).

The Re-Si bond lengths (2.534 Å) are in close agreement with those found in $Re_2(CO)_8H_2Si(C_6H_5)_2$[62,65] and $Re_2(CO)_8[Si(C_6H_5)_2]_2$,[64] (2.544 Å and 2.542 Å respectively). This was not expected if bridging hydrogens were present in the two hydrides. Rather a difference in bridged and unbridged Re-Si bonds, analogous to that observed in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$[66] was expected. A complete discussion of this phenomenon follows in Chapter IV, with emphasis on the existence of bridging hydrogens and their relation to the transition metal-silicon bonds.

CHAPTER III: THE CRYSTAL AND MOLECULAR STRUCTURE OF DIHYDRIDO TRICARBONYL RHENIUM *BIS* (μ-DIETHYLSILICON) TETRACARBONYL RHENIUM, $[Re_2(CO)_7H_2(Si(C_2H_5)_2)_2]$.

EXPERIMENTAL

The sample of $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, supplied by Dr. Graham and Mr. Hoyano,[63] was sublimed in a sealed tube to give crystals that were suitable for a single crystal diffraction study. The crystals produced were clear colourless plates. Preliminary photographs showed $\bar{1}$ Laué symmetry and no systematic absences, consistent with the triclinic space groups P1 and P$\bar{1}$. Precise lattice parameters were obtained at 22°C from the 2θ angles of 17 reflections centred on a Picker manual four circle diffractometer using CuK_{α_1} X-radiation (λ = 1.54051 Å). The parameters are: a = 8.664(1) Å, b = 14.066(2) Å, c = 9.343(1) Å, α = 96.57(2)°, β = 93.86(1)°, γ = 91.63(1)°. A Delaunay reduction[69] showed no higher symmetry. The experimental density [2.21(2) g cm^{-3}] determined by floatation in aqueous Clerici's solution, is in acceptable agreement with that calculated (2.23 g cm^{-3}) assuming two molecules of molecular weight 742.9

a.m.u. in a unit cell of volume 1107 $\mathring{A}^3$.

Intensity data were collected on the Picker manual diffractometer using CuK_α X-radiation monochromated using the (002) reflecting plane of an oriented graphite crystal and using a 2° take-off angle. The crystal was aligned with its a^* axis coincident with the ϕ axis of the diffractometer. The crystal faces were identified and the perpendicular distances between parallel faces of the same form measured as: {1,0,0}, 7.7×10^{-2} mm; {0,1,0}, 5.3×10^{-2} mm; {0,0,1}, 1.9×10^{-2} mm. A coupled $\omega/2\theta$ scan technique was used with a 2θ scan speed of 2°/min to collect all reflections with $2\theta \leq 125°$. Initially a peak scan of 90 secs. (3 deg.) and a stationary background count of 20 secs. at the limits of the scan were used, however as the crystal decomposed and the mosaic spread increased this was changed to 99 sec. peak scans and 19 sec. backgrounds.[85] A scintillation counter in conjunction with a pulse height analyser, tuned to accept 95% of the CuK_α peak, was used to detect the scattered X-rays. Nine well distributed standard reflections were monitored at approximately 10 hr. intervals to assess decomposition effects. The 2836 unique reflections collected were reduced to

2020 significant observations using the criterion that a peak was significantly above background for $I/\sigma(I) \geq 3.0$, where $\sigma(I)$ was computed as described in Chapter II. The data were then reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. The decomposition was approximately linear with time and no significant $\sin\theta/\lambda$ dependence was observed. Total decomposition for the data collection was about 13%. Standard deviations, $\sigma(F)$, in the structure factors were computed as described in the previous chapter using a "p factor" of 0.03.

The high linear absorption coefficient[86] of 216.78 cm^{-1} for CuK_α X-radiation, and the platey habit of the crystals gave rise to a considerable range of transmission factors (0.14 - 0.47). The absorption correction was verified experimentally by investigation of the behavior of I_{h00} as a function of ϕ. The internal consistency of the corrected intensities showed maximum deviations of less than 10% from the mean and was considered acceptable.

TABLE 8: PATTERSON VECTORS[a] FOR $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$

u	v	w	Multiplicity	Relative Peak Height[c]	Assignment[b]
0.167	0.200	0.080	2	523	$(x_1-x_2),(y_1-y_2),(z_1-z_2)$
0.210	0.500	0.500	2	520	$(x_2+x_1),(y_2+y_1),(z_2+z_1)$
-0.384	0.300	0.403	1	288	$2x_1,\ 2y_1,\ 2z_1$
0.036	0.325	0.414	1	231	$2x_2,\ 2y_2,\ 2z_2$
0.090	-0.150	0.070	2	184	$-(x_1-x_4),-(y_1-y_4),-(z_1-z_4)$
0.254	0.050	0.145	2	169	$(x_1-x_3),(y_1-y_3),(z_1-z_3)$

[a] Centrosymmetrically related vectors are not listed.

[b] (x_1,y_1,z_1), (x_2,y_2,z_2), (x_3,y_3,z_3), and (x_4,y_4,z_4) are the coordinates of the Re1, Re2, Si1 and Si2 atoms respectively.

[c] Expected Peak Heights calculated as in Chapter II.

Re_1-Re_2, 444; 2Re, 222; Re-Si, 166.

STRUCTURE SOLUTION AND REFINEMENT

A Patterson[73,74] map was computed between the limits $-0.5 \leq u \leq 0.5$, $-0.5 \leq v \leq 0.5$, and $0.0 \leq w \leq 0.5$. The rhenium-rhenium vectors were readily identified in the Patterson map and a consistent solution for the coordinates of the two independent rhenium atoms was found to be: Re1, (0.185, 0.363, 0.287) and Re2, (0.018, 0.163, 0.207). Image seeking around the origin and Re-Re vectors provided consistent solutions for the silicon atom coordinates as: Si1, (-0.069, 0.313, 0.142), and Si2, (0.275, 0.213, 0.357). The major vectors and their assignments are shown in Table 8.

A resumé of the refinement is shown in Table 9.

TABLE 9: REFINEMENT OUTLINE

MODEL	R_1	R_2
1) Rhenium and Silicon atoms isotropic	0.166	0.238
2) All non-hydrogen atoms isotropic	0.106	0.131
3) Decomposition and Absorption Corrections	0.061	0.078
4) Re and Si anisotropic temperature factors	0.047	0.064
5) All non-hydrogen atoms with anisotropic temperature factors	0.040	0.057

Structure factors were calculated using the atomic scattering factors[75] for the neutral atoms for rhenium, silicon, carbon, and oxygen. The real and imaginary parts of anomalous dispersion corrections[76] were applied to the rhenium and silicon scattering factors.[77] All non-hydrogen atoms were located from an electron density difference map phased on model 1 . Refinement of the model with all temperature factors anisotropic was suggested by features on an electron density difference map phased on model 4 , and was verified by a Hamilton's R Test[79] at the 0.005 significance level. Anisotropic temperature factors were of the form:

$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)\right].$$

In an attempt to locate the hydrogen atoms an electron density difference map was calculated, phased on model 5 . The highest features were of the approximate magnitude 1.1e Å^{-3} and were located in the vicinity of the rhenium atoms, but could not be interpreted as hydrogen atom peaks. Similarly no peaks were observed in the positions predicted for the methylene hydrogens of the ethyl groups. The inability to locate hydrogens in this structure is due to similar problems as encountered for $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$.

The scattering is dominated too much by the heavy r m atoms and hampers location of the hydrogens. A it is probable that residual absorption effects severely limit the data. This is especially true in this structure due to the wide range of transmission factors.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 10. Table 11 contains the final fractional coordinates of all atoms except hydrogen, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic thermal parameters[80] (U's) and equivalent isotropic B's[81] of all atoms are shown in Table 12 and bond lengths and angles are given in Tables 13 and 14 respectively. The bond lengths and angles along with their standard deviations were obtained from ORFFE. Fig. 5 shows a three dimensional representation of the molecule. Least squares plane calculations are shown for the Re_2Si_2 plane (Table 15) showing the deviations of the Re and Si atoms from the plane and also the distances of the carbonyl groups, C202, C303 and C606, from

this plane. Also the plane through the four carbonyl groups perpendicular to the Re_2Si_2 plane is calculated and also selected atom distances from this plane.

TABLE 10: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
				6	0	384	413	-7	-1	983	1006	0	5	355	355	7	-2	637	648	-10	6	961	907
-13	5	357	378	7	-2	488	508	-7	0	627	627	0	6	345	362	7	-1	279	256	-10	7	456	431
-12	4	575	599	7	-1	1655	1623	-7	1	1659	1731	0	7	611	606	7	1	334	319	-9	-7	355	381
-12	5	357	377	7	0	497	498	-7	2	421	440	0	8	524	518	7	2	833	835	-9	-6	396	387
-12	6	339	350	7	1	627	606	-7	3	967	978	0	9	344	358	7	3	556	610	-9	-5	669	659
-11	4	372	373	7	3	525	563	-7	4	288	283	1	-9	189	185	7	4	1097	1149	-9	-4	312	312
-11	5	311	298	7	4	350	366	-7	5	873	883	1	-8	334	332	7	5	461	468	-9	-3	197	182
-10	4	426	415	7	5	845	865	-7	6	179	175	1	-7	658	665	7	6	705	716	-9	0	207	190
-10	6	177	184	7	6	394	406	-7	7	628	618	1	-6	668	670	7	7	253	257	-9	1	355	361
-10	7	263	256	7	7	508	546	-6	-8	192	203	1	-5	914	921	7	8	293	328	-9	2	599	593
-10	8	386	418	8	-2	634	663	-6	-6	548	551	1	-4	1275	1278	8	-8	312	342	-9	4	633	633
-9	5	339	367	8	2	636	632	-6	-3	300	281	1	-3	2069	2025	8	-7	563	575	-9	5	720	848
-9	6	285	310	8	3	551	567	-6	-2	1610	1648	1	-2	1176	1178	8	-6	330	320	-9	6	547	551
-9	7	571	598	8	4	962	1016	-6	-1	755	748	1	-1	1616	1557	8	-5	625	600	-9	7	615	643
-9	8	287	326	8	5	673	567	-6	0	2049	2042	1	0	889	828	8	-4	259	283	-9	8	315	340
-8	4	583	687	8	6	699	787	-6	1	663	668	1	1	239	228	8	-3	253	244	-8	-8	261	249
-8	5	316	316	8	7	268	269	-6	2	1359	1479	1	2	392	385	8	-1	239	226	-8	-7	360	397
-8	6	813	821	9	-2	334	344	-6	3	233	231	1	3	686	696	8	0	348	340	-8	-6	289	338
-8	7	247	261	9	-1	831	798	-6	4	265	272	1	4	1044	1055	8	1	1016	962	-8	-5	290	291
-8	8	644	658	9	0	384	349	-6	5	880	855	1	5	1045	1068	8	2	618	627	-8	-3	251	253
-7	3	1264	1239	9	1	798	783	-5	-7	323	317	1	6	740	722	8	3	1249	1281	-8	-2	824	823
-7	4	666	655	9	2	596	596	-5	-6	190	178	1	7	648	668	8	4	919	936	-8	-1	896	850
-7	5	989	987	9	3	1056	1072	-5	-5	862	872	1	8	600	595	8	5	786	850	-8	0	627	624
-7	6	225	217	9	4	537	550	-5	-4	291	277	1	9	351	336	8	6	213	234	-8	1	1004	966
-7	7	648	596	9	5	721	741	-5	-3	1547	1528	2	-9	393	399	8	7	230	243	-8	2	969	1009
-7	8	196	168	9	6	336	335	-5	-2	781	751	2	-8	617	601	9	-8	348	358	-8	3	996	1051
-6	3	213	204	9	7	228	237	-5	-1	1548	1577	2	-7	760	761	9	-7	206	194	-8	4	563	594
-6	5	188	184	10	-2	325	333	-5	0	908	875	2	-6	998	971	9	-6	436	446	-8	5	753	769
-6	6	888	895	10	-2	996	963	-5	1	1585	1629	2	-5	781	833	9	-3	231	238	-8	6	380	387
-6	7	1821	1811	10	-1	705	660	-5	2	167	176	2	-4	751	767	9	-2	617	595	-8	7	289	299
-6	8	198	206	10	0	1061	984	-5	3	958	946	2	-3	1242	1203	9	-1	370	367	-7	-8	189	252
-5	3	385	378	10	1	698	693	-5	5	647	648	2	-2	371	391	9	0	1277	1226	-7	-6	671	684
-5	4	580	583	10	2	818	785	-5	6	326	315	2	-1	297	231	9	1	401	363	-7	-3	527	543
-5	5	1160	1130	10	3	699	682	-5	7	732	712	2	0	202	66	9	2	1101	1058	-7	-2	1142	1176
-5	6	182	265	10	4	553	540	-5	8	339	308	2	1	782	675	9	3	327	305	-7	-1	1032	1031
-5	7	682	654	10	5	239	229	-5	9	658	658	2	2	631	648	9	4	711	723	-7	0	1147	1072
-5	9	617	617	10	6	226	236	-4	-8	637	665	2	3	1234	1233	9	5	270	230	-7	1	841	850
-4	2	646	678	11	-3	827	796	-4	-7	680	678	2	4	1465	1457	9	6	152	138	-7	2	1140	1218
-4	3	213	204	11	-2	665	615	-4	-6	1136	1118	2	5	1344	1398	10	-5	645	640	-7	3	561	582
-4	5	188	184	11	-1	1001	920	-4	-5	682	679	2	6	888	876	10	-4	488	390	-7	4	559	550
-4	6	888	895	11	0	547	508	-4	-4	1049	1013	2	7	694	702	10	-3	883	877	-7	5	357	360
-4	7	231	210	11	1	663	655	-4	-3	698	671	2	8	444	437	10	-2	605	651	-7	6	228	213
-4	8	948	891	11	2	197	213	-4	-2	1138	1079	2	9	168	153	10	-1	1226	1160	-7	8	196	190
-3	3	788	648	11	3	255	241	-4	-1	227	244	3	-9	564	603	10	0	337	310	-6	-6	239	193
-3	3	692	584	12	-3	684	631	-4	0	1249	1153	3	-8	615	592	10	1	712	686	-6	-5	622	586
-3	4	352	368	12	-2	648	654	-4	1	131	109	3	-7	784	733	10	2	247	219	-6	-4	662	651
-3	5	1458	1448	12	-1	564	519	-4	2	192	234	3	-6	709	717	10	3	668	668	-6	-3	1251	1276
-3	6	196	186	12	0	268	254	-4	3	147	172	3	-5	300	304	11	-6	511	510	-6	-2	1009	1063
-3	7	1367	1351	12	1	181	162	-4	4	1136	1136	3	-3	227	210	11	-5	210	258	-6	-1	1645	1694
-3	8	177	116	12	2	259	254	-4	5	715	736	3	-2	558	528	11	-4	998	975	-6	0	596	566
-3	9	552	560	13	-4	372	326	-4	6	1241	1238	3	-1	688	569	11	-3	276	295	-6	1	758	758
-2	3	182	135	13	-3	632	627	-4	7	544	512	3	0	783	694	11	-2	929	882	-6	2	333	355
-2	3	1071	1056	13	-2	361	313	-4	8	726	730	3	1	1326	1273	11	-1	173	182	-6	3	135	89
-2	3	625	628	13	-1	176	167	-4	9	238	244	3	2	952	912	11	0	687	671	-6	5	228	211
-2	4	1482	1480	13	1	195	151	-3	-8	399	371	3	3	1323	1262	11	1	238	252	-6	6	188	163
-2	6	1265	1297	13	2	385	388	-3	-7	1850	1830	3	4	1636	1634	12	-6	169	146	-6	7	643	639
-2	8	638	631	13	3	662	631	-3	-6	636	635	3	5	1802	1881	12	-5	742	709	-6	8	267	256
-2	11	2981	3048	14	-4	152	120	-3	-5	1664	1670	3	6	757	761	12	-4	177	166	-6	9	685	677
-1	2	167	188	14	0	199	195	-3	-4	697	681	3	7	328	326	12	-3	638	623	-5	-8	328	338
-1	3	1644	1634	14	1	267	284	-3	-3	719	730	4	-9	686	696	12	-1	227	236	-5	-7	266	218
-1	4	311	301	14	2	401	408	-3	-2	233	201	4	-8	652	619	12	1	297	278	-5	-6	585	583
-1	5	897	919					-3	-1	191	185	4	-7	369	375	12	3	459	464	-5	-5	631	610
-1	7	459	458	-14	-2	221	273	-3	1	1443	1386	4	-5	208	198	13	-5	156	88	-5	-4	1165	1156
0	2	1965	1858	-14	2	282	229	-3	2	658	655	4	-4	671	684	13	-4	362	364	-5	-3	728	731
0	3	298	287	-14	3	337	332	-3	3	1062	1133	4	-3	1198	1185	13	0	416	408	-5	-2	1961	1873
0	4	708	735	-13	-3	205	216	-3	4	989	990	4	-2	978	938	13	1	182	156	-5	-1	830	849
0	6	322	333	-13	-1	275	263	-3	5	1764	1715	4	-1	1306	1313	13	2	432	423	-5	0	338	392
1	1	2223	2065	-13	1	560	574	-3	6	811	814	4	0	1458	1386	14	-1	544	521	-5	2	180	163
1	2	172	186	-13	3	703	708	-3	7	861	821	4	1	1440	1424	14	1	635	630	-5	3	488	375
1	3	745	688	-13	5	687	685	-3	8	326	343	4	2	758	728					-5	4	781	801
1	4	291	226	-12	-2	336	332	-3	9	248	253	4	3	1891	1813	-14	0	184	180	-5	5	568	559
1	5	576	551	-12	0	791	806	-2	-9	308	299	4	4	648	686	-14	2	365	374	-5	6	860	831
1	6	163	135	-12	2	1836	1867	-2	-8	661	620	4	5	594	555	-14	3	291	262	-5	7	329	329
1	7	862	800	-12	4	672	673	-2	-7	678	651	4	6	278	248	-13	-3	151	168	-5	8	652	641
1	9	683	688	-12	6	262	233	-2	-6	977	968	4	7	173	148	-13	-1	657	662	-5	9	154	196
2	0	1262	1192	-11	-5	236	184	-2	-5	252	332	4	8	167	167	-13	0	348	335	-4	-9	682	660
2	2	388	377	-11	-3	696	695	-2	-4	213	200	4	9	265	282	-13	1	552	527	-4	-8	292	290
2	3	159	158	-11	-1	853	867	-2	-2	159	162	5	-9	168	182	-13	2	392	382	-4	-7	638	601
2	4	1266	1237	-11	1	1136	1118	-2	-1	806	759	5	-8	268	252	-13	3	566	518	-4	-6	661	629
2	5	278	285	-11	3	633	637	-2	0	1468	1536	5	-7	632	635	-13	4	275	283	-4	-5	912	862
2	6	1678	1665	-11	7	236	278	-2	1	817	868	5	-6	1965	1839	-13	5	321	314	-4	-4	300	305
2	7	265	255	-10	-6	689	668	-2	2	1854	1808	5	-5	1265	1218	-12	-6	261	248	-4	-3	907	920
2	8	719	718	-10	-4	763	779	-2	3	717	748	5	-4	1252	1326	-12	-3	289	304	-4	-2	673	662
2	9	216	217	-10	-2	931	912	-2	4	1918	1830	5	-3	1310	1372	-12	-2	610	586	-4	-1	314	306
3	1	829	717	-10	0	873	821	-2	5	866	865	5	-2	1963	1867	-12	-1	557	548	-4	1	831	809
3	2	238	232	-10	2	538	518	-2	6	876	886	5	-1	636	648	-12	0	687	683	-4	2	782	771
3	3	1618	1562	-10	4	235	264	-2	7	285	286	5	0	567	553	-12	1	510	468	-4	3	1650	1615
3	4	383	398	-10	6	566	596	-2	8	178	177	5	1	367	323	-12	2	560	525	-4	4	736	720
3	5	1598	1591	-9	-7	678	620	-1	-9	621	592	5	2	231	217	-12	3	273	250	-4	5	1667	1650
3	6	297	265	-9	-5	926	957	-1	-7	625	616	5	3	316	329	-11	-5	292	310	-4	6	936	883
3	7	1825	998	-9	-4	190	128	-1	-6	669	631	5	4	586	589	-11	-4	390	391	-4	7	669	678
3	8	269	289	-9	-3	806	841	-1	-3	1229	1217	6	-7	509	498	-11	-3	591	586	-4	8	215	183
4	-1	726	716	-9	-1	325	338	-1	-2	986	1073	6	-6	438	445	-11	-2	672	668	-4	9	175	189
4	0	2221	2135	-9	2	152	152	-1	-1	2115	2058	6	-5	977	965	-11	-1	795	783	-3	-9	360	360
4	2	1335	1279	-9	3	680	678	-1	0	1676	1678	6	-4	1877	1870	-11	0	727	695	-3	-8	695	663
4	3	546	521	-9	6	159	116	-1	1	1928	2061	6	-3	1498	1489	-11	1	622	621	-3	-7	315	323
4	4	1561	1492	-9	5	915	959	-1	2	1262	1268	6	-2	865	864	-11	2	319	319	-3	-6	607	618
4	5	237	265	-9	7	785	811	-1	3	291	302	6	-1	1231	1256	-11	4	168	177	-3	-5	209	182
4	6	986	965	-8	-8	789	918	-1	4	552	551	6	0	629	620	-11	5	291	282	-3	-4	145	136
4	8	178	166	-8	-5	177	161	-1	5	666	667	6	1	215	226	-11	6	276	263	-3	-2	726	698
5	-1	2922	2967	-8	-4	622	680	-1	6	156	142	6	2	368	380	-11	7	317	318	-3	-1	615	615
5	0	765	691	-8	0	587	586	-1	8	322	256	6	3	369	367	-10	-6	317	346	-3	0	690	686
5	1	1986	1998	-8	1	187	178	-1	9	238	247	6	5	631	629	-10	-5	606	576	-3	1	1106	1116
5	2	567	526	-8	2	1269	1316	0	-9	511	516	6	6	217	208	-10	-4	566	570	-3	2	2315	2368
5	3	1183	1092	-8	3	275	258	0	-8	357	366	6	7	666	697	-10	-3	536	532	-3	3	706	701
5	5	392	368	-8	4	859	862	0	-6	1686	1689	6	8	223	282	-10	-2	560	567	-3	4	1617	1608
5	6	688	679	-8	5	322	345	0	-3	1763	1698	7	-9	282	283	-10	-1	660	588	-3	5	663	678
6	-1	615	829	-8	6	996	976	0	-2	2057	2115	7	-8	665	651	-10	0	660	628	-3	6	831	822
6	0	2299	2696	-8	7	285	221	0	-1	1839	1778	7	-7	669	626	-10	1	165	166	-2	-9	533	553
6	1	616	686	-8	8	518	585	0	0	2295	2383	7	-6	628	626	-10	3	258	259	-2	-8	266	221
6	2	666	678	-7	-7	678	699	0	1	1167	1238	7	-5	545	529	-10	5	688	697	-2	-7	385	322
6	4	387	489	-7	-5	638	673	0	2	293	300	7	-4	1266	1258	-10	9	511	510	-2	-6	178	133
6	7	218	282	-7	-3	262	278	0	4	223	200	7	-3	617	668								

Table 10 (continued)

H	L	FOBS	FCAL
-2	-5	317	335
-2	-3	1206	1168
-2	-2	812	783
-2	-1	1628	1521
-2	0	595	610
-2	1	2557	2564
-2	2	546	553
-2	3	1611	1651
-2	4	303	298
-2	5	761	767
-2	6	150	126
-2	7	181	182
-2	9	505	510
-1	-6	625	598
-1	-5	313	340
-1	-4	1637	1670
-1	-3	706	705
-1	-2	3068	2965
-1	-1	561	537
-1	0	1358	1465
-1	1	126	103
-1	2	1395	1375
-1	3	213	206
-1	4	197	190
-1	6	281	282
-1	7	159	170
-1	8	722	705
0	-7	438	427
0	-6	350	345
0	-5	1410	1390
0	-4	558	580
0	-3	2238	2221
0	-2	676	686
0	-1	1286	1219
0	1	606	567
0	2	278	260
0	3	253	282
0	4	129	116
0	5	749	745
0	7	913	913
0	9	591	615
1	-8	690	695
1	-7	213	184
1	-6	1155	1146
1	-5	187	189
1	-4	1525	1535
1	-3	346	356
1	-2	605	660
1	-1	856	826
1	0	1838	1806
1	1	190	190
1	2	1484	1479
1	3	925	933
1	4	575	583
1	5	693	677
2	-9	793	780
2	-7	670	680
2	-5	155	163
2	-2	325	309
2	-1	281	306
2	0	2958	2935
2	1	671	662
2	2	1927	2006
2	3	197	194
2	5	1510	1511
2	7	463	464
2	8	665	647
3	-6	256	253
3	-4	385	357
3	-2	1803	957
3	-1	394	386
3	0	1884	1842
3	2	2558	2426
3	3	227	211
3	4	1310	1316
3	5	188	188
3	6	181	186
3	8	306	289
4	-9	369	367
4	-5	1078	1103
4	-3	1715	1682
4	-1	1847	1854
4	0	233	226
4	1	1777	1826
4	3	708	696
4	7	657	668
5	-6	1805	976
5	-4	1833	1797
5	-2	1940	1898
5	0	1032	961
5	2	208	208
5	4	626	646
5	6	808	846
5	8	665	705
6	-9	256	245
6	-7	798	801
6	-5	1378	1364
6	-3	1126	1138
6	-2	160	115
6	-1	277	284
6	0	219	179
6	1	883	834
6	3	788	736
6	5	916	905
6	7	700	727
7	-8	668	670
7	-6	822	786
7	-4	711	717
7	-2	1281	1225
7	0	313	288
7	2	1362	1369
7	3	239	268

H	L	FOBS	FCAL
7	4	1085	1083
7	5	212	201
7	6	482	503
8	-7	636	602
8	-3	361	356
8	-1	1056	1046
8	0	421	418
8	1	1888	1806
8	2	349	325
8	3	958	985
8	5	368	392
9	-6	303	317
9	-4	621	632
9	-2	867	868
9	-1	333	328
9	0	1378	1329
9	1	462	450
9	2	943	918
9	4	386	327
9	6	221	247
10	-7	356	380
10	-5	797	816
10	-4	263	217
10	-3	823	786
10	-2	225	192
10	-1	722	708
10	0	261	222
10	1	455	446
10	2	333	361
10	3	167	160
11	-7	200	225
11	-6	669	648
11	-5	316	301
11	-4	655	703
11	-3	272	232
11	-2	213	201
11	-1	178	154
11	0	697	520
11	1	203	207
12	-6	248	250
12	-5	538	525
12	-4	228	228
12	-3	225	202
12	-1	255	248
12	0	273	234
12	1	607	611
12	2	225	198
12	3	595	588
12	4	265	245
13	-5	160	85
13	-2	291	292
13	-1	262	269
13	0	681	654
13	1	360	358
13	2	530	525
13	3	231	243
14	-3	292	299
14	-2	277	265
14	-1	590	565
14	0	443	428
14	1	495	497

H	L	FOBS	FCAL
-14	1	820	833
-14	2	138	163
-13	-3	163	166
-13	-1	207	198
-13	0	578	576
-13	1	165	168
-13	2	672	669
-13	4	394	363
-12	-6	173	162
-12	-3	648	653
-12	-2	183	172
-12	-1	777	758
-12	1	326	318
-11	-6	659	683
-11	-3	163	131
-11	-2	776	769
-11	0	297	272
-11	3	176	162
-11	4	586	579
-11	6	667	679
-10	-5	880	888
-10	-3	566	570
-10	-1	291	279
-10	1	637	641
-10	3	1030	1042
-10	5	716	756
-10	7	600	623
-9	-6	238	262
-9	-4	246	179
-9	-2	200	208
-9	0	633	616
-9	2	1075	1069
-9	4	1956	1185
-9	6	396	432
-8	-7	203	192
-8	-5	277	218
-8	-3	693	775
-8	-1	1067	1006
-8	1	970	948
-8	3	1066	1345
-8	5	685	653
-7	-6	300	326
-7	-4	1098	1149
-7	-2	1459	1512
-7	0	853	817
-7	2	556	589
-7	4	196	205
-7	6	361	318
-7	8	572	563
-6	-7	378	399
-6	-5	1189	1083

H	L	FOBS	FCAL
-6	-4	484	462
-6	-3	1638	1664
-6	-1	1090	1085
-6	1	159	161
-6	3	455	465
-6	5	586	587
-6	6	155	93
-6	7	848	813
-5	-8	523	562
-5	-6	652	630
-5	-5	165	140
-5	-4	1306	1319
-5	-2	790	811
-5	0	276	287
-5	2	1166	1209
-5	3	215	199
-5	4	1160	1162
-5	5	218	211
-5	6	845	828
-5	7	181	198
-5	8	499	503
-4	-8	165	85
-4	-7	670	670
-4	-5	693	667
-4	-3	190	182
-4	-1	523	564
-4	1	1649	1565
-4	2	478	475
-4	3	2105	2097
-4	4	496	399
-4	5	829	818
-4	6	197	176
-4	7	392	382
-3	-8	686	636
-3	-6	253	229
-3	-2	1065	1075
-3	0	1626	1662
-3	1	539	557
-3	2	2364	2606
-3	3	549	536
-3	4	1019	980
-3	5	163	153
-3	8	331	331
-2	-9	306	273
-2	-6	263	223
-2	-5	1031	1026
-2	-4	621	615
-2	-3	1621	1667
-2	-2	664	669
-2	-1	1212	1307
-2	0	600	652
-2	1	1166	1179
-2	2	572	575
-2	3	753	762
-2	6	279	293
-2	7	656	661
-2	8	240	236
-2	9	617	618
-1	-8	243	293
-1	-7	229	232
-1	-6	998	956
-1	-5	721	736
-1	-4	1918	1905
-1	-3	674	673
-1	-2	1862	1816
-1	-1	688	702
-1	0	353	422
-1	1	232	248
-1	2	154	115
-1	4	355	346
-1	5	216	220
-1	6	1031	1040
-1	7	396	387
-1	8	778	786
-1	9	300	301
0	-9	351	357
0	-8	213	173
0	-7	654	633
0	-6	678	659
0	-5	1813	1791
0	-4	631	631
0	-3	1196	1195
0	-2	578	561
0	-1	627	596
0	0	257	259
0	1	650	658
0	2	599	598
0	3	911	897
0	4	379	368
0	5	862	869
0	6	536	521
0	7	878	856
0	8	315	317
0	9	462	471
1	-9	201	193
1	-8	536	532
1	-7	326	283
1	-6	709	779
1	-5	666	688
1	-4	655	645
1	-3	662	689
1	0	696	812
1	1	1051	1233
1	2	1027	1067
1	3	860	863
1	4	1013	992
1	5	516	528
1	6	696	698
1	7	308	306
1	8	320	238
2	-9	462	483
2	-8	211	283
2	-7	293	323

H	L	FOBS	FCAL
2	-3	611	630
2	-2	452	450
2	-1	1297	1327
2	0	748	778
2	1	2391	2368
2	2	1358	1355
2	3	1186	1203
2	4	575	558
2	5	366	369
3	-6	379	367
3	-5	686	678
3	-4	687	689
3	-3	585	616
3	-2	1360	1390
3	-1	987	922
3	0	1481	1511
3	1	1238	1230
3	2	1616	1681
3	3	381	367
3	4	396	385
3	5	262	231
3	6	660	639
3	7	272	275
3	8	621	631
4	-8	187	212
4	-7	349	359
4	-6	705	694
4	-5	1128	1158
4	-4	628	644
4	-3	1336	1372
4	-2	1072	1068
4	-1	861	906
4	0	647	650
4	1	779	783
4	2	645	638
4	3	228	223
4	5	683	668
4	6	641	646
4	7	637	633
5	-9	199	198
5	-8	389	398
5	-7	678	702
5	-6	383	398
5	-4	893	895
5	-3	723	782
5	-2	550	568
5	2	229	262
5	3	344	381
5	4	665	627
5	5	711	712
5	6	734	758
5	7	548	572
5	8	606	636
6	-9	291	322
6	-8	377	383
6	-7	608	583
6	-6	673	672
6	-5	708	730
6	-4	681	698
6	-3	264	226
6	-1	336	323
6	0	646	637
6	1	939	928
6	2	767	806
6	3	799	783
6	4	654	641
6	5	529	538
6	6	566	526
7	7	295	333
7	-8	332	340
7	-7	238	247
7	-6	366	312
7	-5	288	278
7	-3	253	282
7	-2	531	579
7	-1	725	781
7	0	1061	1035
7	1	1439	1396
7	2	778	775
7	3	648	696
7	4	606	613
7	5	283	283
8	-5	203	218
8	-4	356	391
8	-3	544	573
8	-2	926	975
8	-1	861	889
8	0	1234	1181
8	2	715	701
8	3	309	313
9	-7	269	309
9	-6	363	395
9	-5	500	523
9	-4	650	523
9	-3	846	852
9	-2	686	653
9	-1	839	807
9	0	557	537
9	1	728	698
9	2	306	223
9	5	332	361
9	6	265	277
10	-7	318	303
10	-6	560	576
10	-5	602	621
10	-4	537	561
10	-3	366	348
10	-2	650	636
10	-1	293	281
10	0	295	296
10	1	193	165

H	L	FOBS	FCAL
10	2	180	160
10	3	210	238
10	4	658	660
10	5	345	340
10	6	755	730
10	7	685	676
10	8	712	719
11	0	501	521
11	1	698	536
11	2	182	223
11	3	216	197
11	4	319	345
11	5	208	258
11	6	422	427
11	7	498	529
11	8	781	796
12	-7	599	621
12	-6	540	575
12	-5	350	353
12	-4	690	681
12	-3	586	606
12	-2	278	288
12	-1	199	186
12	1	345	350
12	2	399	436
12	3	753	785
12	4	635	667
12	5	575	563
12	6	669	660
12	7	682	682
12	8	619	627
13	-8	392	395
13	-7	631	619
13	-6	383	398
13	-5	907	906
13	-4	682	683
13	-1	905	877
13	0	762	758
13	1	818	895
13	2	976	1004
13	3	1136	1129
13	4	756	759
13	5	592	566
13	6	637	627
14	-6	258	279
14	-5	397	437
14	-4	188	158
14	-3	614	616
14	-2	360	293
14	-1	597	505
14	0	280	279
14	1	351	370
14	2	264	290
15	0	686	671
15	1	366	349
15	2	521	522
15	3	236	247
15	-3	671	659
15	-2	291	262
15	-1	668	633
15	0	290	289
15	1	584	580
15	2	182	188
15	-1	190	161

H	L	FOBS	FCAL
-13	-1	166	160
-13	0	623	612
-13	2	216	223
-13	3	185	170
-12	-3	564	569
-12	-2	262	253
-12	-1	359	336
-12	3	176	187
-11	-4	668	667
-11	-3	247	231
-11	-2	278	276
-11	0	229	219
-11	1	178	128
-11	2	516	475
-11	3	279	275
-11	4	542	550
-11	5	257	263
-10	-5	244	229
-10	-1	382	371
-10	0	367	361
-10	1	726	706
-10	2	523	505
-10	3	773	787
-10	4	605	635
-10	5	363	381
-10	6	155	168
-9	-3	388	377
-9	-2	593	525
-9	-1	676	655
-9	0	955	926
-9	1	726	697
-9	2	842	868
-9	3	596	635
-9	4	519	541
-8	-6	163	172
-8	-5	271	328
-8	-4	339	356
-8	-3	686	736
-8	-2	488	466

H	L	FOBS	FCAL
-5	7	378	354
-5	8	192	181
-4	-8	297	306
-4	-7	233	236
-4	-6	489	492
0	-2	618	606
0	-1	232	239
0	0	1052	1010
0	1	682	677
0	2	1228	1238
0	3	679	671
0	4	1042	1026
0	5	637	636
0	6	879	869
0	7	210	216
0	8	625	606
1	-9	636	639
1	-8	288	255
1	-7	689	667
1	-6	208	218
1	-5	316	361
1	-4	167	64
1	-3	662	661
1	-2	382	388
1	-1	1213	1692
1	0	737	779
1	1	1565	1576
1	2	598	613
1	3	1652	1430
1	4	334	339
1	5	682	695
1	7	214	235
2	-8	197	201
2	-6	591	588
2	-3	610	625
2	-2	1665	1668
2	-1	778	791
2	0	1541	1606
2	1	518	520
2	2	1230	1253
2	3	372	378
2	4	212	206
2	7	147	81
2	8	311	303
3	-7	600	606
3	-6	168	170
3	-5	800	796
3	-4	320	341
3	-3	1133	1128
3	-2	666	661
3	-1	1316	1375
3	0	298	296
3	1	359	360
3	2	699	700
3	3	397	390
3	4	699	505
4	-1	1032	1030
4	0	1665	1628
4	1	976	1036
4	2	1339	1351
4	3	803	797
4	4	763	772
4	5	169	171
4	6	167	108
5	-5	361	349
5	-4	592	588
5	-3	793	801
5	-2	811	819
5	-1	1516	1536
5	0	1157	1226
5	2	586	602
5	3	710	689
5	4	199	203
5	5	273	264
6	-7	277	255
6	-6	378	368
6	-5	290	289
6	-4	278	263
6	-3	275	259
6	-2	639	635
6	-1	661	628
6	0	1036	1011
6	1	656	662
6	2	1001	1058
6	3	533	565
6	4	669	694
6	5	376	379
6	6	325	333
6	8	378	351
7	-5	662	625
7	-4	789	798
7	-3	626	648
7	-2	615	600
7	-1	303	289
7	-0	337	342
7	-1	735	689
7	-2	581	552
7	-5	1095	1070
7	-6	649	635
7	-3	797	792
7	-1	196	246
7	2	337	298
7	3	931	905
7	4	665	635
7	5	968	969
7	6	583	565
7	7	789	779
8	-8	280	297
8	-7	268	258
8	-6	717	706
8	-5	626	591
8	-4	827	780
8	-3	562	582

Table 10 (continued)

K	L	FOBS	FCAL
3	1	824	820
3	2	140	104
3	3	144	145
3	4	158	158
3	5	758	736
3	6	172	170
3	7	643	633
4	-8	572	572
4	-6	856	871
4	-5	290	293
4	-4	1007	1042
4	-3	215	207
4	-2	893	952
4	0	396	368
4	2	661	678
4	3	276	262
4	4	998	978
4	5	333	310
4	6	987	961
5	-8	172	171
5	-7	694	673
5	-6	226	236
5	-5	763	785
5	-3	263	269
5	-1	231	265
5	1	525	559
5	2	166	165
5	3	1212	1248
5	4	216	209
5	5	995	1005
5	7	552	572
6	-8	546	569
6	-6	906	892
6	-2	799	828
6	0	1031	1065
6	2	1267	1257
6	4	643	637
6	6	454	470
7	-7	177	165
7	-5	205	229
7	-3	942	1007
7	-1	1332	1308
7	1	1096	1076
7	3	473	492
8	-6	308	347
8	-4	763	811
8	-2	1210	1227
8	0	892	906
8	2	292	336
8	4	353	403
9	-5	611	691
9	-3	793	817
9	-1	552	508
9	0	158	38
9	3	471	475
9	5	581	589
10	-6	478	507
10	-4	388	364
10	-2	205	205
10	2	758	758
10	4	606	697
11	-3	176	175
11	-1	609	600
11	1	692	702
11	3	622	638
12	-6	329	342
12	-2	532	526
12	0	616	596
12	2	456	453
13	-3	581	612
13	-2	192	160
13	-1	689	506
13	0	138	108

K	L	FOBS	FCAL
-12	-2	173	168
-12	2	253	252
-11	-1	306	297
-11	0	212	225
-11	1	523	517
-11	2	250	234
-11	3	682	685
-11	4	198	206
-10	-2	636	615
-10	-1	209	226
-10	0	773	758
-10	1	275	235
-10	2	633	628
-10	4	326	346
-9	-5	265	270
-9	-2	578	591
-9	-1	916	878
-9	0	220	230
-9	1	810	798
-9	3	262	295
-8	-6	662	696
-8	-4	575	595
-8	-3	247	223
-8	-2	767	756
-8	0	785	752
-8	2	252	247
-8	4	273	336
-7	1	161	167
-7	3	557	567
-7	5	496	548
-6	-3	525	589
-6	-1	306	283
-6	1	478	506
-6	3	906	915
-6	5	562	578
-5	-6	593	606
-5	-4	316	286
-5	-2	318	309

K	L	FOBS	FCAL
-6	0	592	601
-6	2	665	684
-6	4	962	968
-6	6	676	662
-5	-7	822	826
-5	-3	670	677
-5	-1	1155	1
-5	0	181	1
-5	1	1101	1179
-5	3	889	922
-5	5	502	486
-4	-8	618	613
-4	-2	1306	1362
-4	0	1664	1673
-4	2	718	698
-4	4	153	106
-3	-7	827	828
-3	-5	506	526
-3	-3	1280	1281
-3	-1	1336	1360
-3	1	627	656
-3	3	184	151
-3	5	491	461
-3	7	581	572
-2	-8	506	520
-2	-6	748	737
-2	-4	1038	998
-2	-3	188	176
-2	-2	802	799
-2	0	367	396
-2	2	685	662
-2	4	1231	1183
-2	5	163	80
-2	6	798	779
-1	-7	850	817
-1	-5	490	501
-1	-3	382	325
-1	-1	160	172
-1	1	663	690
-1	2	133	115
-1	3	1346	1326
-1	4	171	170
-1	5	1118	1097
-1	6	163	165
-1	7	534	545
0	-8	603	589
0	-6	385	338
0	-4	239	255
0	-3	259	265
0	-2	833	803
0	-1	253	260
0	0	1133	1097
0	1	221	201
0	2	1166	1128
0	3	346	344
0	4	953	939
0	5	244	236
0	6	638	626
1	-5	378	362
1	-4	250	261
1	-3	1270	1303
1	-2	389	385
1	-1	1000	1782
1	0	616	660
1	1	973	977
1	2	325	301
1	3	699	690
1	4	179	177
1	5	236	231
1	7	179	170
2	-6	280	273
2	-5	187	183
2	-4	1203	1188
2	-3	397	408
2	-2	1513	1529
2	-1	484	492
2	0	1310	1295
2	2	309	306
2	4	359	327
2	6	379	372
2	7	243	214
3	-7	512	501
3	-5	690	703
3	-4	627	607
3	-3	1034	1056
3	-2	601	618
3	-1	713	763
3	0	236	200
3	2	260	267
3	3	829	793
3	4	366	356
3	5	682	663
3	6	386	353
3	7	587	510
4	-8	560	568
4	-7	200	203
4	-6	658	686
4	-5	252	226
4	-4	556	582
4	-3	218	225
4	-2	267	220
4	1	203	203
4	2	1066	1125
4	4	1017	1029
4	5	916	920
4	6	552	567
4	7	200	195
5	-8	215	224
5	-7	683	622
5	-6	172	89
5	-5	206	185
5	-3	218	231
5	-1	634	661
5	0	352	333

K	L	FOBS	FCAL
5	1	879	892
5	2	577	600
5	3	965	980
5	4	685	680
5	5	569	569
5	6	175	169
6	-8	245	257
6	-5	201	218
6	-4	568	610
6	-3	365	412
6	-2	780	839
6	-1	631	660
6	0	820	791
6	1	672	650
6	2	698	723
6	3	622	638
6	4	605	607
7	-5	505	556
7	-4	517	575
7	-3	833	932
7	-2	599	639
7	-1	852	856
7	0	382	361
7	1	312	305
7	2	200	200
8	-7	171	159
8	-6	330	381
8	-5	617	659
8	-4	670	735
8	-3	559	599
8	-2	600	612
8	-1	331	343
8	0	175	225
8	2	229	199
8	3	193	197
8	4	298	306
8	5	230	255
9	-6	222	232
9	-5	326	391
9	-4	305	356
9	-3	375	388
9	1	358	392
9	2	646	635
9	3	519	526
9	4	619	623
10	-1	316	356
10	0	383	391
10	1	497	490
10	2	572	566
10	3	554	582
11	-6	208	211
11	-3	302	276
11	-2	389	359
11	-1	656	647
11	0	396	392
11	1	646	649
11	2	531	536
12	-3	368	381
12	-2	358	361
12	-1	358	358
12	0	244	244

K	L	FOBS	FCAL
-11	-1	535	525
-11	0	154	166
-11	1	536	529
-11	2	162	138
-10	-2	620	611
-10	-1	251	252
-10	0	660	663
-10	1	208	211
-10	2	358	346
-10	4	136	55
-9	-3	658	685
-9	-2	269	267
-9	-1	662	623
-9	0	242	231
-9	1	325	305
-9	3	361	352
-8	-5	196	161
-8	-4	366	362
-8	-2	609	602
-8	0	181	142
-8	2	260	291
-8	3	185	176
-8	4	675	658
-7	-5	279	296
-7	-3	233	280
-7	1	570	516
-7	2	327	332
-7	3	675	737
-7	4	639	661
-7	5	698	725
-6	-4	376	306
-6	-3	253	255
-6	-2	649	666
-6	-1	328	295
-6	0	680	646
-6	1	608	610
-6	2	647	713
-6	3	619	664
-6	4	695	655
-5	-6	699	696
-5	-5	238	292
-5	-4	220	238
-5	-3	703	696
-5	-2	566	556
-5	-1	846	868
-5	0	560	566
-5	1	573	579
-5	2	357	375
-5	3	252	263
-5	4	181	193

K	L	FOBS	FCAL
-4	-6	300	315
-4	-5	256	278
-4	-4	639	614
-4	-3	689	668
-4	-2	979	981
-4	-1	611	650
-4	0	539	551
-4	1	242	239
-4	4	274	296
-4	5	212	193
-4	6	265	254
-3	-7	378	406
-3	-6	308	310
-3	-5	459	433
-3	-4	502	502
-3	-3	694	706
-3	-2	606	571
-3	-1	381	432
-3	0	397	368
-3	1	549	569
-3	3	550	555
-3	4	263	258
-2	0	539	546
-2	1	102	156
-2	2	711	706
-2	4	244	255
-2	5	542	548
-2	6	658	659
-2	7	533	507

K	L	FOBS	FCAL
-10	0	171	164
-9	-2	436	411
-9	-1	178	165
-9	0	158	144
-9	2	200	165
-9	3	183	208
-8	-3	191	184
-8	1	350	356
-8	2	278	254
-8	3	500	517
-8	4	192	227
-7	-2	210	234
-7	-1	230	209
-7	0	495	501
-7	1	296	301
-7	2	662	696
-7	4	513	553
-6	-5	189	220
-6	-3	620	643
-6	-2	259	278
-6	-1	650	675
-6	0	258	257
-6	1	661	723
-6	2	200	208
-6	3	457	455
-5	-6	158	162
-5	-5	197	181
-5	-4	548	556
-5	-3	221	214
-5	-2	718	776
-5	0	699	515
-5	2	275	267
-4	-6	165	165
-4	-5	653	626
-4	-3	708	649
-4	-1	343	397
-4	3	336	298
-3	-7	447	512
-3	-6	675	641
-3	-2	219	218
-3	0	382	419
-3	2	693	648
-3	4	655	636
-2	-5	217	202
-2	-1	676	668
-2	1	1073	1020
-2	2	190	157
-2	3	883	830
-2	5	506	501
-1	-6	267	281
-1	-2	753	712
-1	0	897	957
-1	2	864	825
-1	4	668	667
0	-5	576	533
0	-3	952	795
0	-1	888	839
0	1	791	738
0	3	358	317
0	5	231	226
1	-6	632	613
1	-4	708	698
1	-2	806	748
1	0	255	248
1	4	375	373
1	5	602	576
2	-3	421	403
2	1	662	650
2	3	587	556
2	4	178	164
2	5	595	606
3	-6	618	602
3	-4	229	226
3	-2	380	345
3	0	931	926
3	2	797	798
3	4	606	631
4	-3	662	635
4	-1	762	825
4	0	276	206
4	1	630	620
4	3	579	571

K	L	FOBS	FCAL
5	-6	215	246
5	-4	373	408
5	-3	197	182
5	-2	692	730
5	0	776	727
5	1	272	233
5	2	426	447
6	-5	661	678
6	-3	528	548
6	-1	379	363
6	0	177	170
6	1	271	249
6	-6	355	395
7	2	221	237
7	3	188	161
8	-1	339	331
8	0	173	168
8	1	429	427
8	2	191	202
9	-2	400	421
9	-1	290	251
9	0	561	561

K	L	FOBS	FCAL
-7	-2	267	317
-7	0	549	573
-7	1	232	190
-7	2	651	687
-6	-3	330	378
-6	-1	439	462
-6	0	175	152
-6	1	346	356
-5	-4	453	465
-5	-3	174	163
-5	-2	323	346
-4	-3	226	213
-4	1	299	290
-4	3	352	359
-3	-4	167	133
-3	-2	224	225
-3	1	229	206
-3	0	597	566
-3	1	255	262
-3	2	577	550
-3	3	270	257
-3	4	394	373
-2	-3	218	246
-2	-2	277	249
-2	-1	716	640
-2	0	357	393
-2	1	669	658
-2	2	368	352
-2	3	406	376
-2	4	186	143
-1	-5	205	161
-1	-4	335	271
-1	-3	271	243
-1	-2	591	549
-1	-1	434	389
-1	0	515	592
-1	1	619	381
-1	2	371	323
0	-5	436	433
0	-4	23	242
0	-3	395	399
0	-2	314	331
0	-1	396	343
0	0	329	294
0	1	202	229
1	-5	329	332
1	-4	338	321
1	-3	178	181
1	-2	178	167
1	2	270	261
1	3	255	286
1	4	630	622
2	-5	286	255
2	-1	303	323
2	0	300	307
2	1	406	377
2	2	462	415
2	3	904	357
3	-3	285	273
3	-2	466	426
3	-1	541	497
3	0	696	681
3	1	495	516
3	2	325	335
3	3	277	277
4	-4	274	253
4	-3	385	382
4	-2	520	533
4	-1	628	662
4	0	568	530
4	1	290	315
4	2	177	206
5	-6	278	255
5	-3	387	433
5	-2	289	309
5	-1	616	648
5	0	219	236
5	1	180	175

K	L	FOBS	FCAL
-3	-1	690	689
-3	0	215	230
-2	-2	510	571
-2	-1	235	219
-2	0	675	658
-1	-1	502	476
0	-2	265	206
1	-1	191	198
1	1	661	693
2	-2	666	611
2	0	687	665

TABLE 11: FRACTIONAL COORDINATES

Atom	x	y	z
Re1	0.02212(8)	0.16212(5)	0.20948(7)
Re2	0.19138(8)	0.35578(5)	0.29300(7)
Si1	0.2768(5)	0.1950(3)	0.3623(5)
Si2	-0.0608(5)	0.3230(3)	0.1359(5)
C1	0.143(2)	0.141(1)	0.040(2)
C2	-0.166(2)	0.123(1)	0.093(2)
C3	0.054(2)	0.037(1)	0.266(2)
C4	-0.092(2)	0.187(1)	0.381(2)
C5	0.309(2)	0.342(1)	0.117(2)
C6	0.303(2)	0.479(2)	0.351(2)
C7	0.078(2)	0.378(1)	0.470(2)
C8	0.460(2)	0.147(1)	0.284(2)
C9	0.273(2)	0.172(1)	0.560(2)
C10	0.479(2)	0.040(1)	0.287(2)
C11	0.426(2)	0.216(2)	0.650(2)
C12	-0.057(2)	0.342(1)	-0.061(2)
C13	-0.242(2)	0.369(1)	0.208(2)
C14	-0.198(2)	0.292(2)	-0.157(2)
C15	-0.288(2)	0.469(2)	0.169(2)
O1	0.212(2)	0.130(1)	-0.059(1)
O2	-0.281(2)	0.097(1)	0.027(1)
O3	0.081(2)	-0.041(1)	0.293(2)
O4	-0.164(2)	0.199(1)	0.482(1)
O5	0.378(1)	0.336(1)	0.019(1)
O6	0.362(2)	0.550(1)	0.393(2)
O7	0.015(2)	0.394(1)	0.574(1)

TABLE 12: THERMAL PARAMETERS ($\AA^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B(\AA^2)^a$
Re1	0.0497(5)	0.0456(5)	0.0432(5)	-0.0010(4)	-0.0004(3)	0.0031(4)	3.67
Re2	0.0448(5)	0.0436(5)	0.0483(4)	0.0010(4)	-0.0038(4)	0.0039(4)	3.63
Si1	0.0585(30)	0.0501(26)	0.0519(26)	0.0069(23)	-0.0042(21)	0.0098(21)	4.22
Si2	0.0512(28)	0.0553(27)	0.0483(25)	-0.0024(23)	-0.0051(21)	0.0101(21)	4.09
C1	0.070(13)	0.058(11)	0.071(14)	0.003(10)	0.014(11)	-0.013(11)	5.33
C2	0.076(13)	0.056(10)	0.040(10)	-0.017(9)	0.005(9)	-0.012(8)	4.68
C3	0.087(14)	0.053(11)	0.051(11)	-0.017(10)	-0.020(10)	0.008(9)	5.13
C4	0.055(12)	0.060(11)	0.059(13)	0.009(9)	0.006(10)	0.001(10)	4.58
C5	0.050(10)	0.054(10)	0.051(9)	-0.008(8)	-0.005(8)	0.014(8)	4.08
C6	0.038(10)	0.096(15)	0.067(12)	0.001(10)	-0.014(8)	0.001(11)	5.39
C7	0.074(12)	0.051(11)	0.052(10)	0.003(9)	-0.001(9)	0.006(8)	4.68
C8	0.057(12)	0.075(12)	0.082(14)	0.021(10)	0.012(10)	0.019(10)	5.50
C9	0.083(13)	0.077(12)	0.044(10)	-0.004(11)	-0.010(9)	0.015(9)	5.40

TABLE 12 CONTINUED

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B(Å^2)[a]
C10	0.091(15)	0.065(13)	0.111(15)	0.027(11)	0.011(12)	0.025(12)	6.88
C11	0.092(15)	0.111(17)	0.069(13)	-0.014(13)	-0.033(11)	0.019(12)	7.28
C12	0.091(14)	0.067(12)	0.049(10)	-0.012(11)	-0.003(9)	0.008(8)	5.50
C13	0.054(11)	0.065(12)	0.089(13)	0.011(9)	0.000(9)	0.008(10)	5.48
C14	0.095(15)	0.101(15)	0.057(11)	-0.026(13)	-0.023(10)	0.019(11)	6.75
C15	0.066(13)	0.060(12)	0.115(16)	0.021(10)	0.004(11)	-0.000(11)	6.38
O1	0.111(12)	0.099(11)	0.074(10)	-0.009(9)	0.033(9)	-0.012(8)	7.52
O2	0.084(10)	0.093(10)	0.074(9)	-0.015(9)	-0.009(8)	-0.011(8)	6.79
O3	0.124(13)	0.063(9)	0.120(11)	0.007(9)	-0.006(9)	0.021(8)	8.06
O4	0.089(11)	0.107(11)	0.060(9)	-0.013(9)	0.008(8)	0.011(8)	6.75
O5	0.070(9)	0.101(10)	0.078(9)	0.007(8)	0.021(7)	0.010(8)	6.48
O6	0.087(11)	0.069(9)	0.124(12)	-0.020(8)	-0.024(9)	-0.002(9)	7.61
O7	0.108(11)	0.085(10)	0.076(9)	0.012(9)	0.031(8)	-0.018(7)	7.15

[a]Equivalent isotropic thermal parameter.

TABLE 13: INTRAMOLECULAR DISTANCES[a] (Å)

Atoms	Distance	Atoms	Distance
Re1-Re2	3.052(1)	Re2-Si1	2.539(4)
Re1-Si1	2.547(5)	Re2-Si2	2.549(4)
Re1-Si2	2.548(5)	Re1-C1	1.96(2)
Re1-C2	1.93(2)	Re1-C3	1.92(2)
Re1-C4	1.94(2)	Re2-C5	1.98(2)
Re2-C6	1.97(2)	Re2-C7	1.98(2)
C1-O1	1.13(2)	C2-O2	1.15(2)
C3-O3	1.18(2)	C4-O4	1.16(2)
C5-O5	1.12(2)	C6-O6	1.12(2)
C7-O7	1.15(2)	Si1-C8	1.90(2)
Si1-C9	1.91(2)	Si2-C12	1.89(2)
Si2-C13	1.85(2)	C9-C11	1.59(2)
C8-C10	1.53(2)	C12-C14	1.56(2)
C13-C15	1.54(2)		

[a]Standard deviations in parentheses refer to last digit quoted.

TABLE 14: INTRAMOLECULAR ANGLES (DEGREES)

Atoms	Angle	Atoms	Angle
Si1-Re2-Re1	53.3(1)	Si1-Re1-Re2	53.0(1)
Si2-Re2-Re1	53.2(1)	Si2-Re1-Re2	53.2(1)
Re2-Si1-Re1	73.7(1)	Re2-Si2-Re1	73.5(1)
Si1-Re1-C3	80.4(5)	Si2-Re1-C2	79.8(5)
Re2-Re1-C1	89.7(5)	Re2-Re1-C4	88.2(5)
Re1-Re2-C5	92.4(5)	Re1-Re2-C6	178.6(5)
Re1-Re2-C7	91.1(5)	Re1-C1-O1	179(2)
Re1-C2-O2	178(2)	Re1-C3-O3	175(2)
Re1-C4-O4	178(2)	Re2-C5-O5	178(2)
Re2-C6-O6	175(2)	Re2-C7-O7	178(2)
C8-Si1-C9	110.4(8)	C12-Si2-C13	109.6(8)
C10-C8-Si1	115(1)	C11-C9-Si1	110(1)
C14-C12-Si2	114(1)	C15-C13-Si2	116(1)
Si1-Re2-C6	125.5(5)	Si2-Re2-C6	128.0(5)

TABLE 15: LEAST SQUARES PLANE CALCULATIONS [a]

FOR $Re_2(CO)_7H_2(SiEt_2)_2$

(A) ATOMS DEFINING PLANE: Re1, Re2, Si1, Si2

EQUATION OF PLANE:

$$-0.5693X + 0.0653Y + 0.8195Z - 1.6898 = 0.0$$

DISTANCES OF ATOMS FROM PLANE:

Re1	0.0029		
Re2	0.0031		
Si1	-0.020	Si2	-0.020
C6	0.026	O6	0.127
C2	-0.017	O2	0.002
C3	0.179	O3	0.184
C5	-1.980		

(B) ATOMS DEFINING PLANE: Re1, Re2, C1, C4, C5, C7.

EQUATION OF PLANE:

$$0.6782X - 0.5229Y + 0.5163Z + 0.0354 = 0.0$$

DISTANCES OF ATOMS FROM PLANE:

Re1	0.0004	Re2	0.0004
C1	0.049	C4	-0.029
C5	-0.049	C7	0.016
O1	0.065	O4	-0.055
O5	-0.077	O7	0.038
C6	0.043	O6	0.089
Si1	-2.041		

[a] X, Y, and Z are orthogonal coordinates (Å) with X along the a-axis, Y in the (a,b) plane, and Z along the c^*-axis.

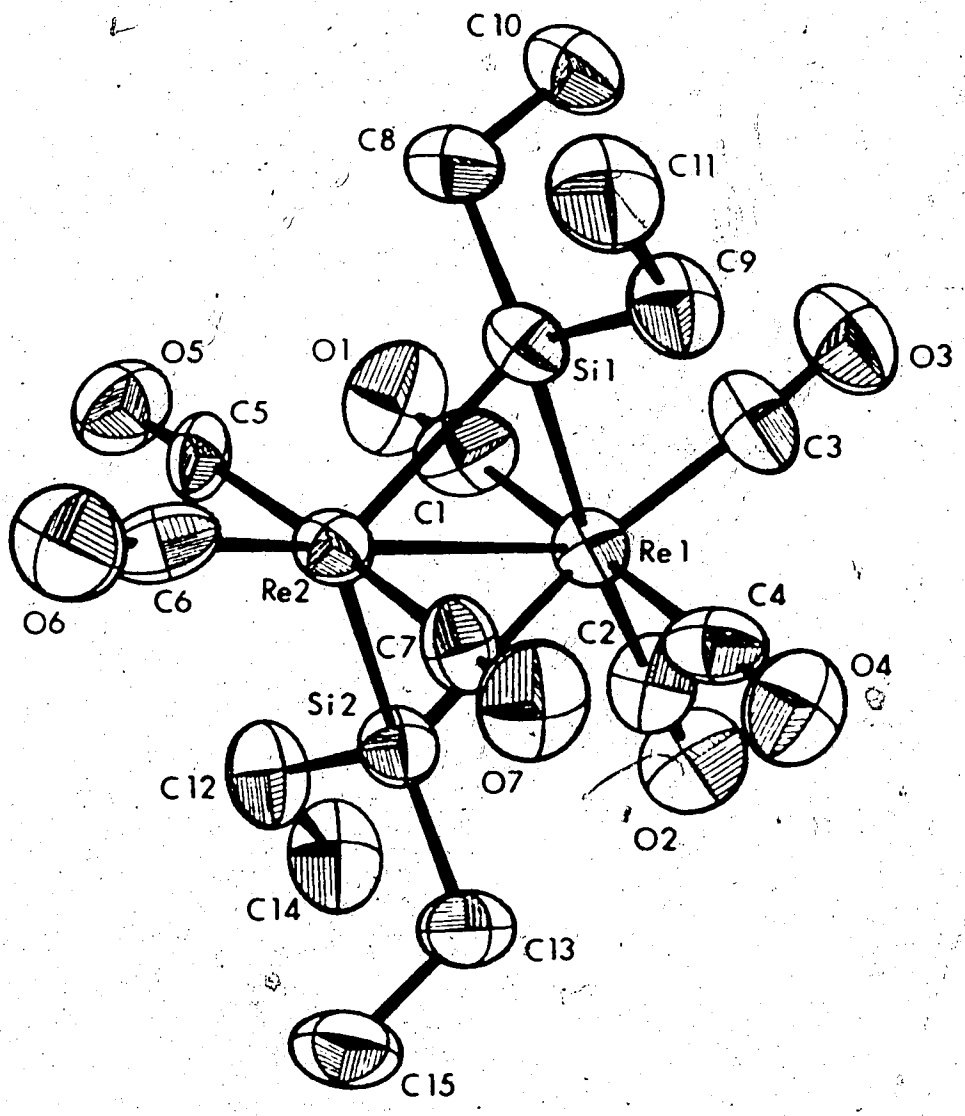


Fig. 5: A PERSPECTIVE VIEW OF $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$.

DESCRIPTION OF STRUCTURE

$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ has approximate C_s symmetry. A perspective view of the molecule is shown in Fig. 5. The central cluster is similar to that of $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ shown in Chapter II. The two rhenium atoms and two silicon atoms are planar and located at the corners of a rhombus, with like atoms at opposing corners, and a rhenium-rhenium bond across the shorter diagonal. Two carbonyl groups (C303 and C202) on Re1 are also approximately in this plane and *trans* to the Re1-Si1 and Re1-Si2 bonds, while one carbonyl group (C606), also in this plane and bonded to Re2, lies along the Re-Re bond. The two remaining carbonyls on each rhenium are perpendicular to the Re_2Si_2 plane above and below the rhenium atoms.

The rhenium-carbon (carbonyl) and carbon-oxygen distances are regular and similar to those observed in $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and other rhenium carbonyl compounds.[64,65,82,83,87,88,89] The coordination around the silicon atoms is a distorted tetrahedron due to the small Re1-Si-Re2 angles. There are no unusual distances in the silicon-carbon (ethyl) or carbon-carbon (ethyl) bonds (compare Chapter II). The rhenium-rhenium distance [3.052(1) Å] is consistent with a rhenium-rhenium single bond, and this is further

substantiated by the acute Re1-Si1-Re2 and Re1-Si2-Re angles of 73.7(1)° and 73.5(1)°. It is also interesting that there is a progression in Re-Re bond lengths through the series $Re_2(CO)_8[Si(C_6H_5)_2]_2$,[64] $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_8H_2Si(C_6H_5)_2$,[65] whereas the Re-Si bonds are approximately constant (Table 16).

The longer Re-Re bond in $Re_2(CO)_8H_2Si(C_6H_5)_2$ reflects the fact that only one Si bridge is constraining the rhenium atoms together and also that the two extra eclipsed carbonyls are present causing added repulsion of the two $Re(CO)_4$ moieties. It is believed however that the Re-Re bond length differences in the other three compounds indicate that there is significant π bonding present in the Re-Re bonds whereas the Re-Si bonds are primarily σ. Thus varying the number of π-withdrawing carbonyl groups in the molecules would be expected to affect the Re-Re bonds if π bonding is important, but have little effect on the Re-Si bonds if the π bonding contribution here is not great.

Using the covalent radii of Pauling[27] for Si (1.17 Å) and Re (1.283 Å) a single bonded Re-Si distance of 2.45 Å is predicted, which is less than the observed value of approximately 2.54 Å in these

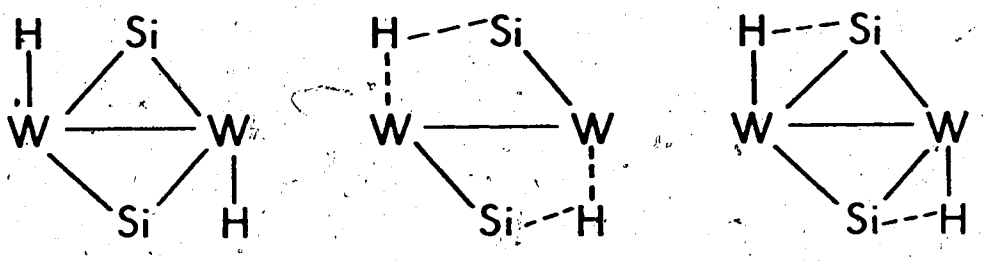
compounds (Table 16). Although the radius used for rhenium may not be suitable, the larger observed Re-Si bond length does not weaken the argument that rhenium-silicon π bonding is of little significance in these compounds. A similar trend was observed[90] in $Cl(\pi C_5H_5)_2ZrSi(C_6H_5)_3$ where the observed Zr-Si distance [2.813(2) Å] exceeded the value calculated with Pauling radii (2.62 Å). Here Zr(IV) is formally d^0 so no back-donation into empty silicon d orbitals can occur. Thus it was postulated that only σ bonding was important. This contrasts with $Co(SiCl_3)(CO)_4$[91] and $RhHCl(SiCl_3)(PPh_3)_2$,[92] where the Co-Si [2.254(3) Å] and Rh-Si [2.303(4) Å] distances are both less than the values predicted using Pauling's covalent radii (2.33 Å and 2.42 Å respectively). It seems therefore that metal-silicon π bonding is present in these two compounds, whereas it is minimal in the zirconium and rhenium compounds. Any explanation of bond shortening as due to π bonding in these transition metal silyl compounds should be approached cautiously, however, since it is difficult to separate these effects from a σ-inductive effect. Thus the changes in metal-silicon distances in the series $(\pi\text{-}C_5H_5)(CO)_2HMnSi(C_6H_5)_3$,[93] [2.424(2) Å]; $(\pi\text{-}C_5H_5)(CO)_2HMnSiCl_2(C_6H_5)$,[94] [2.310(2) Å]; and also

the series $Co(SiH_3)(CO)_4$,[95] [2.381(7) Å]; $Co(SiCl_3)(CO)_4$,[91] [2.254(3) Å]; and $Co(SiF_3)(CO)_4$,[96] [2.226(5) Å]; can be attributed to shrinkage of the silicon orbitals by the more electronegative substituents, thereby shortening the metal-silicon bonds.

However uncertain the mode of bonding between the rhenium and silicon atoms, it is still possible to compare the distances within the series mentioned in Chapter II since all substituents are similar. Thus the most interesting feature of $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ is the similarity in the Re-Si bond lengths and their similarity to the other members of the series. The Re2-Si1 and Re2-Si2 bonds are adjacent to the hydrogen ligands whereas the Re1-Si1 and Re1-Si2 bonds are "hydrogen-free". As was explained in Chapter II, the similarity of these bonds in the two differing environments is not expected in view of the proposed hydrogen bridging.[62,63] Again, complete discussion of this phenomenon is deferred until Chapter IV.

CHAPTER IV: MODE OF BONDING OF THE HYDRIDE LIGANDS IN $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ AND $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$

Although location of the hydrogen atoms in this series of hydrides was not possible due to high dominance of the rhenium and tungsten scattering and also large absorption effects, location of the central framework, in particular the transition metal-silicon bond, has proved exceedingly valuable in obtaining information about the bonding exhibited by the hydrogens attached to the metals.[66] Three possibilities exist for the hydrogen bonding in these compounds as shown for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ in Fig. 6: (1) the hydrogen is terminally bonded to the transition metal with no interaction with the silicon, (2) the hydrogen bridges the transition metal-silicon bond thus forming a three centre two electron bond, and (3) the hydrogen is terminally bonded to the transition metal, but with weak attractive interaction with the silicon. A hydrogen bridge of type (2) was postulated[66] for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ in which the W-Si distances differed significantly (Table 16), with the hydrogen presumably bridging the longer distance. However,



(1) (2) (3)

Fig. 6: Possible Bonding Schemes for the Hydrogen Ligand in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$.

in $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ the Re-Si bond lengths are not consistent with a three centre Si-H-Re bond, but rather seem consistent with a terminally bound hydrogen ligand.

It was expected that if the hydrogen was involved in a three centre Si-H-Re bond, a significant lengthening of this Si-Re distance would be observed, analogous to $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$. There is no significant difference in Re-Si bond lengths, however, between the two hydrides $Re_2(CO)_8H_2Si(C_6H_5)_2$[65] and $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$, and $Re_2(CO)_8[Si(C_6H_5)_2]_2$[64] which contains no hydrogen ligand. Moreover these Re-Si distances are similar to the shorter (unbridged) W-Si distance in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$, and therefore

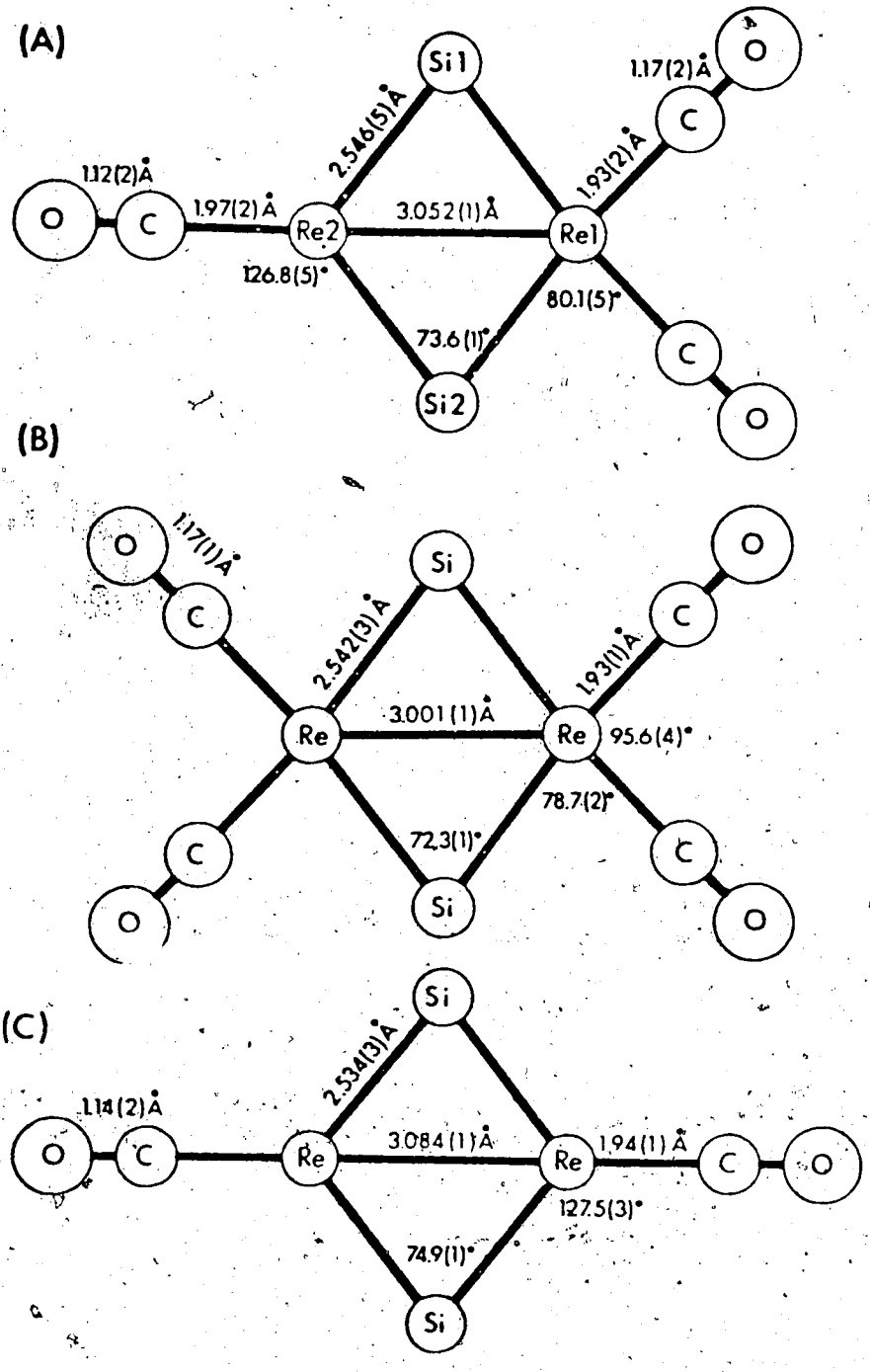


Fig. 7: A COMPARISON OF THE GEOMETRIES OF (A) $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, (B) $Re_2(CO)_8[Si(C_6H_5)_2]_2$, AND (C) $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$.

are more consistent with terminal hydrides.

The ambiguity in comparison of the Re-Si bond lengths in the hydrides and $Re_2(CO)_8[Si(C_6H_5)_2]_2$, in which the disorder problem existed (Appendix 1), was overcome with the structural determination of $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, which, like the tungsten complex, was an internal standard containing metal-silicon bonds both adjacent to hydrogen ligands and "hydrogen-free". The similarity of the Re-Si bonds in this structure was added proof that the hydrogen ligands were not bonded in a fashion analogous to $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ and were therefore probably bound terminally to the rhenium atom. This reinforced the previous argument that the other rhenium hydrides in this series were also terminal. Fig. 7 shows $Re_2(CO)_8[Si(C_6H_5)_2]_2$, $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ and $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ viewed perpendicular to the Re_2Si_2 planes and including only those atoms lying approximately in this plane. Included are relevant bond lengths and angles for ready comparison of the three.

To explain why the hydrogen ligands seem to be terminally bound for the rhenium compounds, but bridging in the case of the tungsten compound, it is useful to consider the coordination about the metal atoms, as shown in Fig. 8. In each compound there are two mutually *trans* carbonyl groups on each metal which are not shown. These are perpendicular to the

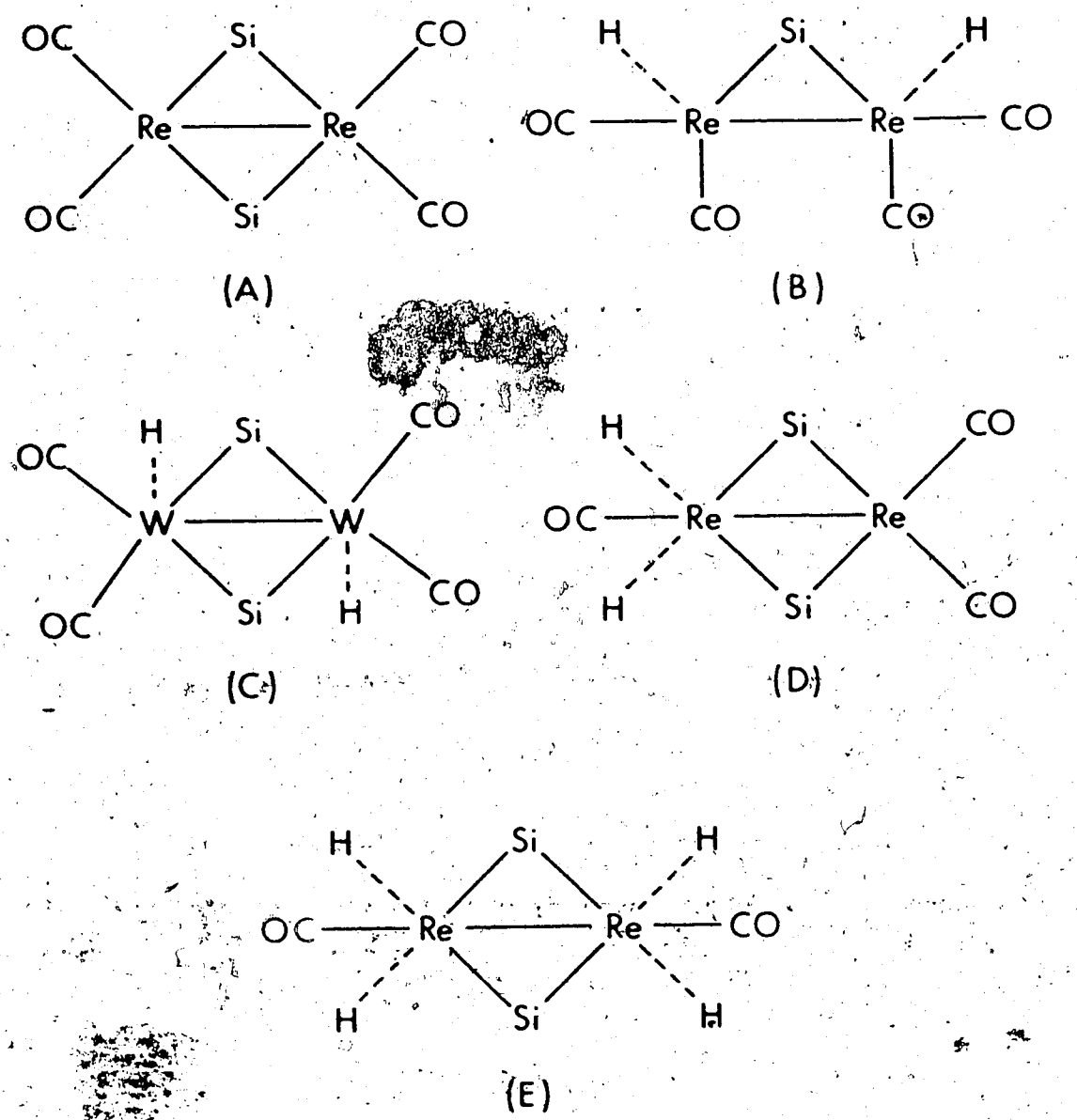


Fig. 8: HYDROGEN LIGAND ENVIRONMENTS IN THE SILICON BRIDGED TRANSITION METAL HYDRIDES.

TABLE 16: RELEVANT BOND LENGTHS (Å)

IN SOME TRANSITION METAL SILICON-BRIDGED COMPLEXES

COMPOUND	M-Si	M-M	REFERENCE
$W_2(CO)_8H_2[Si(C_2H_5)_2]_2$	2.586(5), 2.703(4)	3.183(1)	66
$Re_2(CO)_8H_2Si(C_6H_5)_2$	2.544(9)	3.121(2)	65
$Re_2(CO)_8[Si(C_6H_5)_2]_2$	2.542(3)	3.001(1)	64
$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$	2.533(2), 2.535(3)	3.084(1)	THIS WORK
$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$	2.547(5), 2.548(5) 2.539(4), 2.549(4)	3.052(1)	THIS WORK

TABLE 17: RELEVANT ANGLES (DEGREES) IN SOME TRANSITION METAL SILICON-BRIDGED COMPLEXES

COMPOUND	Si-M-M	M-Si-M	Si-M-C
$W_2(CO)_8H_2[Si(C_2H_5)_2]_2$	53.02(10)	73.97(12)	109.1(5)
$Re_2(CO)_8H_2Si(C_6H_5)_2$	53.9(1)	72.3(1)	124.8(13)
$Re_2(CO)_8[Si(C_6H_5)_2]_2$	52.2(2)	75.7(3)	78.7(2)
$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$	52.6(1)	74.9(1)	127.5(3)
$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$	53.2(1)	73.6(1)	126.8(5)

plane of the central cluster and are a constant feature of all the structures. Hydrogen atoms, although not located experimentally, are positioned in what are thought to be their approximate locations.

Viewing the hydrogen ligand environments in the examples shown, it is obvious that in the tungsten hydride (C), the hydrogen is more crowded than in the rhenium hydrides. The Si-W-C (carbonyl) angle, which encloses the hydrogen ligand is 109.1(5)° in the tungsten hydride, compared to the analogous angles of 124.8(13)°, 126.8(5)°, and 127.5(3)° in the rhenium hydrides (B), (D), and (E) respectively. It has been shown[93,94,97] that a normal non-bonded H-C (carbonyl) contact can be as low as 2.0 Å. For a Re-H distance[29] of 1.68 Å calculations show that in the rhenium hydrides, maintaining the minimum C-H contact, a H-Si contact of greater than 2.2 Å arises. However the situation is much different for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$. If no hydrogen bridging concept is utilized, then using the unbridged W-Si distance of 2.586 Å, and maintaining the minimum C-H contact, a very short Si-H contact of 1.72 Å occurs (this calculated assuming a W-H distance[98] of 1.70 Å). Even using the larger W-Si distance, a short Si-H contact of 1.81 Å arises. Therefore the hydrogen

ligands are constrained to be considerably closer to the silicon atoms in the tungsten compound. It is believed that the crowding of the hydrogen by the carbonyl group is then responsible for the appearance of the three centre W-H-Si bond, since it is possible that the three centre bond is favoured energetically over a terminal hydride involving the high repulsion energy which must be associated with the very short Si-H non-bonded contacts mentioned.

The non-bonded Si-H contact of 2.2 Å calculated for the rhenium hydrides is believed to be reasonable. In $(\pi\text{-}C_5H_5)(CO)HFe(SiF_3)_2$ the hydrogen was not believed[99] bonded to either silicon atom and was located at 2.06(7) Å from both silicons. Although seemingly short, these non-bonded contacts can occur because in these systems the hydrogens approach the silicon atoms in electron density nodes, for example between the F-Si-F covalent bonds in $(\pi\text{-}C_5H_5)(CO)HFe(SiF_3)_2$, or between the C-Si-C bonds in the rhenium hydrides discussed. The repulsion is minimized in these bonding nodes thus facilitating the approach of the hydrogen ligand to the silicon atom.

There seems therefore to be no inherent stability of the hydrogen-bridged metal-silicon bond. Rather, the three centre bond is the result of steric crowding

by an adjacent carbonyl group and only appears, as for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$, when the hydrogen ligand is restricted to be close to the silicon atom.

Although evidence obtained from the structural investigations of $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ combined with that obtained from[64,66] $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ and $Re(CO)_8[Si(C_2H_5)_2]_2$ exclude the possibility of a three centre Re-H-Si bond, it does not exclude the existence of weak attractive interaction of the hydrogen ligand with the silicon atom. An insight into this possibility is gained from the structural investigations[93,94,97] of $(\pi\text{-}C_5H_5)(CO)_2HMnSi(C_6H_5)_3$, $(\pi\text{-}C_5H_5)(CO)_2HMnSiCl_2(C_6H_5)$ and $(CO)_4FeHSi(C_6H_5)_3$, in which the hydrogen ligands were located experimentally. In both manganese compounds the hydrogens were located at 1.55(4) Å and 1.49(6) Å respectively from the manganese atoms and 1.76(4) Å and 1.79(6) Å respectively from the silicon atoms. However, in the iron compound the hydrogen atom was 1.64(10) Å from the iron atom and 2.73(10) Å from the silicon atom. In the two manganese hydrides the hydrogen ligands are constrained to be close to the silicon atoms due to steric crowding, the hydrogen being only 2.08(4) Å from the carbonyl in $(\pi\text{-}C_5H_5)(CO)_2HMnSi(C_5H_5)_3$ and 1.98(6) Å from the carbonyl

in $(\pi\text{-}C_5H_5)(CO)_2HMnSiCl_2(C_6H_5)$. There is no possibility of increasing the H-Si distance without increasing the hydrogen contact with the carbonyl groups. However in $(CO)_4FeHSi(C_6H_5)_3$ the hydrogen is not constrained to be close to the silicon atom, since it is in a sterically less crowded environment than the manganese hydrides. Thus the long Si-H contact observed is indicative of a terminally bound hydrogen with no attraction to the silicon atom. This is interpreted as meaning that there is no inherent stability of the weakly bridged hydrogen in this series in preference to a simple terminal hydrogen.

Thus in conclusion, in this series of transition metal hydrides, the hydrogen atoms are bound terminally to the transition metals in all the rhenium complexes. The hydrogens only approach the silicon atoms, as in the tungsten and manganese complexes, as a result of steric crowding and not as a result of any unusual attraction to the silicon atoms.

CHAPTER V: DITHIOLENE[100] INTRODUCTION

Interest in the bidentate dithiolene ligands began in the mid 1930's when R. E. D. Clark discovered[101,102] that toluene-3,4-dithiol and 1-chlorobenzene-3,4-dithiol reacted with zinc, cadmium, mercury and tin halides to form complexes of the type $[M(dithiol)_2]$. This reaction was found to be especially effective in the analytical determination of tin[103,104] and of molybdenum and tungsten[105,106,107] and most attention was directed towards this end. By the early 1960's several dithiolene complexes had been characterized[108,109,110] and were found to be of the form $M(dithiol)_2$ involving a variety of dithiolene ligands combined with nickel, cobalt, palladium, and molybdenum. These *bis* dithiol complexes were found to possess two unusual properties. Firstly, they exhibited the unusual square planar geometry[111,112,113,114] with the sulfur atoms in an almost perfect square about the metal. And secondly, they underwent facile reversible oxidation-reduction reactions[115] without changes in coordination geometry. The oxidized and reduced species were found to be related simply by one electron transfers and could be detected using polarography and voltammetry.

Attempts to produce the *bis* complexes of $S_2C_2Ph_2$ with V, Cr, Mo, Re, W, Ru, and Os[116] instead yielded

the six coordinate *tris* complexes[117,118,119] which were similar to the *bis* complexes in that they also underwent the facile oxidation-reduction reactions.[119,120,121] The discovery[122] that $Co[S_2C_2(CN)_2]_2^-$ reversibly added one mole of ligand to form the complex $Co[S_2C_2(CN)_2]_3^{3-}$ led to the interesting suggestion that the six coordinate cobalt complex and possibly even the other *tris* complexes could be trigonal prismatic. In addition doubt about the octahedral coordination of these complexes was raised because of the inability to separate $Co[S_2C_2(CN)_2]_3^{3-}$ and $Mo[S_2C_2(CF_3)_2]_3$ into their optical enantiomers.[123] The possibility of trigonal prismatic coordination was extremely unusual since no six coordinate molecular complexes had been observed with non-octahedral coordination. Trigonal prismatic coordination *had* been observed[125] as early as 1923 in the compounds MoS_2 and WS_2 and later[126] in NiAs. However these were infinitely extended lattices and molecular packing was believed responsible for their unusual coordination.[124] It is noteworthy that on the basis of "directed valence" calculations, it had even been predicted by Hultgren[127] in 1932, that the only stable six coordinate complexes were trigonal prismatic and octahedral, the former being preferred for low lying d orbitals and the latter being preferred

for higher energy d orbitals. In addition octahedral coordination would be favoured by increasing ionic character in the metal-ligand bonds and by the bulkiness of large ligands.

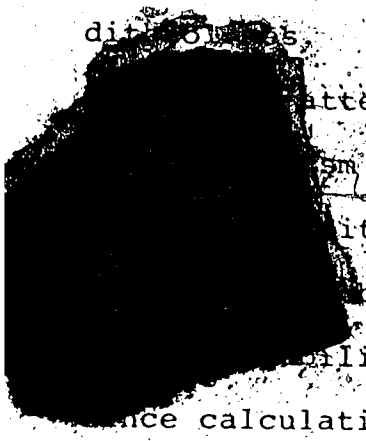
The existence of trigonal prismatic coordination in a molecular complex was not observed until 1965 when the X-ray structure determination[128,129] of $Re[S_2C_2(C_6H_5)_2]_3$ was completed. The subsequent structural determinations of $Mo(S_2C_2H_2)_3$[130] and $V[S_2C_2(C_6H_5)_2]_3$[131,132] also showed trigonal prismatic geometry and verified that the rhenium compound was not an isolated example but only one of a possible series of trigonal prismatic structures. In all three compounds the metals were surrounded by six sulfur atoms at the corners of a trigonal prism, with the dithiolene ligands radiating from the metals in a "paddle-wheel" arrangement. There was also a striking similarity in the prism dimensions of the three compounds (Table 48). The intra- and interligand sulfur-sulfur distances are similar in all cases with the approximate values 3.06 Å and 3.08 Å respectively. The shortness of these "non-bonded" contacts led to the speculation that some sulfur-sulfur bonding was involved[124] in stabilizing the trigonal prism. Another remarkable feature of the three complexes was

the similarity in the metal-sulfur bond lengths, averaging 2.33 Å, despite the fact that the covalent and ionic radii[133] of vanadium differed from those of molybdenum and rhenium by 0.07 Å. This similarity was viewed as an added consequence of the interligand S-S bonding.[124] In addition the S-C distances, averaging 1.69 Å were found to be consistent with considerable double bond character as seen from a comparison with the S=C double bond in thiourea[134] $[SC(NH_2)_2]$ and its derivatives,[135] measuring 1.720 Å.

Slight differences are, however, present in the three compounds which lead to distortions from the idealized D_{3h} symmetry. $Re[S_2C_2(C_6H_5)_2]_3$ and $Mo[S_2C_2(CN)_2]_3$ both have approximate C_{3h} symmetry caused by twisting of the phenyl groups out of the ligand planes in the former and by a deviation of the S_2C_2 planes from the MS_2 planes by 18° in the latter. In $V[S_2C_2(C_6H_5)_2]_3$ the unique ligand on the crystallographic two-fold differs slightly from the other two, however the molecule still closely approximates D_{3h} symmetry.

Comparison of the electron spin resonance and electronic spectra in the solid state and in solution[136] confirmed that the trigonal prismatic coordination was also present in solution and therefore was a

consequence of intramolecular phenomena rather than intermolecular effects. It was also apparent in all the electronic spectra that the dominant feature was an intense two-band pattern in the visible region,[137] the first at about 15,000 cm^{-1} (ε ~ 25000) and the second at about 24,000 cm^{-1} (ε ~ 15000). This was believed to be characteristic of all trigonal prismatic di[illegible]



[illegible]ttempt to explain the stability of the [illegible]sm over the octahedron, two separate [illegible]ital treatments were presented. In [illegible]y Schrauzer and Mayweg[138] no reason [illegible]ility of the trigonal prism is obvious [illegible]nce calculations performed on a hypothetical octahedral complex $MS_6C_6R_6$ yielded the same orbital ordering as the trigonal prismatic calculations. Also objections based on electron spin resonance spectra have been raised[139] concerning the ordering of the highest occupied and lowest unoccupied levels for this scheme. The scheme by Gray *et. al.*,[137] which seems more consistent with electron spin resonance spectra, electronic spectra and polarographic work is therefore favoured in this work. Both schemes are discussed further in Chapter IX where a detailed explanation of the trigonal prism is given based on

Gray's molecular orbital calculations.

Although the neutral *tris* dithiolenes were found to be trigonal prismatic, subsequent structural determinations on $V[S_2C_2(CN)_2]_3^{2-}$,[142] $Mo[S_2C_2(CN)_2]_3^{2-}$,[141] and $Fe[S_2C_2(CN)_2]_3^{2-}$[142] showed coordinations which varied from highly distorted octahedrons for the vanadium and molybdenum dianions to an almost regular octahedral coordination for the iron dianion. Interligand sulfur-sulfur distances in the three were greater than for the neutral trigonal prisms and thus were consistent with a breakdown in the sulfur-sulfur bonding which had been proposed[124] as a stabilizing factor in the prism. In addition the extra electrons in the molybdenum dianion as compared to the neutral molybdenum complex were located in an orbital which was said to be antibonding in the trigonal prism[141] thus offering an explanation of the deviation from the trigonal prismatic coordination. The trend therefore emerged that the neutral *tris* 1,2-dithiolenes were trigonal prismatic whereas the dianions were octahedral or distorted octahedral. The reasons for the trigonal prismatic and octahedral coordination in these dithiolenes was not obvious however and little was published correlating the observed structures to the molecular orbital descriptions of either Gray or

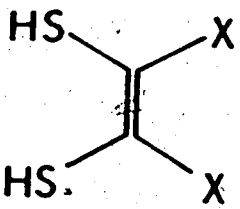
Schrauzer.

The compounds $Mo(S_2C_6H_4)_3$, $[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$, and $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$, which form the subject matter for the remainder of this thesis, therefore constitute an interesting and potentially informative series. Firstly the $M(S_2C_6H_4)_3^{n-}$ (n = 0, 1, 2 for M = Mo, Nb, Zr, respectively), moeities form an isoelectronic series so that the only differences are in the central metal. From a molecular orbital viewpoint, this means only the d orbital energies vary throughout the series. Hence, the effect that varying the central metal, and thus the metal d orbitals, will have on the coordination of the metals can be observed, and hopefully correlated to Gray's molecular orbital description for trigonal prismatic geometry. Also since identical ligands ($S_2C_6H_4^{2-}$) are involved, subtle geometry changes involving angles and bond lengths can be more readily compared, than if differing ligands are used.

From a comparison of their electronic spectra[137,143] in Table 18 it is obvious that gross differences exist within the three compounds. For the molybdenum[137,144] and niobium[143] complexes the spectra were similar, both having absorptions which were believed characteristic of trigonal prismatic

coordination.[137] The spectrum[143] of $Zr(S_2C_6H_4)_3^{2-}$ however, was found to be vastly different and was not indicative of a trigonal prism. Thus on the basis of the electronic spectral results it seems that varying the central metal from Mo to Nb to Zr causes changes in the coordination, presumably destabilizing the trigonal prism and favouring a tendency towards octahedral coordination as was observed in $Mo[S_2C_2(CN)_2]_3^{2-}$ and $V[S_2C_2(CN)_2]_3^{2-}$. It was believed that a complete structural determination of this series of *tris* 1,2-dithiolene complexes would prove useful in understanding further the factors which stabilize trigonal prismatic coordination. It was also of interest to discover whether the electronic spectra were reliable indicators of the coordination geometry in these compounds.

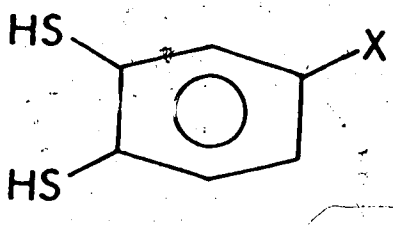
The common 1,2-dithiol ligands and their normal abbreviations, which will be used in this thesis, are shown below.



X = H dithioglyoxal

= CN maleonitrile-dithiol (mnt)

= C_6H_5 *cis* 1,2-diphenyl-ethene-1,2-dithiol (sdt)



X = H benzene-1,2-dithiol (bdt)

= CH_3 toluene-3,4-dithiol (tdt)

TABLE 18: ELECTRONIC SPECTRA FOR MOLYBDENUM, NIOBIUM, AND ZIRCONIUM BENZENE DITHIOLS[137,143]

COMPLEX	COLOUR	BAND MAXIMA, cm^{-1} (ε in parentheses)
$Mo(S_2C_6H_4)_3$ [144]	Dark Green	11,500 sh (1000); 14,463 (20,900); 22,990 (17,400).
$[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$	Dark Purple	17,700 (10,700); 27,200 (13,800); 30,700 sh (9,120).
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_4)_3]$	Red	20,000 sh (2,030); 35,800 sh (25,200).

CHAPTER VI: THE CRYSTAL AND MOLECULAR STRUCTURE OF *TRIS* (BENZENE-1,2-DITHIOLATO) MOLYBDENUM, $[Mo(S_2C_6H_4)_3]$.

EXPERIMENTAL

Dark green crystals of $Mo(bdt)_3$ suitable for X-ray diffraction study, prepared by the reaction of molybdenum pentachloride with benzene dithiol,[137] were kindly supplied by Dr. Takats and Mr. Martin.[143] Preliminary photography revealed mmm Laué symmetry, indicating an orthorhombic space group. The systematic absences as determined from Weissenberg ($0k\ell$, $1k\ell$; CuK_α X-radiation) and Precession ($h0\ell$, $h1\ell$, $hk0$, hkl; MoK_α X-radiation) photographs are $0k\ell$: $k + \ell = 2n + 1$ and $h0\ell$: $h = 2n + 1$, consistent with the space groups Pnam and $Pna2_1$. Precise lattice parameters were obtained at 22°C from a least squares refinement of the setting angles of 12 reflections which were accurately centred on a Picker automatic four-circle diffractometer, using CuK_{α_1} X-radiation (λ = 1.54051 Å). The cell parameters and their standard deviations are: a = 16.093(3) Å, b = 10.177(1) Å, and c = 11.906(2) Å.

The observed density, obtained by floatation in aqueous zinc bromide solution, is 1.74(2) g cm^{-3} and

is in good agreement with the calculated value of 1.75 g cm^{-3}, obtained assuming four molecules of molecular weight 516.60 a.m.u. per unit cell of volume 1952.84 $Å^3$. For space group $Pna2_1$ there are 4 general equivalent positions and no restrictions are possible. However for Pnam there are 8 general equivalent positions so the molecules are restricted to lie either on the mirror planes or inversion centres. The *tris* chelate structure cannot have an inversion centre, hence for space group Pnam, the molecule must possess symmetry m.

Intensity data were collected on the Picker automatic four circle diffractometer using CuK_α X-radiation, filtered with 0.0005" thick nickel foil (in preference to a graphite monochromator[145]) and using a 2° take-off angle. The crystal was aligned in a general orientation but with its a^* axis approximately coincident with the diffractometer ϕ axis. The crystal faces were identified and the perpendicular distances between parallel faces of the same form were measured as: {1,0,0}, 0.206 mm; {0,1,0}, 0.055 mm; {0,0,1}, 0.077 mm. A coupled $2\theta/\omega$ scan was used, with a 2θ scan speed of 1°/min to collect all reflections with $2\theta \leq 125°$. The peak scan was approximately two minutes (2°), increasing as the $\alpha_1\alpha_2$ resolution

increased. Stationary background counts of 40 secs. were collected on either side of the peak. Assuming approximate linearity of background, the intensities and standard deviations were calculated as shown previously in Chapter II. The detector was a scintillation counter and was used in conjunction with a pulse height analyzer tuned to accept 95% of the CuK_α peak. Three standard reflections were collected automatically every 100 data reflections. In addition data collection was interrupted periodically to collect a further five standard reflections to investigate possible decomposition. No significant decomposition was observed over the duration of the data collection. Of the 1806 reflections collected, 1050 were significantly above background with $I/\sigma(I) \geq 3.0$. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization, and absorption effects. Terms used in the Zachariasen extinction correction were calculated at this stage. Standard deviations, $\sigma(F)$, in the structure factors were again computed using a "p factor"[70] of 0.03.

The linear absorption coefficient[86] using CuK_α radiation is 110.67 cm^{-1}, giving rise to a range of transmission factors between 0.5768 and 0.3099.

STRUCTURE SOLUTION AND REFINEMENT

A sharpened 3-dimensional Patterson map[146] was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, $0 \leq w \leq 0.5$. The Mo-Mo vectors for both $Pna2_1$ and Pnam (with the molybdenum atom on the crystallographic mirror) are shown in Table 19. It is obvious that the two space groups cannot be distinguished in the Patterson on the basis of the Mo-Mo vectors alone. However, the molybdenum position was obtained as follows. The most intense peak was situated at (0.500, 0.0, 0.0) and was attributed to the vector (1/2, 1/2-2y, 0); thus the y coordinate was obtained as ± 0.25. The accidentally special y coordinate leads to an ambiguity in the assignment of the next most intense peaks, observed at (0.325, 0.500, 0.500) and (0.182, 0.500, 0.500), as vectors of the form (1/2-2x, 1/2, 1/2) and (2x, 2y, 1/2). Because of this failure to identify the true Harker line vector, two possible solutions for molybdenum coordinates had to be tested by subsequent structure factor calculations and least squares refinement. The solutions to be tested were (a) x = 0.09, y = 0.25, z = 0.25, and (b) x = 0.16, y = 0.25 and z = 0.25.

The fourth largest peak on the map, at (0.0, 0.0,

TABLE 19: HARKER VECTORS FOR $Mo(bdt)_3$

$Pna2_1$		Pnam (z=1/4), SPECIAL POSITION "C"	
VECTOR FORM	WEIGHT	VECTOR FORM	WEIGHT
1/2-2x,1/2,1/2	2	1/2-2x,1/2,1/2	2
1/2+2x,1/2,1/2	2	1/2+2x,1/2,1/2	2
1/2,1/2-2y,0	2	1/2,1/2-2y,0	2
1/2,1/2+2y,0	2	1/2,1/2+2y,0	2
2x,2y,1/2	1	2x,2y,1/2	1
-2x,-2y,1/2	1	-2x,-2y,1/2	1
2x,-2y,1/2	1	2x,-2y,1/2	1
-2x,2y,1/2	1	-2x,2y,1/2	1

0.255), was located at 3.04 Å from the origin and was consistent with a build-up of S-S vectors between sulfur atoms related by a mirror perpendicular to z. Since this was the largest S-S vector, the possibility of the mirror bisecting the triangular faces was excluded and the space group was probably Pnam with the mirror relating the two triangular faces of the trigonal prism. If this were the case, then Mo-S vectors should be observed at w coordinates of about 1/2(0.255) = 0.13. Three vectors at 2.3 - 2.4 Å from the origin were located with w coordinates 0.136 and were consistent with the trigonal prismatic geometry. In addition three vectors were located in the w = 0 plane at 3.04 - 3.17 Å from the origin and these were consistent with vectors between the sulfur atoms within the triangular faces. From the Mo-S and S-S vectors the sulfur positions were calculated as either: S1(0.11, 0.14, 0.38), S2(0.16, 0.42, 0.38) and S3(0.29, 0.21, 0.38) corresponding to Mo position (b) or S1(0.04, 0.14, 0.38), S2(0.09, 0.42, 0.38) and S3(0.22, 0.21, 0.38) corresponding to Mo position (a).

To obtain the proper x coordinates a least squares refinement was performed with the model based on Mo positions (b). This model showed no signs of successful

refinement and converged after two cycles to give $R_1 = 0.424$ and $R_2 = 0.516$. However the model based on Mo coordinates (a) refined to $R_1 = 0.349$ and $R_2 = 0.435$ in two cycles. Temperature factors were fixed in these cycles, so further refinement of the second model, varying the temperature factors yielded $R_1 = 0.209$ and $R_2 = 0.294$ after the three cycles and thus the model was assumed to be correct. An outline of the solution and refinement is shown in Table 20.

TABLE 20: REFINEMENT OUTLINE

	Model	R_1	R_2
(1)	Mo and S atoms based on Mo coordinates (0.16,0.25,0.25)	0.424	0.516
(2)	Mo and S atoms based on Mo coordinates (0.09,0.25,0.25)	0.349	0.435
(3)	Mo and S atoms of model (2) - varying temperature factors	0.209	0.294
(4)	Mo, S, and C atoms; isotropic B's	0.079	0.086
(5)	Absorption Correction	0.065	0.075
(6)	Mo and S atoms anisotropic	0.050	0.062
(7)	H positions added	0.046	0.051
(8)	Extinction correction[147]	0.042	0.042
(9)	Carbon atoms anisotropic	0.035	0.034

Structure factors were calculated using the atomic scattering factors of the neutral atoms for molybdenum,

sulfur and carbon compiled by Cromer and Mann.[75] The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.[149] In addition anomalous dispersion corrections,[76] both real and imaginary, were applied to the molybdenum and sulfur scattering factors ($\Delta f'_{Mo} = -0.54$, $\Delta f''_{Mo} = 2.89$, $\Delta f'_{S} = 0.31$, $\Delta f''_{S} = 0.58$).

The carbon atoms were located from an electron density difference map phased on model (3). Anisotropic temperature factors for the different groups of atoms were introduced, as indicated by features in electron density difference maps, and can be justified, at the 0.005 significance level, by the subsequent application of Hamilton's R factor ratio test.[79] In the difference map, phased on model (6), the hydrogen atoms were visible so they were included in subsequent refinements, their positions calculated from the known geometry and orientation of the benzene rings, and using a C-H distance of 1.0 Å. The hydrogen atoms were assigned thermal parameters approximately 15% higher than those of the attached carbon atoms. Although they were included in the structure factor calculations, their parameters were not refined.

Extinction corrections[147] were applied since comparison of $|F_o|$ and $|F_c|$ for low angle reflections suggested the problem may exist. Verification of the

importance of the extinction correction is evident in the results of the refinements before and after this correction. Before the correction, all reflections except one with $\sin\theta/\lambda \leq 0.084$ were rejected from the refinement on the basis that $|\Delta F/\sigma(F)| > 5.0$, and in all cases $|F_o|$ was less than $|F_c|$ for these reflections. After the extinction correction, only one of these reflections previously rejected was still rejected from the refinement. The final refined value of the extinction scale factor, C, is 2.371×10^{-6}.

Anomalous features in the thermal parameters (*vide infra*) suggested that the scattering factors could be inadequate. Several refinements were attempted using various alternative scattering factors [Mo(IV),[150] Mo(VI),[150] S^{-} [75]] but no better agreement in R factor and no more reasonable thermal parameters were obtained. Thus the results from the original refinement are reported.

Programmes used in solution, refinement and presentation of data are listed in Appendix 2.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 21. The final fractional coordinates of all atoms and their isotropic temperature factors are shown in Table 22, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic thermal parameters[80] (U_{ij}'s) of all anisotropic atoms are shown in Table 23. Relevant intramolecular bond lengths are shown in Table 24 and the intramolecular angles in Table 25. Intermolecular contacts which are close to the predicted van der Waals separations[151] are listed in Table 26. These bond lengths, intermolecular contacts and bond angles, along with their standard deviations were obtained from ORFFE (See Appendix 2). Several least squares plane calculations are shown in Table 27, along with the deviations of the atoms from the planes. In addition, Table 28 shows the dihedral angles between selected planes.

In the three dimensional drawings of the molecule, 50% probability thermal ellipsoids are shown for molybdenum and sulfur atoms. For the carbon atoms artificially low isotropic thermal parameters were used

for clarity of the diagram. Similarly the hydrogen atoms were excluded from the plot for clarity. The hydrogen atoms are numbered from H1 to H6, and are bonded sequentially to the second and third carbon atoms in the rings. In the packing diagram in Fig. 13, the open bonds represent molecules at z = 0.25 whereas the dark bonds represent molecules at z = 0.75.

TABLE 21: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

K	L	FOBS	FCAL
**H =	0	****	
0	2	3512	3133
0	4	2258	2159
0	6	628	664
0	8	2010	1969
0	12	404	428
1	1	2346	2421
1	3	278	258
1	5	440	459
1	7	2098	2060
1	9	1115	1098
1	13	245	276
2	0	520	515
2	2	836	852
2	4	1147	1168
2	6	1371	1333
2	8	1089	1067
2	10	608	604
2	12	420	429
3	1	798	823
3	3	1888	1895
3	5	1397	1365
3	7	421	416
3	9	474	477
3	11	742	740
3	13	460	444
4	0	666	679
4	2	902	900
4	4	1148	1166
4	6	779	765
4	8	640	631
4	10	790	793
4	12	550	539
5	1	974	992
5	3	823	835
5	5	811	803
5	7	761	766
5	9	617	627
5	11	456	435
6	0	1262	1263
6	2	1248	1228
6	4	923	891
6	6	568	544
6	8	331	303
6	10	184	233
7	1	902	888
7	3	785	786
7	5	611	600
7	7	440	430
7	9	383	386
8	2	411	392
8	4	749	765
8	6	565	585
8	8	464	457
8	10	504	515
9	1	583	583
9	3	656	648
9	5	461	463
9	7	280	267
10	0	227	256
10	2	381	380
10	4	485	479
10	6	368	391
11	1	395	407
11	3	263	297
**H =	1	****	
1	0	128	157
2	0	581	590
2	1	721	741
2	3	400	416
2	4	335	335
2	5	455	442
2	6	148	108
2	11	240	241
3	0	856	850
3	1	642	635
3	2	136	143
3	3	370	383
3	4	912	911
3	5	390	395
3	7	205	157
3	8	371	379
3	10	257	266
3	11	265	286
3	12	374	347
4	0	577	587
4	1	164	149
4	2	472	457
4	3	1447	1417
4	4	996	996
4	5	651	671
4	7	718	708
4	8	549	541
4	9	312	333
4	10	190	142
4	11	452	413
4	12	319	307
5	0	230	213
5	1	281	290
5	3	655	652
5	4	389	402
5	5	400	402
5	6	172	131
5	7	340	335
5	10	238	255
5	11	358	331
5	12	164	169
6	0	230	242
6	1	551	557
6	2	196	235
6	4	553	535
6	7	519	484
6	9	295	310
7	0	1080	1110
7	2	206	193
7	3	239	268
7	4	525	501
7	5	207	195
7	6	347	314
7	8	687	668
8	1	370	360
8	4	299	304
8	7	408	434
8	9	172	219
9	2	276	279
9	3	282	282
9	4	533	525
9	5	284	299
10	3	588	601
10	4	320	300
10	5	388	397
10	7	168	173
11	0	164	76
11	1	175	177
11	2	240	241
11	3	180	193
11	4	443	457
**H =	2	****	
0	0	1296	1329
0	1	2124	2030
0	2	417	434
0	3	195	185
0	5	579	582
0	6	646	663
0	7	1625	1585
0	8	815	803
0	9	896	868
0	13	288	300
1	0	1800	1761
1	1	604	620
1	2	961	978
1	3	373	363
1	4	442	440
1	5	443	445
1	6	1153	1160
1	7	594	591
1	8	1205	1190
1	9	395	379
1	10	429	422
1	12	217	206
1	13	161	168
2	0	435	420
2	1	2428	2530
2	2	775	794
2	3	774	800
2	4	980	990
2	5	494	520
2	6	250	226
2	7	763	760
2	9	696	699
2	10	421	393
2	11	367	380
2	12	375	384
2	13	247	264
3	0	709	698
3	1	586	573
3	2	1079	1095
3	3	1578	1579
3	4	1260	1256
3	5	1119	1113
3	6	788	785
3	7	374	368
3	8	470	479
3	10	492	498
3	11	634	656
3	12	431	437
3	13	306	296
4	0	665	656
4	1	882	874
4	2	703	686
4	3	1181	1175
4	4	1494	1476
4	5	923	922
4	6	211	188
4	7	597	587
4	8	378	382
4	9	475	443
4	10	347	335
4	11	411	422
4	12	500	486
5	0	1245	1235
5	1	341	356
5	2	840	827
5	3	699	697
5	4	487	476
5	5	483	487
5	6	741	729
5	8	813	778
5	10	436	422
5	11	318	299
5	12	216	238
6	0	535	541
6	1	859	869
6	2	338	294
6	3	331	332
6	5	488	454
6	6	350	339
6	7	825	809
6	9	639	630
6	10	220	201
6	11	304	270
7	0	766	777
7	1	451	468
7	2	720	714
7	4	627	619
7	6	528	490
7	7	496	472
7	8	395	383
7	9	312	317
7	10	327	338
8	0	303	323
8	3	935	920
8	5	745	765
8	6	321	322
8	8	351	338
8	9	174	157
9	0	314	323
9	1	546	532
9	2	585	587
9	4	684	681
9	6	246	233
9	7	341	334
10	0	640	654
10	1	271	276
10	2	201	197
10	3	397	415
10	4	174	190
10	5	351	378
10	6	168	191
10	7	265	268
11	0	357	383
11	1	458	442
11	2	305	295
11	4	218	215
**H =	3	****	
1	1	1486	1493
1	3	623	619
1	5	532	515
1	7	325	320
1	9	214	129
1	11	301	286
2	0	1679	1671
2	1	258	258
2	2	628	624
2	4	388	401
2	8	188	225
3	0	276	275
3	4	207	171
3	5	256	241
3	7	201	211
4	0	571	555
4	2	177	174
4	4	652	670
4	6	245	214
4	10	209	200
4	12	225	214
5	0	711	702
5	4	551	532
5	7	428	403
5	8	294	293
5	9	405	436
5	11	192	180
5	12	232	204
6	0	846	843
6	1	578	579
6	2	345	335
6	3	804	776
6	5	505	483
6	6	285	273
6	7	617	595
6	8	472	442
6	9	255	268
6	11	384	393
7	0	911	914
7	1	883	933
7	4	852	853
7	7	532	508
7	8	565	560
7	9	244	254
8	0	604	673
8	1	363	366
8	2	294	317
8	3	391	414
8	5	269	281
8	6	266	272
8	7	292	299
8	8	362	319
9	1	209	205
9	3	330	339
9	5	273	305
10	2	224	234
10	3	171	160
10	4	435	428
10	6	180	193
11	0	263	246
11	1	165	132
11	3	333	329
11	4	162	190
**H =	4	****	
0	0	672	672
0	1	2552	2546
0	2	1074	1093
0	3	705	719
0	4	1255	1262
0	5	357	372
0	6	319	311
0	7	630	635
0	9	591	610
0	10	508	504
0	11	366	334
0	12	500	515
0	13	257	239
1	0	275	242
1	1	456	459
1	2	593	637
1	3	1224	1240
1	4	1351	1297
1	5	1131	1142
1	6	653	698
1	7	231	235
1	8	542	529
1	9	242	270
1	10	556	568
1	11	559	582
1	12	462	481
1	13	295	317
2	0	449	443
2	2	792	798
2	3	1652	1708
2	4	946	937
2	5	1444	1451
2	6	530	515
2	8	270	267
2	9	247	218

Table 21. (continued)

K	L	FOBS	FCAL
**H =		4****	
2	10	369	350
2	11	777	783
2	12	329	340
2	13	416	424
3	1	1205	1190
3	2	1503	1472
3	3	614	606
3	4	2093	2040
3	5	399	383
3	6	298	291
3	7	462	475
3	8	391	395
3	9	356	331
3	10	519	486
3	12	673	682
4	0	1485	1495
4	1	590	594
4	2	616	605
4	3	990	1000
4	5	781	783
4	6	480	488
4	7	306	298
4	8	719	734
4	9	446	451
4	10	234	232
4	11	558	568
5	0	723	730
5	1	928	921
5	2	424	441
5	4	329	353
5	5	265	236
5	6	756	756
5	7	742	733
5	8	824	807
5	9	413	440
5	10	409	414
5	12	175	200
6	0	575	577
6	1	915	937
6	2	465	444
6	3	386	395
6	4	351	321
6	5	400	411
6	6	431	449
6	7	665	675
6	8	421	402
6	9	352	360
7	0	886	861
7	1	330	313
7	2	563	565
7	3	386	396
7	4	288	295
7	5	396	391
7	6	483	466
7	7	325	300
7	8	453	459
7	9	277	274
7	10	220	223
8	1	358	340
8	2	254	265
8	3	395	435
8	4	563	554
8	5	484	456
8	6	311	295
8	7	380	375
8	9	295	303
9	0	710	722
9	1	291	295
9	2	532	538
9	3	496	515
9	4	237	280
9	5	308	327
9	6	239	230
9	8	228	255
10	1	379	420
10	2	229	257
10	4	380	395
10	5	175	193
10	6	177	176
11	0	569	571
11	1	224	258
11	2	159	177
11	3	179	187
**H =		5****	
1	0	1106	1070
1	1	670	673
1	2	125	132
1	3	176	214
1	4	624	620
1	5	228	223
1	6	206	182
1	7	169	208
1	8	435	436
1	11	210	185
1	12	196	223
2	1	581	602
2	2	285	293
2	3	971	970
2	4	295	291
2	5	381	384
2	6	273	253
2	7	969	951
2	8	309	349
2	9	433	449
2	11	322	353
3	0	1563	1561
3	4	1085	1074
3	6	291	307
3	8	878	874
3	12	312	302
4	0	237	217
4	1	1109	1074
4	2	315	292
4	3	206	170
4	4	550	555
4	7	200	175
4	8	317	324
4	12	163	166
5	0	206	173
5	3	185	189
5	5	177	176
5	6	244	258
5	8	241	288
5	11	165	98
6	0	526	544
6	1	213	190
6	4	238	222
6	5	213	237
6	7	226	274
6	8	295	253
7	0	605	602
7	1	670	664
7	2	261	274
7	3	282	290
7	5	247	248
7	7	351	341
7	8	322	300
8	0	200	210
8	1	241	257
8	6	189	204
8	7	291	288
8	8	247	263
8	9	207	212
9	0	219	242
9	2	216	228
9	3	165	190
9	5	236	248
9	6	197	223
10	1	412	422
10	4	330	315
11	0	427	440
11	2	242	232
**H =		6****	
0	0	1346	1359
0	1	542	554
0	2	1742	1663
0	3	1265	1274
0	4	1566	1540
0	5	738	753
0	6	531	533
0	7	645	659
0	9	257	263
0	10	479	470
0	11	498	506
0	12	541	564
1	0	949	914
1	1	474	476
1	2	265	265
1	3	1719	1733
1	4	1059	1057
1	5	1352	1316
1	7	330	299
1	8	408	427
1	9	361	346
1	10	251	226
1	11	707	693
1	12	352	362
2	0	663	677
2	2	1009	1042
2	3	318	328
2	4	1291	1296
2	5	275	252
2	6	651	647
2	8	434	431
2	10	719	746
2	12	554	568
3	0	173	192
3	1	342	346
3	2	1034	1072
3	5	1054	1060
3	6	229	220
3	7	644	654
3	8	243	240
3	9	604	613
3	11	572	589
4	0	941	953
4	1	227	220
4	2	797	795
4	4	625	631
4	6	805	793
4	8	781	773
4	10	442	440
4	12	227	270
5	1	1460	1458
5	2	218	175
5	3	308	273
5	4	317	318
5	5	330	296
5	7	688	940
5	9	601	608
5	10	177	87
6	0	1456	1486
6	2	796	783
6	3	245	261
6	4	201	161
6	5	223	196
6	6	580	573
6	8	701	666
6	10	195	214
7	0	284	267
7	1	805	803
7	3	589	584
7	5	526	500
7	7	450	442
7	9	324	314
8	0	219	167
8	1	236	231
8	2	401	409
8	4	902	910
8	6	496	463
8	7	293	270
9	0	356	346
9	1	260	257
9	3	636	640
9	4	205	180
9	5	508	521
10	0	308	305
10	2	324	339
10	4	359	358
11	1	513	523
**H =		7****	
1	0	1099	1049
1	2	252	248
1	3	310	282
1	4	999	978
1	6	212	194
1	7	210	230
1	8	689	698
1	12	257	264
2	0	354	339
2	1	678	677
2	3	477	474
2	5	280	262
2	7	520	535
2	8	250	240
2	9	221	216
2	11	274	261
3	1	262	293
3	3	296	310
3	4	167	140
3	7	400	415
4	0	805	791
4	1	295	302
4	2	180	191
4	3	707	714
4	4	323	329
4	5	466	464
4	6	209	159
4	7	357	335
4	8	335	345
4	11	262	261
5	0	295	276
5	1	603	585
5	2	218	23
5	3	301	262
5	4	605	605
5	5	188	153
5	7	345	375
5	8	242	240
5	9	190	205
5	10	236	217
6	0	385	386
6	2	239	232
6	3	459	501
6	5	391	395
7	0	236	225
7	3	193	142
7	4	398	396
7	6	190	186
8	3	336	322
8	5	260	293
8	8	197	196
9	1	286	305
9	2	194	234
9	4	360	331
9	7	220	249
10	0	327	337
10	3	247	237
**H =		8****	
0	0	1116	1124
0	1	1307	1282
0	2	297	293
0	3	798	815
0	4	334	331
0	5	634	621
0	6	246	261
0	7	603	604
0	8	479	475
0	9	566	568
0	11	418	422
1	1	450	440
1	2	688	695
1	3	148	62
1	4	873	879
1	6	808	815
1	7	449	451
1	8	638	651
1	9	278	252
1	10	501	494
1	12	353	363
2	1	1130	1137
2	3	773	776
2	4	196	203
2	5	623	634
2	6	268	268
2	7	644	650
2	8	224	240
2	9	531	523
2	11	332	328
3	0	1256	1240
3	1	430	418
3	2	986	980
3	3	267	245
3	4	620	604
3	5	181	128
3	6	579	559
3	8	535	534
3	10	321	343
4	0	883	883
4	1	990	973
4	2	229	254
4	3	505	489
4	4	309	286
4	5	463	456
4	6	217	188
4	7	722	695
4	8	428	443
4	9	540	567
4	11	296	273
5	0	818	815
5	1	721	728
5	2	602	596
5	3	422	411

Table 21 (continued)

K	L	FOBS	FCAL
**H =	8****		
5	4	435	445
5	5	214	223
5	6	650	639
5	7	648	632
5	8	653	637
5	9	306	360
5	10	327	351
6	0	667	683
6	1	571	581
6	2	207	187
6	3	583	569
6	4	216	215
6	5	574	536
6	6	201	205
6	7	460	466
6	8	383	345
6	9	348	350
7	0	444	477
7	2	519	519
7	3	271	245
7	4	556	534
7	5	241	259
7	6	418	416
7	8	288	327
8	0	628	665
8	1	261	268
8	3	575	575
8	4	697	714
8	5	537	519
8	7	253	247
8	8	259	257
9	0	460	471
9	1	251	231
9	2	520	512
9	3	567	568
9	4	455	452
9	5	316	345
9	6	239	221
10	1	211	170
10	2	177	174
10	3	369	371
10	4	296	324
**H =	9****		
1	0	812	809
1	1	572	574
1	3	332	294
1	4	685	673
1	7	187	172
1	8	442	430
1	9	222	243
2	1	338	336
2	3	696	718
2	5	375	374
2	7	535	549
2	9	256	271
2	11	251	282
3	0	270	250
3	4	251	248
4	0	326	292
4	2	361	330
4	4	710	705
4	7	227	238
4	8	309	300
4	10	178	143
5	0	377	384
5	1	624	647
5	3	507	486
5	4	302	306
5	5	523	542
5	6	224	140
5	8	305	290
6	0	369	359
6	1	201	210
6	2	215	204
6	4	630	640
7	1	390	390
7	3	411	410
7	5	201	153
8	2	211	207
8	4	326	349
8	6	179	142
9	0	214	203
9	3	300	333
9	5	342	339
10	2	235	223
**H =	10****		
0	0	1334	1351
0	1	965	965
0	2	508	547
0	3	299	269
0	5	288	282
0	6	550	552
0	7	589	570
0	8	801	793
0	9	345	348
0	10	189	213
1	0	479	472
1	1	776	795
1	2	391	403
1	4	391	393
1	5	270	251
1	6	525	531
1	7	848	846
1	8	465	449
1	9	536	536
1	10	255	238
2	0	1338	1329
2	1	486	470
2	2	560	560
2	3	526	516
2	5	472	460
2	6	457	476
2	7	375	333
2	8	695	730
2	9	265	265
2	10	182	212
2	11	257	273
3	0	610	609
3	1	859	840
3	2	661	641
3	3	323	316
3	4	525	541
3	5	310	285
3	6	262	297
3	7	545	524
3	9	310	330
3	10	203	209
4	0	485	517
4	1	577	575
4	2	598	557
4	3	305	270
4	4	528	525
4	5	276	270
4	6	3..	328
4	7	477	449
4	8	202	213
4	9	347	354
4	10	200	244
5	0	640	625
5	2	221	247
5	3	729	717
5	5	592	597
5	6	487	463
5	8	555	603
5	9	195	177
6	1	528	532
6	2	350	361
6	3	293	229
6	4	707	716
6	5	249	241
6	6	283	279
6	7	392	388
6	9	237	239
7	0	319	315
7	1	365	347
7	2	369	357
7	3	379	375
7	4	347	353
7	5	282	298
7	6	194	219
7	7	254	225
8	0	402	375
8	2	202	226
8	3	532	520
8	5	422	421
8	6	267	291
9	1	476	459
9	2	325	327
9	4	456	460
**H =	11****		
1	0	362	354
1	1	418	462
1	3	460	502
1	4	271	260
1	5	290	341
1	7	403	379
1	10	179	166
2	0	669	658
2	1	358	379
2	3	548	559
2	4	546	558
2	5	357	387
2	7	318	317
2	8	427	418
3	0	497	522
3	3	221	185
3	4	566	575
3	8	239	245
4	3	415	407
4	5	239	238
4	7	216	126
5	0	375	348
6	0	272	312
6	3	241	183
7	1	233	218
7	4	230	215
8	3	199	207
8	5	170	187
9	0	213	205
**H =	12****		
0	0	1012	1017
0	1	503	526
0	2	750	736
0	4	402	412
0	6	421	409
0	7	213	225
0	8	323	351
0	10	189	204
1	0	576	537
1	1	614	623
1	2	205	194
1	3	556	564
1	5	509	525
1	6	220	233
1	7	450	455
1	8	335	336
1	9	291	303
2	0	5..	564
2	1	600	592
2	2	526	539
2	3	197	208
2	4	549	524
2	6	452	467
2	7	499	498
2	8	407	411
2	9	273	273
2	10	346	363
3	0	524	503
3	3	649	663
3	4	239	176
3	5	633	651
3	6	298	298
3	7	315	313
3	8	467	445
3	9	325	313
4	2	453	454
4	4	798	798
4	6	438	409
4	9	175	128
5	1	370	385
5	2	288	242
5	3	654	644
5	4	490	470
5	5	524	506
6	0	465	477
6	2	494	505
6	3	381	391
6	4	463	449
6	5	239	263
6	6	270	255
7	1	441	458
7	3	307	297
7	4	221	153
7	5	220	270
8	0	341	357
8	1	210	270
8	2	277	266
8	4	166	205
**H =	13****		
1	1	300	346
1	3	329	297
1	5	271	254
2	0	475	461
2	4	397	408
4	0	393	404
4	1	355	306
5	0	231	203
5	1	249	260
5	7	231	216
6	0	221	224
6	1	295	284
6	3	253	249
7	0	656	665
7	4	342	357
8	1	198	229
**H =	14****		
0	0	632	610
0	1	501	499
0	3	628	646
0	4	282	298
0	5	458	484
0	8	218	222
1	2	419	416
1	4	691	688
1	6	372	419
2	0	225	259
2	1	371	360
2	3	568	574
2	5	495	502
2	7	271	272
3	0	457	464
3	2	562	571
3	3	362	353
3	4	579	575
3	6	311	305
3	7	218	237
4	0	205	149
4	1	359	356
4	3	542	528
4	4	272	227
4	5	474	432
4	7	236	203
5	2	346	328
5	4	614	592
5	6	383	349
6	1	220	229
6	3	511	500
6	5	435	427
7	0	476	469
7	2	321	320
**H =	15****		
1	3	225	126
2	1	220	199
3	0	353	361
3	4	247	302
4	1	303	284
4	3	309	279
5	0	223	234
5	1	243	237
5	4	216	185
6	0	230	273
**H =	16****		
0	0	298	293
0	1	327	328
0	2	350	337
0	4	846	814
1	0	487	459
1	3	607	601
1	5	491	498
2	0	411	395
2	1	399	404
2	2	345	363
2	4	284	285
3	0	227	174
3	1	425	431
3	2	210	186
3	3	202	220
3	4	205	178
3	5	255	199
4	0	403	400
4	2	305	305
4	3	265	264
4	4	215	206
4	5	236	246
5	1	245	245
5	3	315	267
**H =	17****		
2	0	280	272
3	0	216	203
3	3	199	182
4	0	272	214
**H =	18****		
0	0	527	544
0	2	357	405
0	3	337	323
1	1	241	249
1	2	201	199
1	3	225	212
2	0	272	271
2	1	221	206

TABLE 22: ATOM COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

ATOM	x	y	z	B
Mo	0.08815(5)	0.25886(7)	0.25	2.46*
S1	0.0077(1)	0.1371(1)	0.3802(1)	3.28*
S2	0.0632(1)	0.4286(1)	0.3808(1)	3.48*
S3	0.1939(1)	0.2047(1)	0.3808(1)	3.36*
C1	-0.0757(4)	0.0681(5)	0.3096(5)	3.19*
C2	-0.1390(5)	0.0016(7)	0.3648(7)	4.51*
C3	-0.1989(4)	-0.0638(7)	0.3087(7)	4.94*
C4	0.0787(4)	0.5741(5)	0.3091(5)	3.32*
C5	0.0872(5)	0.6936(6)	0.3659(6)	4.55*
C6	0.0959(5)	0.8080(6)	0.3088(7)	6.00*
C7	0.2557(4)	0.0951(6)	0.3091(5)	3.26*
C8	0.3073(4)	0.0067(7)	0.3677(7)	4.30*
C9	0.3565(4)	-0.0801(7)	0.3096(7)	5.30*
H1	-0.1389	0.0016	0.4488	5.2
H2	-0.2438	-0.1121	0.3518	6.0
H3	0.0873	0.6937	0.4499	5.2
H4	0.1023	0.8921	0.3514	6.0
H5	0.3074	0.0066	0.4516	5.2
H6	0.3925	-0.1429	0.3523	6.0

*These values are equivalent isotropic temperature factors[81] corresponding to the anisotropic thermal parameters shown in Table 23.

TABLE 23: ANISOTROPIC TEMPERATURE FACTORS ($Å^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.0389(4)	0.0259(3)	0.0287(3)	-0.0003(4)	0.0	0.0
S1	0.0489(10)	0.0400(8)	0.0356(8)	-0.0053(8)	-0.0006(9)	0.0033(8)
S2	0.0547(11)	0.0364(8)	0.0409(9)	0.0026(8)	0.0030(9)	-0.0070(8)
S3	0.0455(10)	0.0461(9)	0.0358(8)	0.0015(8)	-0.0049(8)	-0.0027(7)
C1	0.039(4)	0.034(3)	0.048(4)	0.002(3)	0.000(3)	-0.001(3)
C2	0.051(5)	0.064(5)	0.056(5)	-0.006(4)	0.014(4)	0.016(4)
C3	0.039(4)	0.074(5)	0.075(6)	-0.019(4)	0.012(4)	0.008(4)
C4	0.034(4)	0.033(3)	0.059(4)	0.004(3)	-0.002(3)	-0.007(3)
C5	0.057(5)	0.040(3)	0.075(5)	0.015(4)	0.004(5)	-0.013(4)
C6	0.079(6)	0.037(4)	0.111(7)	0.011(4)	0.005(5)	-0.010(4)
C7	0.034(4)	0.044(4)	0.046(4)	-0.000(3)	-0.002(3)	-0.004(3)
C8	0.048(5)	0.061(4)	0.054(5)	0.005(4)	-0.001(4)	0.004(4)
C9	0.045(5)	0.068(5)	0.088(7)	0.011(4)	-0.009(4)	0.014(4)

TABLE 24: INTRAMOLECULAR CONTACTS (Å)

ATOMS	DISTANCE (Å)	ATOMS	DISTANCE (Å)
Mo-S1	2.370(2)	Mo-S2	2.360(2)
Mo-S3	2.371(2)	S1-S1'	3.100(3)
S2-S2'[a]	3.115(3)	S3-S3'	3.114(3)
S1-S2	3.099(2)	S1-S3	3.074(2)
S2-S3	3.101(2)	S1-C1	1.731(6)
S2-C4	1.728(6)	S3-C7	1.721(6)
C1-C1'	1.419(11)	C1-C2	1.388(8)
C2-C3	1.349(10)	C3-C3'	1.394(16)
C4-C4'	1.408(12)	C4-C5	1.398(8)
C5-C6	1.355(8)	C6-C6'	1.400(16)
C7-C7'	1.408(12)	C7-C8	1.410(8)
C8-C9	1.373(10)	C9-C9'	1.418(16)

[a]Primed atoms are related by a mirror at z = 1/4.

TABLE 25: INTRAMOLECULAR ANGLES (DEGREES)

ATOMS	ANGLES	ATOMS	ANGLES
S1-Mo-S1'[a]	81.70(8)	S2-Mo-S2'	82.57(8)
S3-Mo-S3'	82.09(8)	S1-Mo-S2	81.85(5)
S1-Mo-S3	80.85(6)	S2-Mo-S3	81.89(6)
S1-Mo-S2'	136.17(7)	S1-Mo-S3'	134.43(6)
S2-Mo-S3'	136.51(7)	Mo-S1-C1	108.5(2)
Mo-S2-C4	106.1(2)	Mo-S3-C7	103.9(2)
S1-C1-C1'	119.0(2)	S2-C4-C4'	119.6(2)
S3-C7-C7'	119.7(2)	C2-C1-C1'	118.2(4)
C1-C2-C3	122.1(8)	C2-C3-C3'	119.7(5)
C5-C4-C4'	118.9(4)	C4-C5-C6	120.9(7)
C5-C6-C6'	120.1(4)	C8-C7-C7'	119.7(4)
C7-C8-C9	120.0(7)	C8-C9-C9'	120.3(5)
S3-S1-S2	60.30(5)	S1-S3-S2	60.24(5)
S1-S2-S3	59.46(5)		

[a]Primed atoms are related by a mirror at z = 1/4.

TABLE 26: INTERMOLECULAR CONTACTS (Å)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
S1	H4	x, y-1, z	2.941
S1	H3	$\bar{x}$, $\bar{y}$+1, $\bar{z}$+1	3.065
S2	H5	1/2-x, 1/2+y, $\bar{z}$+1	2.992
S3	H1	$\bar{x}$, $\bar{y}$, $\bar{z}$+1	3.051
S1	C6	x, y-1, z	3.736(7)
S1	C5	$\bar{x}$, $\bar{y}$+1, $\bar{z}$+1	3.800(7)
S2	C8	1/2-x, 1/2+y, $\bar{z}$+1	3.734(8)
S2	C9	1/2+x-1, 1/2-y, z	3.763(7)
S3	C2	$\bar{x}$, $\bar{y}$, $\bar{z}$+1	3.791(7)
S2	S2	$\bar{x}$, $\bar{y}$+1, $\bar{z}$+1	3.782(3)
C3	C4	1/2+x-1, 1/2-y, z	3.581(9)
C3	C9	1/2+x-1, 1/2-y-1, z	3.[illegible]33(10)
C3	C5	1/2+x-1, 1/2-y, z	[illegible]749(10)
C4	C9	1/2+x-1, 1/2-y, z	3.577(9)
C4	C3	1/2+x, 1/2-y, z	3.581(9)
C4	H6	1/2+x-1, 1/2-y, z	3.120
C5	H6	1/2+x-1, 1/2-y, z	3.180
C4	H2	1/2+x, 1/2-y, z	2.927
C5	H2	1/2+x, 1/2-y, z	2.848

TABLE 27: LEAST SQUARES PLANE CALCULATIONS[a]

(A) ATOMS DEFINING PLANE: S1, Mo, S1'

EQUATION OF PLANE: $-0.6913X + 0.7225Y - 0.9227 = 0.0$

(B) ATOMS DEFINING PLANE: S2, Mo, S2'

EQUATION OF PLANE: $-0.9740X - 0.2266Y + 1.9797 = 0.0$

(C) ATOMS DEFINING PLANE: S3, Mo, S3'

EQUATION OF PLANE: $-0.3080X - 0.9514Y + 2.9444 = 0.0$

(D) ATOMS DEFINING PLANE: S1, S2, S3

EQUATION OF PLANE: $-0.0016X - 0.0019Y + 1.0Z - 4.5264 = 0.0$

DISTANCE OF Mo FROM PLANE (Å): -1.556

(E) ATOMS DEFINING PLANE: S1', S2', S3'

EQUATION OF PLANE: $0.0016X - 0.0019Y + 1.0Z - 1.4298 = 0.0$

DISTANCE OF Mo FROM PLANE (Å): 1.556

(F) ATOMS DEFINING PLANE: S1, S1', C1, C1', C2, C2', C3, C3'

EQUATION OF PLANE: $0.5094X - 0.8605Y + 1.1429 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S1	0.005(2)	S1'	0.005(2)
C1	-0.074(6)	C1'	-0.074(6)
C2	-0.011(7)	C2'	-0.011(7)
C3	0.071(8)	C3'	0.071(8)
Mo	-0.4017(7)		

TABLE 26 (Continued)

(G) ATOMS DEFINING PLANE: S2, S2', C4, C4', C5, C5', C6, C6'

EQUATION OF PLANE: $-0.9899X + 0.1420Y + 0.3898 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S2	0.002(2)	S2'	0.002(2)
C4	-0.035(6)	C4'	-0.035(6)
C5	0.001(7)	C5'	0.001(7)
C6	0.028(8)	C6'	0.028(8)
Mo	-0.6412(7)		

(H) ATOMS DEFINING PLANE: S3, S3', C7, C7', C8, C8', C9, C9'

EQUATION OF PLANE: $0.7424X + 0.6700Y - 3.7136 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S3	0.000(2)	S3'	0.000(2)
C7	-0.008(6)	C7'	-0.008(6)
C8	0.006(7)	C8'	0.006(7)
C9	0.001(7)	C9'	0.001(7)
Mo	-0.8942(7)		

[a] X, Y, and Z are in Å and refer to the orthogonal coordinates along a, b, and c^*.

TABLE 28: DIHEDRAL ANGLES BETWEEN SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE
S1,Mo,S1'	S2,Mo,S2'	120.7°
S1,Mo,S1'	S3,Mo,S3'	118.2°
S2,Mo,S2'	S3,Mo,S3'	121.1°
S1,Mo,S1'	S1,S1',C1,C1',C2,C2',C3,C3'	13.1°
S2,Mo,S2'	S2,S2',C4,C4',C5,C5',C6,C6'	21.1°
S3,Mo,S3'	S3,S3',C7,C7',C8,C8',C9,C9'	30.0°

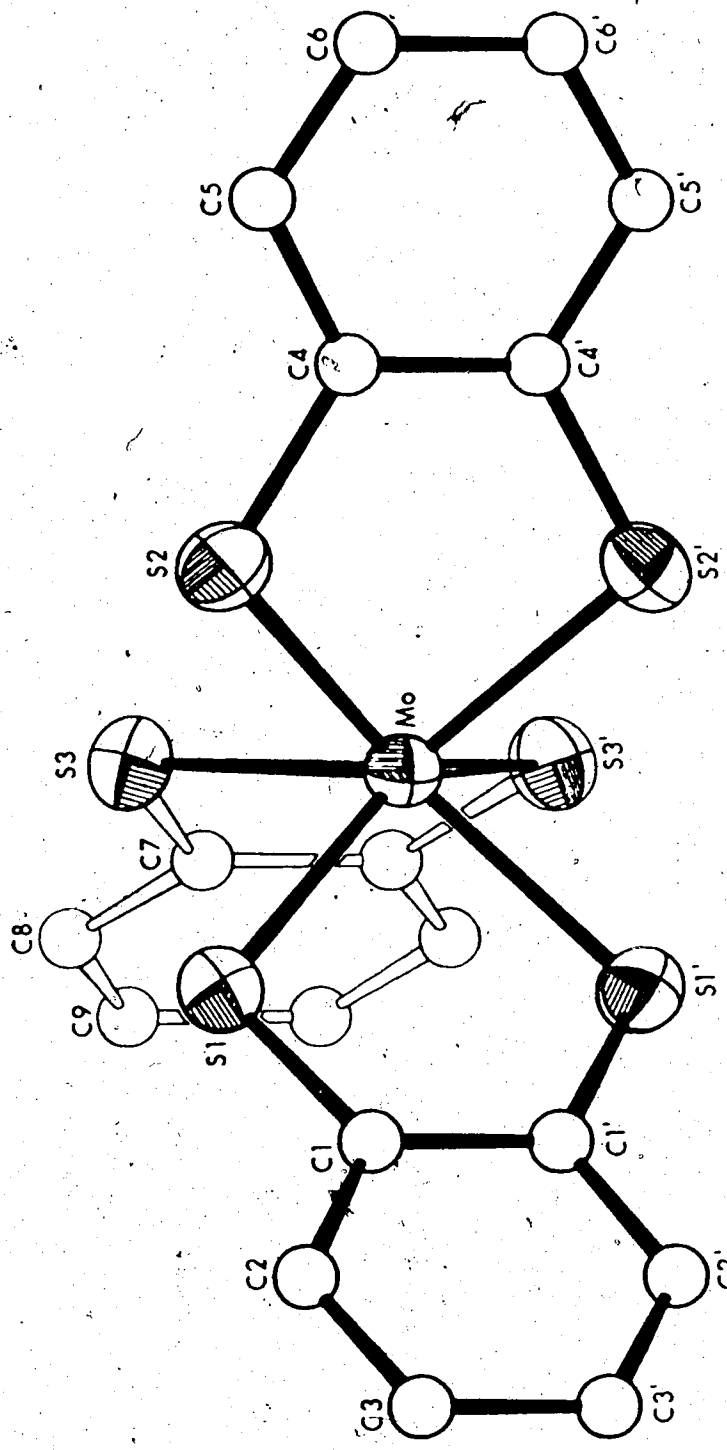


Fig. 9: A PERSPECTIVE VIEW OF $Mo(S_2C_6H_4)_3$.

DESCRIPTION OF STRUCTURE

A 3-dimensional view of $Mo(bdt)_3$ is shown in Fig. 9. The sulfur atoms surround the molybdenum in an almost perfect trigonal prismatic coordination with the dithiolene ligands radiating from the molybdenum atom in a "paddle-wheel" arrangement. The molecule deviates from approximate D_{3h} symmetry due to the bending of the $(S_2C_6H_4)$ planes from the MoS_2 planes by an average of 21.4°. In addition C_{3h} symmetry is not achieved due to the three differing $(S_2C_6H_4)/MoS_2$ dihedral angles (Fig. 12). The molybdenum atom is located on the crystallographic mirror at z = 1/4, with the two triangular faces of the prism being related by the mirror.

Again, as was the case for the three previous trigonal prismatic structures, $Re(S_2C_2Ph_2)_3$,[129] $Mo(S_2C_2H_2)_3$[130] and $V(S_2C_2Ph_2)_3$,[132] the intra- and interligand sulfur-sulfur distances are approximately equal (3.110 Å and 3.091 Å respectively in the present study). These agree favourably with those observed in other prisms and are especially close to those in $Mo(S_2C_2H_2)_3$ (Table 48). It is interesting that the relative magnitudes of these intra- and interligand S-S distances are reversed to those in the other three

dithiolene trigonal prisms, with the intraligand S-S distances being greater in the present study. This can be attributed to the constraint of the fixed ligand bite holding the intraligand sulfurs apart. That the ligand bite should be greater in the benzene dithiols than in the ethylene dithiols is apparent since the C-C distances in the former are longer, thereby ensuring a larger bite. This was also observed in the trigonal prismatic molecule[152] $Mo[Se_2C_2(CF_3)_2]_3$, which also has intraligand Se-Se distances which exceed the interligand values [3.317(5) Å and 3.222(3) Å respectively].

The mean Mo-S distance (2.367 Å), although similar to the metal-sulfur distance in other trigonal prisms, is significantly longer than their average of approximately 2.33 Å. In fact they are more closely matched by the metal-sulfur distances in the non-trigonal prismatic species $V(mnt)_3^{2-}$ [140] and $Mo(mnt)_3^{2-}$ [141] (Table 48). This difference is again probably due to the difference in ligands, all previous examples being substituted ethylene dithiol ligands. For this reason a rigid comparison of intramolecular distances and angles will prove more worthwhile within the series of compounds which are the topic of part of this thesis, i.e., $Mo(bdt)_3$, $[Ph_4As][Nb(bdt)_3]$, and $[(CH_3)_4N]_2[Zr(bdt)_3]$. In addition the molybdenum-

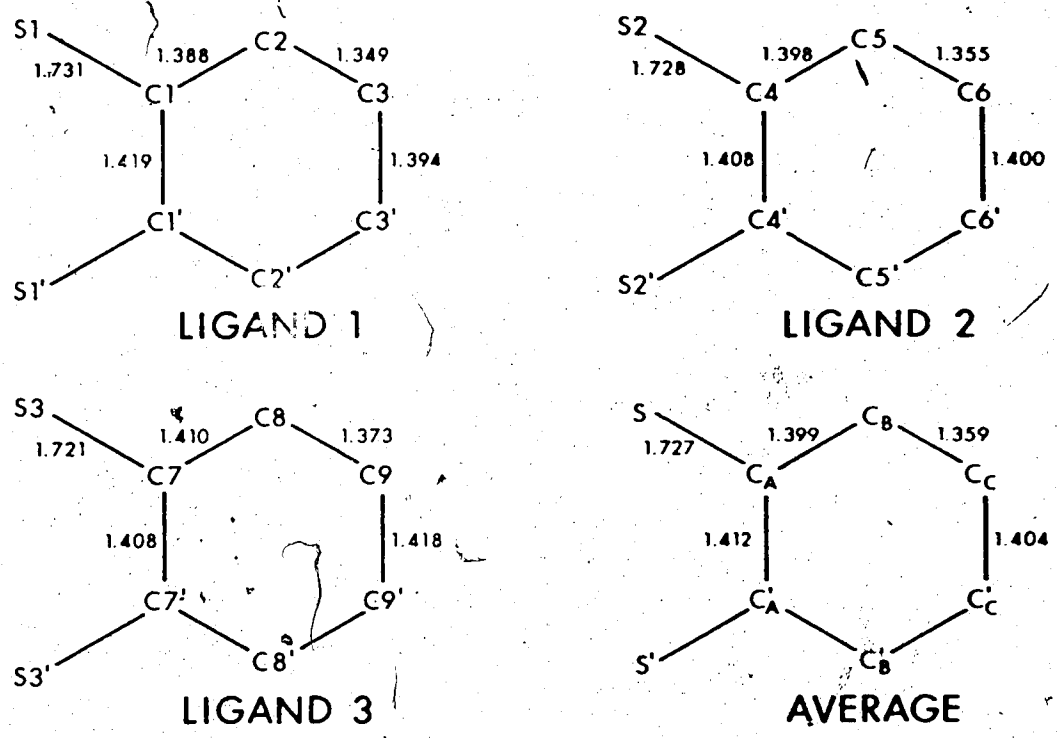


Fig. 10: DIMENSIONS WITHIN THE DITHIOLENE LIGANDS.

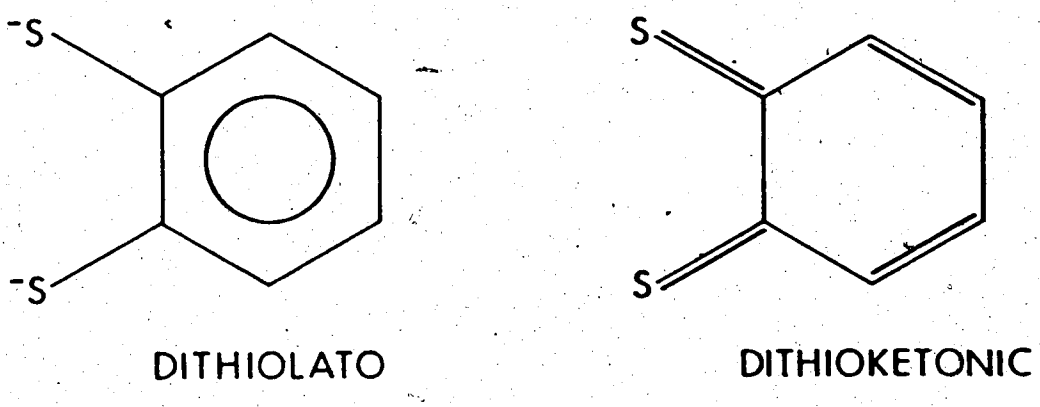


Fig. 11: DITHIOLATO AND DITHIOKETONIC LIMITING FORMULATIONS FOR THE "bdt" LIGAND.

sulfur distances are again shorter than those observed in the 1,1-dithiolato complexes, $Fe[S_2CN(n\text{-}C_4H_9)_2]_3$,[153] $Ru[S_2CN(C_2H_5)_2]_3$,[154] $Cr[S_2P(CH_3)_2]_3$,[155] and $V[S_2P(OC_2H_5)_2]_3$,[156] although the molybdenum covalent radius is greater than any of these metal radii.[133] Thus a difference in the metal-sulfur bonding between the 1,1-dithiolato and 1,2-dithiolene complexes is obvious with the latter having a greater amount of M-S bonding. This is in agreement with the proposed metal-sulfur multiple bonding in the *tris*(1,2-dithiolenes).[157]

The sulfur-carbon distances (mean 1.727 Å) are similar to those in the other trigonal prisms and are once again consistent with a great deal of S=C double bond character, as witnessed by their similarity with the double bonded S=C distance of 1.72 Å in thiourea[134] $[SC(NH_2)_2]$ and its derivatives.[135] The mean carbon-carbon distance (1.393 Å) is similar to that observed in benzene[158] (1.398 Å) and in several di-substituted benzene compounds.[159] However in the benzene dithiol ligands in this structure there is a significant range of C-C distances (Fig. 10). In addition, the C-S distances are consistent with a tendency towards the dithioketonic limit (Fig. 11). However caution must be used since the dithioketonic limit will not be attained due to other resonance

structures, so only a trend towards this limit is noted. Also due to increasing thermal motion of the carbon atoms as the distance from the central atom (Mo) increases, the bonds will appear shorter due to libration of the rings. Thus the shortening of $C_B - C_C$ (Fig. 10) could be partly attributed to thermal motion. However thermal motion of this type cannot cause bond lengthening, so the longer $C_A - C_A'$ bond remains as good evidence of the tendency of the ligand towards its oxidized formulation. At this point it is convenient to note that the thermal parameters in this and similar structures all show an anomalous feature. In molecules of this type it would appear reasonable to expect that the general trend of thermal amplitudes increases steadily as one progresses outward from the centre of gravity of the molecule. This assumes that the thermal motion is dominated by rigid body motion. However the sulfur atoms have larger thermal parameters than their attached carbon atoms. This observation, which appears to be very general for sulfur donor ligands, suggests either the unsuitability of the scattering factors used, or large vibration of the core of the molecule. This feature precludes any attempt at correction of these bond lengths for thermal motion and hence severely restricts the discussion

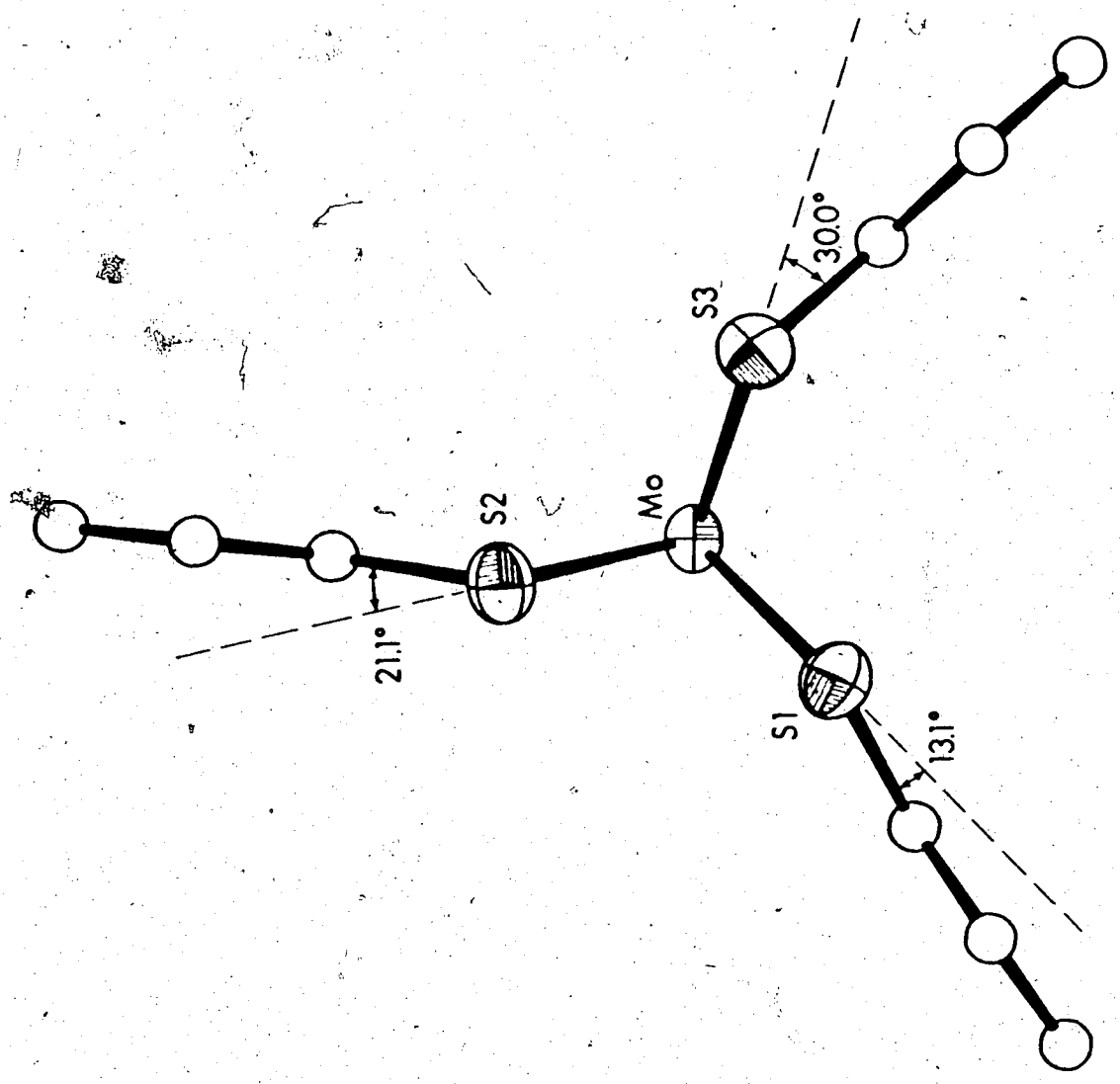


Fig. 12: VIEW OF $Mo(S_2C_6H_4)_3$ DOWN THE CRYSTALLOGRAPHIC *c* AXIS.

of the ligand geometry with respect to the pattern of carbon-carbon bond lengths. A more complete view of the ligand in its reduced and oxidized formulation is presented in Chapter IX, based on molecular orbital calculations performed by Birss and Das Gupta.[160]

The mean S-M-S angle involving *trans* sulfur atoms is 136 ± 1° in the known trigonal prismatic structures,[129,130,132] and assuming the constraint of ligand bite, has been calculated[161] as approximately 173° in octahedral coordination. The mean value of 135.70° observed in $Mo(bdt)_3$ is clearly consistent with trigonal prismatic coordination. The intra- and interligand S-Mo-S angles (82.12° and 81.53°) are similar, as expected, and again agree with those found in other trigonal prismatic structures.[129,130,132]

As mentioned, the molecule deviates from D_{3h} symmetry due to the bend of the ligand planes from the respective S-Mo-S planes, as shown in Fig. 12, in which the molecule is viewed directly down the crystallographic *c* axis and approximate molecular three-fold axis. Similar bending of the ligand planes was observed in $Mo(S_2C_2H_2)_3$[130] and also in $Mo(Se_2C_2(CF_3)_2)_3$,[152] where the ligand planes deviate from the MoS_2 and $MoSe_2$ planes by 18° and 18.6° respectively. Although these deviations are uniform

in these previous two examples, the molecules both having 3/m symmetry, they are irregular for $Mo(bdt)_3$ with the ligand/MoS_2 dihedral angles being 13.1°, 21.1°, and 30.0° (mean 21.4°). Schrauzer[130] has attributed this as being due to intramolecular effects, saying that the sulfur may be in a state between sp^2 and sp^3 hybridization, with possible added stabilization from packing forces. However from the structure of $Mo(bdt)_3$ it is obvious that packing forces contribute significantly, as witnessed by the wide range in dihedral angles observed. Table 26 shows that several intermolecular contacts are comparable to the predicted van der Waals contacts[151] (Predicted values: S···C, 3.70 Å; S···S, 3.70 Å; S···H, 3.05 Å; C···C, 3.70 Å; C···H 3.05 Å; H···H, 2.40 Å). Thus packing is very efficient and will probably be important in the bending of the ligand planes. A packing diagram, viewed down the *c* axis is shown in Fig. 13. The efficient packing is obvious from this diagram with the molecules packing in a gear-wheel arrangement.

As shown in Table 28, a further indication of the regularity of the prism is given by the similarity of the angles between the three MoS_2 planes, all being close to the expected value of 120°. The two tri-

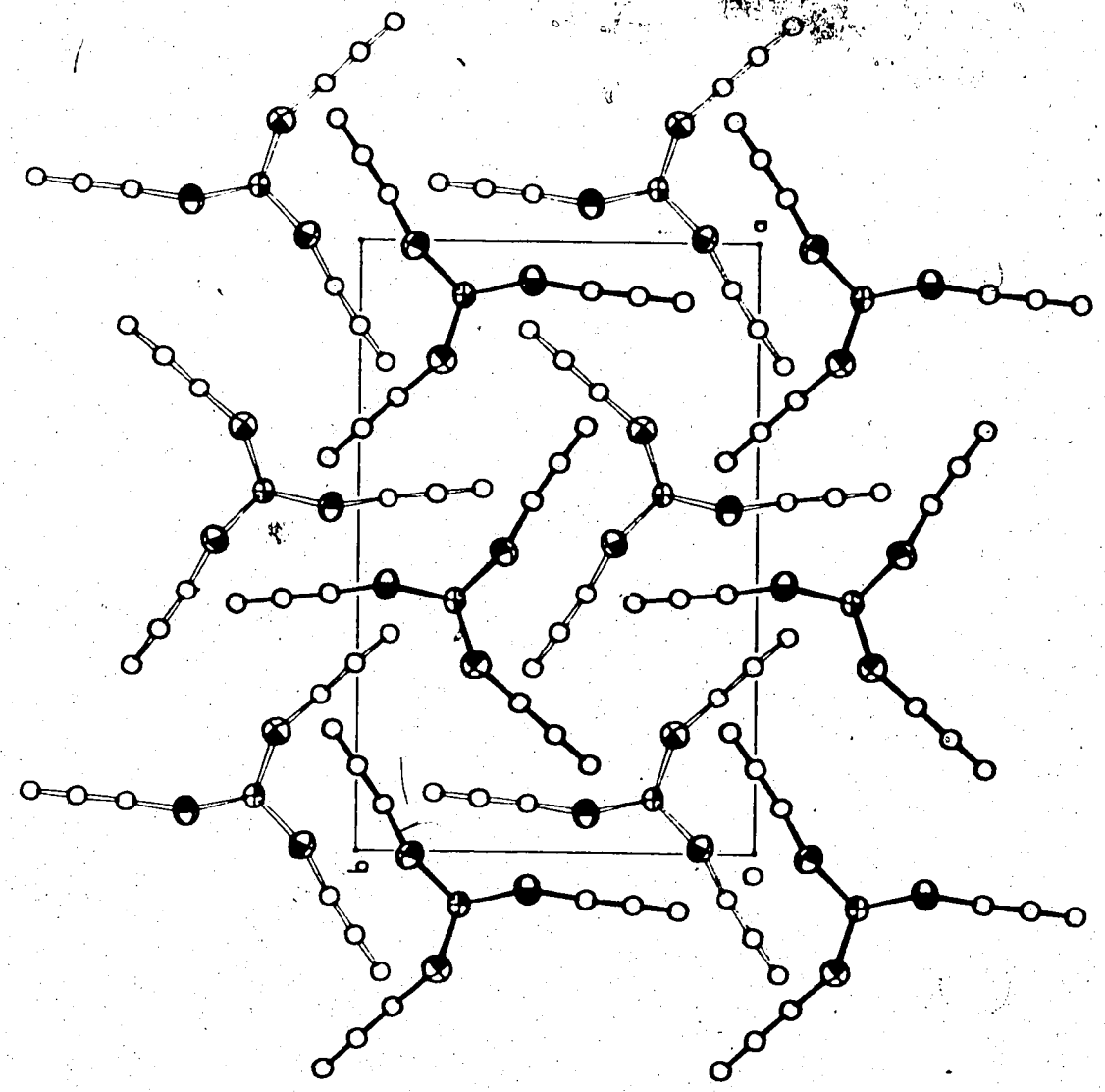


Fig. 13: PACKING DIAGRAM FOR $Mo(S_2C_6H_4)_3$, PROJECTED ON THE *ab* PLANE.

angular faces of the prism are also almost exactly parallel.

The Mo-S-C angles (mean 106.2°) are similar to the values of 109(1)° and 109.9(4)° observed in $Re(S_2C_2Ph_2)_3$ and $V(S_2C_3Ph_2)_3$, however they are significantly smaller, again probably due to differences in the ligands. The S-C-C' angles (mean 119.4°) are in good agreement with the value of 120°. Similarly all C-C-C angles within the benzene rings are close to their expected value of 120°.

CHAPTER VII: THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRAPHENYLARSONIUM *TRIS* (BENZENE-1,2-DITHIOLATO) NIOBIUM, ($[(C_6H_5)_4As][Nb(S_2C_6H_4)]$)

EXPERIMENTAL

Dark purple crystals suitable for single crystal X-ray diffraction study, prepared by the reaction of sodium cyclopentadienide with benzene dithiol and subsequent reaction with $Nb[N(CH_3)_2]_5$ and crystallization with tetraphenylarsonium chloride,[143] were kindly supplied by Dr. Takats and Mr. Martin. Preliminary photography indicated 2/m Laué symmetry consistent with a monoclinic space group. Systematic absences, as determined by Weissenberg ($h0\ell$, $h1\ell$; CuK_α X-radiation) and Precession photographs ($0k\ell$, $1k\ell$, $hk0$, $hk1$; MoK_α X-radiation), are $0k0$: $k = 2n + 1$ and $h0\ell$: $h + \ell = 2n + 1$ indicating the non-standard space group $P2_1/n$, which was retained because of the convenient β angle. The cell parameters obtained at 22°C from a least squares analysis of the setting angles of 12 reflections, which were centred accurately on a Picker automatic four circle diffractometer, using CuK_{α_1} X-radiation (λ = 1.54051 Å), are: a = 22.983(7) Å, b = 12.747(4) Å, c = 13.150(3) Å, β = 92.09(2)°. The observed density, obtained by

floatation in aqueous zinc bromide solution, is 1.52(2) g cm^{-3} and is in reasonable agreement with the theoretical value of 1.54 g cm^{-3} calculated assuming four molecules with formula weight 896.94 a.m.u. per unit cell of volume 3867.12 $\AA^3$.

Intensity data were collected on the Picker automatic diffractometer, using CuK_α X-radiation, filtered using a 0.0005" thick Ni foil, and using a 2° take-off angle. The crystal was aligned in a general orientation but with its b^* axis approximately coincident with the ϕ axis of the instrument. Crystal faces were identified and perpendicular distances between faces of the same form were measured as: {1,0,0}, 0.206 mm; {$\bar{2}$,1,0}, 0.206 mm; {$\bar{2}$,$\bar{1}$,0}, 0.206 mm; {$\bar{1}$,0,1}, 0.155 mm; {1,0,1}, 0.175 mm.

In the data collection a coupled $2\theta/\omega$ scan was used with a 2θ scan speed of 1°/min to collect all reflections with $2\theta \leq 115°$. The peak scan was 2° (2 min) for low angle reflections but increased with increasing 2θ due to compensation for $\alpha_1\alpha_2$ separation. Background counts were measured for 20 seconds at the limits of the two theta scan. The scattered X-rays were detected by a scintillation counter used in conjunction with a pulse height analyzer tuned to accept 95% of the CuK_α peak. Three standard reflections

were collected automatically every 100 data reflections. Another five standard reflections were collected manually every 10 hours to detect more precisely decomposition and crystal centering errors. No significant decomposition was observed but small fluctuations ($\pm$ 1%), due to an instability of the goniometer head, were detected. These fluctuations were not regular and corrections were not made.

Of the 5862 unique reflections collected, 3604 were considered as significantly above background using the criterion $I/\sigma(I) \geq 3.0$. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization and absorption effects. For CuK_α X-radiation, the linear absorption coefficient[86] is 68.42 cm^{-1} which yielded a range of transmission factors of 0.4359 to 0.3128. Standard deviations were estimated using a "p factor" of 0.03 as outlined in Chapter II. Terms used in the Zachariasen[148] extinction correction were calculated at this stage.

TABLE 29: MAJOR PATTERSON PEAKS AND THEIR ASSIGNMENT

OBSERVED VECTOR	RELATIVE INTENSITY	ASSIGNMENT	CALCULATED POSITION[a]
0.500, 0.063, 0.500	250	$1/2,\ 1/2-2y_1,\ 1/2$	0.500, 0.064, 0.500
0.339, 0.500, 0.106	226	$1/2-2x_1,\ 1/2,\ 1/2-2z_1$	0.340, 0.500, 0.114
0.209, 0.377, 0.532	159	$-(x_1+x_2),(y_1+y_2),-(z_1+z_2)$	0.208, 0.374, 0.544
0.287, 0.440, 0.958	148	$1/2+(x_1+x_2),\ 1/2-(y_1-y_2),\ 1/2+(z_1+z_2)$	0.292, 0.438, 0.956
0.130, 0.126, 0.578	146	$1/2-(x_1-x_2),\ 1/2-(y_1+y_2),\ 1/2-(z_1-z_2)$	0.132, 0.126, 0.570
0.500, 0.188, 0.500	140	$1/2,\ 1/2-2y_2,\ 1/2$	0.500, 0.188, 0.500
0.165, 0.424, 0.395	113	$2x_1,\ 2y_1,\ 2z_1$	0.160, 0.436, 0.386
0.078, 0.500, 0.958	103	$1/2-2x_2,\ 1/2,\ 1/2-2z_2$	0.076, 0.500, 0.974
0.418, 0.314, 0.532	63	$2x_2,\ 2y_2,\ 2z_2$	0.424, 0.312, 0.526

[a]Calculated on the basis of the consistent solution:

$x_1 = 0.580,\ y_1 = 0.218,\ z_1 = 0.193;\ x_2 = 0.212,\ y_2 = 0.156,\ z_2 = 0.263.$

STRUCTURE SOLUTION AND REFINEMENT

A sharpened[146] Patterson was calculated between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, $0 \leq w \leq 1.0$. The general positions for space groups $P2_1/n$ are: $x, y, z; \bar{x}, \bar{y}, \bar{z}; 1/2 + x, 1/2 - y, 1/2 + z$; and $1/2 - x, 1/2 + y, 1/2 - z$. For one niobium [coordinates (x_1, y_1, z_1)] and one arsenic atom [coordinates (x_2, y_2, z_2)] per general position, the major peaks in the map can be assigned as shown in Table 29.

A brief outline of the refinement is shown in Table 30.

TABLE 30: REFINEMENT OUTLINE

	MODEL	R_1	R_2
(1)	Nb and As positions, B's fixed	0.421	0.507
(2)	Nb, As, and S positions, isotropic B's	0.270	0.359
(3)	Nb, As, S with isotropic B's, benzene rings as rigid bodies	0.076	0.087
(4)	Absorption and Extinction[147]	0.064	0.072
(5)	Nb, S, and As anisotropic	0.056	0.065
(6)	Nb, S, and As anisotropic, ligand carbons individual isotropic, H atoms and benzene rings on arsenic as rigid bodies	0.049	0.051
(7)	Model (6) but with anisotropic dithiolene carbons	0.047	0.048

Structure factors were calculated using the atomic scattering factors for the neutral atoms for niobium, arsenic, sulfur, and carbon as tabulated by Cromer and Mann.[75] The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.[149] In addition, anomalous dispersion corrections[76] were applied to the niobium, arsenic and sulfur scattering factors ($^{\Delta}f'_{Nb} = -0.58$, $^{\Delta}f''_{Nb} = 2.68$, $^{\Delta}f'_{As} = -1.17$, $^{\Delta}f''_{As} = 1.17$, $^{\Delta}f'_{S} = 0.31$, $^{\Delta}f''_{S} = 0.58$). Features surrounding the Nb, As and S atoms in the electron density difference map suggested the anisotropic refinement, and the validity was verified by a Hamilton's R Test[79] at the 0.005 significance level.

Initially the benzene rings were refined as rigid bodies constrained to their well known geometry. In model (6) the carbon atoms of the benzene dithiol ligands were refined individually with isotropic temperature factors, and the phenyl groups on the arsenic atoms were refined as rigid bodies. The hydrogen positions were calculated from the geometry and orientation of the benzene rings and were also added as rigid bodies, using a C-H distance of 1.0 Å. The hydrogen rigid bodies were not refined however. The final model was refined with anisotropic temperature factors on the carbon atoms of the dithiolene

ligands. This was again justified by a Hamilton's R Test[79] at the 0.005 significance level.

In the final least squares refinement, 284 parameters were varied, and the standard deviation in an observation of unit weight was 1.641. The final value of the refined extinction parameter, C, was 8.74×10^{-7}.

RESULTS

Observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 31. The final fractional coordinates and isotropic B's of all atoms are shown in Table 32. Standard deviations were obtained from the inverse matrix of the final least squares analysis. Table 33 shows the anisotropic thermal parameters (U_{ij}'s).[80] Intra-ionic contacts and angles, shown in Tables 34 and 35, were obtained with their standard deviations from ORFFE. Inter-ionic contacts (also obtained from ORFFE) are shown in Table 36. Selected least squares planes are given in Table 37. In Table 38, the dihedral angles between some selected planes are shown.

In Fig. 14 a three-dimensional view of the $Nb(bdt)_3^-$ anion is shown. Fig. 16 shows the anion and the

$(C_6H_5)_4As^+$ cation together, viewed down the crystallographic *b* axis. The numbering scheme is shown in both diagrams. For the carbon atoms in the phenyl groups, the first number designates the ring number and the second number is the sequence of the atom in the ring. The carbon atoms are numbered sequentially and for the phenyl groups in the cation the first atom in the numbering scheme is always bonded to the arsenic atom. The hydrogen atoms are not shown but are numbered from H1 to H32 and are bonded, four on each dithiolene ligand and five on each phenyl group, sequentially from C12 to C76.

In the three dimensional representations the niobium, sulfur and arsenic atoms are shown with 50% probability thermal ellipsoids. The carbon atoms are shown, however, with artificially low isotropic thermal parameters, for clarity.

TABLE 31: OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (ELECTRONS X 10)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 0***				-24	4	225	284	-18	8	281	254	-13	0	186	178	-4	2	474	465
-24	0	392	416	-22	4	425	428	-16	8	486	518	-12	0	332	347	-3	2	1266	1145
-22	0	258	305	-20	4	1304	1315	-14	8	254	240	-10	0	506	520	-2	2	1583	1514
-20	0	710	740	-14	4	436	441	-12	8	1570	1537	-9	0	698	715	-1	2	940	903
-18	0	825	793	-12	4	361	378	-8	8	307	287	-8	0	714	765	0	2	377	370
-14	0	1586	1593	-10	4	1648	1602	-6	8	1253	1312	-7	0	1381	1406	1	2	600	622
-12	0	601	595	-8	4	460	471	-2	8	1567	1593	-6	0	1944	2032	2	2	2044	2137
-10	0	1771	1779	-6	4	701	712	0	8	1366	1422	-4	0	7895	876	3	2	231	256
-8	0	1451	1521	-4	4	798	708	2	8	1166	1158	-2	0	3003	3089	4	2	566	561
-6	0	177	177	-2	4	811	808	4	8	542	510	-1	0	229	254	5	2	263	266
-4	0	1442	1465	0	4	482	494	6	8	298	326	1	0	249	254	6	2	895	942
-2	0	150	190	2	4	504	535	8	8	1257	1296	2	0	3070	3089	7	2	264	287
2	0	136	190	4	4	940	965	10	8	220	229	4	0	891	876	8	2	642	671
4	0	1432	1445	6	4	799	891	12	8	712	709	6	0	1994	2032	10	2	963	1002
8	0	1475	1521	8	4	978	1046	14	8	2731	243	7	0	1366	1406	12	2	769	820
10	0	1761	1779	10	4	743	813	18	8	795	760	8	0	728	765	13	2	275	214
12	0	609	595	12	4	388	384	20	8	300	318	9	0	708	715	14	2	188	132
14	0	1555	1593	14	4	1021	1058	-17	9	769	814	10	0	505	520	16	2	681	678
18	0	798	793	16	4	275	254	-15	9	404	401	12	0	319	347	18	2	561	578
20	0	729	740	20	4	933	923	-13	9	604	595	13	0	222	178	19	2	705	721
22	0	242	305	22	4	573	553	-9	9	1045	1046	14	0	485	487	20	2	422	382
24	0	381	416	-23	5	826	885	-7	9	319	366	15	0	235	244	22	2	493	497
-23	1	242	313	-21	5	246	239	-5	9	399	338	16	0	1176	1199	23	2	206	143
-21	1	997	1016	-19	5	358	388	-3	9	1204	1213	18	0	305	257	-23	3	408	380
-17	1	1234	1260	-17	5	231	254	-1	9	911	958	19	0	653	627	-21	3	1127	1139
-15	1	618	603	-13	5	705	644	1	9	845	845	22	0	519	570	-19	3	253	265
-13	1	943	991	-11	5	199	169	5	9	1517	1506	24	0	198	120	-18	3	365	318
-11	1	299	289	-9	5	1675	1573	7	9	351	365	-23	1	333	347	-17	3	439	438
-9	1	296	305	-7	5	1103	1042	9	9	289	289	-22	1	223	234	-16	3	575	537
-7	1	621	647	-5	5	571	563	15	9	901	885	-21	1	398	390	-15	3	358	373
-5	1	852	842	-3	5	341	351	17	9	236	225	-19	1	1257	1246	-14	3	260	264
-3	1	2846	2603	-1	5	239	225	19	9	210	200	-18	1	293	283	-13	3	398	380
-1	1	875	841	1	5	1375	1455	-12	10	485	549	-17	1	253	232	-12	3	184	84
1	1	1075	1239	3	5	2539	2662	-10	10	332	326	-16	1	665	687	-11	3	831	787
3	1	2074	2196	5	5	308	320	-8	10	603	608	-15	1	276	268	-9	3	850	826
5	1	3145	3123	7	5	699	740	-6	10	998	1051	-13	1	570	557	-8	3	923	910
7	1	1645	1682	9	5	353	400	-2	10	712	765	-11	1	1367	1369	-7	3	216	201
11	1	1822	1857	11	5	1034	1072	0	10	675	712	-10	1	1061	1036	-6	3	735	706
17	1	1490	1463	15	5	571	536	2	10	1381	1376	-9	1	395	400	-5	3	256	284
19	1	676	707	17	5	817	807	4	10	653	660	-8	1	562	549	-4	3	1281	1192
21	1	280	325	19	5	853	851	6	10	835	798	-7	1	220	211	-3	3	285	262
23	1	350	307	21	5	297	284	8	10	823	801	-5	1	856	916	-2	3	709	671
25	1	211	199	23	5	501	483	12	10	762	751	-4	1	473	468	-1	3	1214	1196
-24	2	566	591	-20	6	950	999	16	10	495	451	-3	1	334	341	0	3	1569	1518
-22	2	274	319	-18	6	380	367	-15	11	231	212	-2	1	1299	1209	1	3	2907	2826
-20	2	360	412	-16	6	532	541	-9	11	681	676	-1	1	1375	1221	2	3	2163	2226
-18	2	872	906	-14	6	218	254	-5	11	497	477	0	1	428	445	3	3	288	317
-16	2	655	625	-12	6	1225	1212	-1	11	399	374	1	1	2029	2240	4	3	252	260
-12	2	720	649	-10	6	1123	1167	1	11	599	542	2	1	653	704	5	3	1000	1061
-10	2	1514	1461	-8	6	509	491	9	11	595	576	3	1	1085	1139	6	3	314	333
-8	2	956	941	-6	6	929	927	11	11	754	811	4	1	174	216	8	3	500	528
-6	2	1294	1249	-4	6	321	312	13	11	284	270	5	1	1885	1918	9	3	1737	1795
-4	2	3766	3379	-2	6	902	943	15	11	483	495	6	1	299	294	10	3	329	312
-2	2	2442	2278	0	6	485	436	-10	12	289	311	7	1	869	909	11	3	958	952
0	2	2486	2421	2	6	848	852	-8	12	280	304	9	1	1626	1699	12	3	633	625
2	2	278	315	4	6	619	627	-6	12	962	1020	10	1	1062	1104	13	3	695	719
4	2	772	770	6	6	352	345	-2	12	221	197	11	1	479	552	14	3	510	528
6	2	1700	1764	10	6	1005	999	4	12	860	925	12	1	289	285	15	3	404	413
8	2	1439	1492	12	6	851	890	6	12	382	356	13	1	923	941	16	3	266	208
12	2	571	594	14	6	538	539	8	12	1028	1048	14	1	658	655	17	3	454	462
14	2	1566	1637	18	6	383	368	10	12	254	197	15	1	305	333	19	3	767	768
18	2	242	288	20	6	570	589	12	12	340	345	16	1	861	885	21	3	302	315
20	2	966	997	22	6	738	719	-9	13	590	603	17	1	243	293	22	3	303	252
24	2	371	375	-21	7	281	327	-5	13	592	633	19	1	1144	1146	-24	4	414	438
-23	3	910	909	-19	7	633	596	-1	13	226	248	21	1	228	193	-23	4	293	268
-21	3	580	554	-17	7	773	791	1	13	203	159	22	1	255	283	-22	4	269	250
-19	3	566	525	-15	7	739	726	3	13	549	591	-24	2	309	307	-21	4	280	257
-15	3	525	526	-13	7	597	604	5	13	638	643	-23	2	203	158	-19	4	312	280
-13	3	453	446	-9	7	1301	1308	7	13	430	438	-21	2	302	312	-18	4	803	825
-11	3	495	503	-7	7	832	833	-6	14	337	368	-20	2	305	307	-16	4	289	270
-9	3	443	332	-5	7	858	844	-2	14	215	238	-19	2	457	440	-14	4	4691	476
-7	3	2384	2290	-3	7	1385	1365	2	14	618	622	-18	2	477	482	-13	4	784	796
-5	3	2812	2643	1	7	2691	2655	**K = 1*****				-16	2	606	587	-12	4	371	385
-3	3	1367	1267	3	7	889	857	-24	0	199	126	-14	2	355	369	-11	4	207	232
-1	3	815	776	5	7	1235	1210	-22	0	568	570	-13	2	511	479	-9	4	647	624
1	3	792	853	7	7	660	690	-21	0	225	197	-12	2	545	544	-8	4	1256	1233
3	3	1740	1918	9	7	796	795	-19	0	621	627	-10	2	215	192	-7	4	1243	1208
7	3	782	812	11	7	218	246	-18	0	277	257	-8	2	1793	1653	-6	4	164	120
11	3	1404	1476	15	7	1095	1043	-16	0	1167	1199	-7	2	700	704	-5	4	448	440
15	3	652	754	19	7	414	413	-15	0	241	244	-6	2	548	536	-4	4	885	856
17	3	1288	1305	21	7	307	306	-14	0	480	487	-5	2	1157	1140	-3	4	148	127
21	3	520	505	-20	8	958	1015												

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
***	=	10000		14	6	458	421	2	9	387	403	-13	0	1290	1294	-15	2	451	466
-2	4	557	545	17	6	331	378	3	9	448	465	-12	0	978	985	-14	2	190	204
-1	4	1372	1341	18	6	426	462	7	9	934	965	-11	0	471	460	-13	2	670	659
0	4	250	224	20	6	825	804	12	9	344	308	-10	0	1501	1478	-12	2	492	503
1	4	1212	1245	22	6	295	303	13	9	719	742	-9	0	533	581	-11	2	1096	1083
2	4	1786	1820	-21	7	578	600	14	9	257	251	-8	0	1617	1622	-10	2	1593	1568
6	4	1503	1570	-19	7	389	384	16	9	465	447	-7	0	502	487	-9	2	337	341
7	4	397	386	-15	7	981	988	17	9	328	353	-6	0	1144	1179	-7	2	985	980
8	4	518	509	-14	7	238	215	-18	10	220	190	-5	0	844	872	-6	2	871	905
9	4	1019	1063	-13	7	493	533	-15	10	318	298	-4	0	1705	1676	-4	2	1961	1797
11	4	190	198	-11	7	556	541	-14	10	567	536	-3	0	1492	1508	-3	2	2767	2514
12	4	986	1011	-10	7	586	575	-11	10	209	233	-2	0	1043	1033	-2	2	1123	1062
13	4	716	719	-9	7	850	836	-8	10	475	463	-1	0	265	282	0	2	444	465
14	4	252	260	-7	7	1510	1485	-6	10	275	287	0	0	2940	2998	1	2	294	341
15	4	204	204	-6	7	196	152	-4	10	712	694	1	0	254	282	2	2	426	466
16	4	625	647	-5	7	585	568	-3	10	385	385	2	0	1026	1033	3	2	1270	1371
17	4	272	264	-4	7	431	449	-2	10	415	397	3	0	1514	1508	4	2	598	665
18	4	310	253	-3	7	232	257	-1	10	469	486	4	0	1676	1676	5	2	863	903
19	4	222	256	-2	7	578	605	0	10	536	537	5	0	878	872	6	2	985	1040
20	4	509	500	-1	7	2165	2142	2	10	1022	1021	6	0	1161	1179	7	2	611	604
22	4	871	863	0	7	228	219	3	10	209	199	7	0	508	487	8	2	2114	2174
-23	5	209	226	1	7	257	276	4	10	361	357	8	0	1599	1622	10	2	557	548
-21	5	686	677	2	7	599	617	5	10	224	213	9	0	538	581	11	2	258	263
-18	5	367	378	3	7	789	791	6	10	593	560	10	0	1487	1478	12	2	454	474
-16	5	424	460	4	7	197	171	10	10	982	962	11	0	457	460	13	2	502	513
-15	5	795	778	5	7	225	251	13	10	370	379	12	0	947	985	14	2	383	405
-12	5	368	262	7	7	951	948	16	10	387	375	13	0	1270	1294	17	2	845	889
-11	5	335	306	8	7	228	238	17	10	326	282	14	0	672	699	20	2	574	579
-10	5	298	228	9	7	950	931	-14	11	231	227	15	0	595	603	21	2	288	277
-9	5	741	723	10	7	222	235	-11	11	709	760	17	0	529	549	-24	3	614	666
-8	5	362	361	11	7	562	582	-8	11	530	596	18	0	316	347	-23	3	314	354
-7	5	642	600	12	7	408	433	-7	11	493	545	20	0	387	409	-21	3	330	365
-6	5	479	470	13	7	325	309	-6	11	539	598	21	0	508	539	-20	3	250	220
-5	5	1165	1077	14	7	246	228	-5	11	220	218	24	0	282	291	-19	3	483	502
-4	5	1361	1271	15	7	241	189	-4	11	427	487	-24	1	389	442	-18	3	218	336
-3	5	157	167	17	7	728	702	-3	11	690	725	-21	1	638	664	-16	3	236	264
-2	5	913	882	20	7	251	178	-1	11	361	403	-18	1	326	332	-14	3	857	874
-1	5	1209	1222	-18	8	892	925	0	11	274	211	-16	1	556	580	-13	3	976	937
0	5	316	295	-16	8	457	410	1	11	317	294	-15	1	589	576	-12	3	270	249
1	5	1543	1546	-14	8	818	809	4	11	230	219	-14	1	520	510	-11	3	715	690
2	5	318	297	-13	8	421	487	5	11	382	364	-13	1	1330	1355	-10	3	1504	1452
3	5	961	993	-12	8	634	616	6	11	237	263	-12	1	692	652	-9	3	1545	1393
5	5	675	652	-11	8	269	286	7	11	992	967	-11	1	708	697	-7	3	880	872
6	5	1281	1276	-10	8	754	738	9	11	544	551	-10	1	484	515	-6	3	205	224
9	5	2000	2030	-9	8	241	254	10	11	402	362	-9	1	1625	1594	-4	3	2231	2045
10	5	897	939	-8	8	412	351	11	11	229	136	-8	1	381	365	-3	3	1107	1040
13	5	344	312	-6	8	299	272	13	11	614	627	-7	1	726	728	-2	3	1970	1862
14	5	522	569	-5	8	698	722	-14	12	203	233	-5	1	248	241	-1	3	536	528
15	5	316	320	-4	8	1452	1436	-11	12	400	413	-4	1	1704	1625	0	3	877	874
17	5	447	450	-3	8	470	460	-8	12	563	584	-3	1	1340	1260	1	3	883	882
19	5	704	696	-2	8	632	616	-6	12	484	511	-2	1	1706	1633	2	3	339	356
21	5	530	562	-1	8	594	611	-3	12	391	398	-1	1	1188	1114	3	3	745	795
22	5	287	239	2	8	1674	1703	0	12	384	428	0	1	2069	2080	4	3	605	649
23	5	427	422	3	8	410	389	1	12	312	295	1	1	255	284	5	3	227	255
-22	6	321	322	4	8	798	800	2	12	373	381	2	1	269	342	6	3	444	458
-20	6	211	198	5	8	630	638	4	12	463	451	3	1	3026	3179	7	3	1316	1375
-18	6	1144	1132	6	8	377	367	6	12	294	255	4	1	1506	1550	8	3	1466	1491
-14	6	343	344	7	8	204	216	10	12	800	802	5	1	711	758	9	3	200	174
-12	6	1078	1071	9	8	200	200	11	12	546	509	6	1	1432	1488	10	3	540	520
-11	6	305	253	10	8	929	975	12	12	270	272	7	1	690	712	11	3	1429	1478
-10	6	847	792	12	8	823	836	-11	13	613	656	8	1	842	885	12	3	1292	1311
-9	6	387	357	13	8	429	437	-9	13	253	292	9	1	543	573	13	3	375	371
-8	6	843	825	14	8	491	489	-8	13	212	269	10	1	1334	1393	14	3	940	950
-7	6	846	776	15	8	411	405	-6	13	498	526	11	1	1477	1476	17	3	543	571
-5	6	682	649	16	8	657	611	-3	13	557	560	12	1	271	244	19	3	340	289
-4	6	2036	1924	17	8	519	479	-1	13	301	313	13	1	462	498	22	3	249	137
-3	6	357	318	18	8	355	298	1	13	315	359	14	1	946	961	23	3	351	342
-2	6	703	649	20	8	521	506	3	13	625	624	16	1	729	763	24	3	328	372
-1	6	486	464	-19	9	477	521	7	13	275	281	17	1	477	447	-23	4	277	309
0	6	497	544	-18	9	265	234	8	13	354	329	18	1	424	468	-22	4	232	245
1	6	483	499	-17	9	327	339	9	13	456	438	19	1	321	360	-21	4	539	535
2	6	470	476	-15	9	220	291	-6	14	342	374	20	1	395	377	-20	4	524	534
3	6	427	415	-14	9	434	412	4	14	694	688	21	1	592	581	-18	4	220	202
4	6	410	403	-13	9	218	326	***	=	20000		22	1	217	165	-16	4	410	395
5	6	406	411	-12	9	229	160	-24	0	321	291	24	1	243	231	-15	4	523	503
6	6	1072	1095	-11	9	1115	1132	-21	0	553	539	-24	2	327	364	-14	4	601	570
7	6	347	328	-10	9	332	341	-20	0	375	409	-22	2	244	234	-13	4	944	929
8	6	740	767	-7	9	860	888	-18	0	348	347	-21	2	536	528	-12	4	312	269
9	6	286	273	-6	9	739	731	-17	0	545	549	-18	2	557	580	-11	4	983	928
10	6	533	566	-2	9	467	466	-15	0	617	603	-17	2	225	166	-10	4	1498	1460
12	6	834	861	-1	9	1726	1742	-14	0	685	699	-16	2	582	566	-9	4	201	191
13	6	716	740	1	9	921	922												

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 2				5	6	509	612	-13	9	277	256	7	13	296	252	-13	2	884	956
-8	4	359	327	6	6	419	421	-9	9	925	902	8	13	562	552	-12	2	1043	1029
-7	4	2817	2643	7	6	886	881	-8	9	865	912	-5	14	540	544	-11	2	971	951
-5	4	1647	1628	8	6	646	639	-7	9	242	197	-2	14	495	541	-10	2	885	849
-4	4	1837	966	9	6	419	445	-4	9	778	777	2	14	559	575	-8	2	644	637
-3	4	561	521	10	6	989	1033	-3	9	588	617	K = 3				-7	2	455	424
-2	4	737	727	11	6	256	221	-2	9	942	918	-22	0	345	319	-6	2	466	428
-1	4	662	651	12	6	491	522	-1	9	670	677	-20	0	682	696	-5	2	1676	1641
0	4	508	495	13	6	414	406	1	9	599	611	-19	0	496	485	-4	2	682	646
1	4	1606	1607	14	6	298	307	2	9	685	676	-18	0	250	195	-3	2	323	281
2	4	387	395	15	6	665	688	3	9	501	493	-16	0	208	144	-2	2	146	168
3	4	1315	1375	16	6	298	283	4	9	577	584	-15	0	724	727	-1	2	854	812
4	4	1355	1379	17	6	493	468	5	9	782	783	-14	0	559	552	0	2	1741	1718
5	4	799	822	18	6	416	381	6	9	765	774	-13	0	455	448	1	2	307	335
7	4	854	887	22	6	528	524	7	9	204	203	-11	0	1145	1151	2	2	797	846
8	4	769	817	-21	7	261	250	9	9	526	534	-10	0	1435	1455	3	2	497	514
9	4	830	920	-20	7	301	270	10	9	562	555	-8	0	991	1009	4	2	780	852
11	4	389	427	-17	7	407	388	12	9	585	550	-7	0	1113	1086	5	2	838	907
12	4	328	374	-15	7	492	490	15	9	221	236	-6	0	207	149	6	2	600	615
14	4	604	597	-13	7	367	328	16	9	178	169	-5	0	710	727	7	2	307	313
15	4	1098	1126	-12	7	611	600	18	9	712	678	-4	0	357	329	9	2	910	944
16	4	433	382	-11	7	523	504	-17	10	227	257	-3	0	1633	1657	10	2	1291	1358
17	4	254	172	-9	7	721	711	-16	10	236	219	-2	0	726	723	11	2	347	380
18	4	282	284	-8	7	1070	1054	-12	10	833	838	-1	0	308	345	13	2	370	438
19	4	311	259	-7	7	766	782	-9	10	594	648	1	0	304	345	14	2	397	425
20	4	565	580	-6	7	438	436	-3	10	387	395	2	0	726	723	15	2	253	246
21	4	290	223	-5	7	959	904	0	10	507	540	3	0	1628	1657	16	2	283	322
22	4	398	395	-4	7	663	660	1	10	560	582	4	0	334	329	17	2	404	390
-23	5	232	269	-3	7	578	598	2	10	801	797	5	0	725	727	18	2	367	380
-20	5	539	540	-2	7	519	525	3	10	261	245	7	0	1106	1086	19	2	580	598
-19	5	338	343	-1	7	687	679	5	10	472	457	8	0	989	1009	20	2	285	297
-18	5	217	232	0	7	327	353	7	10	493	540	10	0	1415	1455	22	2	444	446
-17	5	380	277	1	7	664	685	8	10	542	532	11	0	1110	1151	24	2	227	209
-16	5	238	204	3	7	287	332	9	10	277	274	13	0	452	448	-22	3	324	278
-15	5	379	417	4	7	378	381	10	10	242	200	14	0	550	552	-19	3	424	430
-14	5	400	409	6	7	307	309	12	10	410	427	15	0	713	727	-18	3	569	557
-13	5	811	792	7	7	1160	1165	15	10	862	791	19	0	490	485	-17	3	657	611
-12	5	294	288	8	7	259	191	16	10	303	261	20	0	689	696	-16	3	642	662
-11	5	691	683	9	7	777	771	-13	11	344	395	22	0	318	319	-15	3	622	599
-10	5	1553	1472	11	7	256	248	-12	11	410	419	-23	1	255	292	-14	3	540	559
-8	5	1058	959	13	7	281	286	-9	11	574	604	-22	1	203	243	-12	3	408	413
-7	5	504	469	14	7	583	597	-8	11	453	441	-19	1	318	270	-11	3	841	826
-6	5	1075	1078	15	7	383	425	-6	11	824	808	-18	1	628	632	-9	3	739	715
-5	5	534	468	16	7	239	252	-5	11	281	212	-17	1	283	262	-8	3	1977	1885
-4	5	861	820	17	7	249	254	-4	11	270	306	-16	1	783	775	-7	3	771	732
-3	5	441	429	18	7	483	452	-2	11	303	335	-14	1	441	489	-6	3	387	384
-2	5	1232	1210	21	7	439	441	-1	11	468	489	-13	1	198	162	-5	3	747	734
-1	5	1834	976	-21	8	240	210	0	11	288	275	-12	1	177	159	-4	3	761	740
0	5	194	225	-20	8	437	448	2	11	527	525	-11	1	1435	1444	-3	3	335	353
1	5	1637	1620	-18	8	226	253	3	11	331	272	-10	1	279	279	-2	3	789	772
3	5	365	361	-17	8	345	354	4	11	375	353	-8	1	1224	1179	-1	3	309	293
4	5	1158	1210	-15	8	701	735	5	11	581	574	-7	1	958	944	0	3	760	736
7	5	662	699	-14	8	360	345	7	11	240	225	-6	1	908	890	1	3	742	717
9	5	462	435	-13	8	355	361	8	11	457	486	-5	1	402	395	2	3	494	496
10	5	804	818	-12	8	815	811	9	11	325	303	-4	1	540	527	3	3	911	991
11	5	1446	1473	-11	8	947	947	10	11	280	274	-3	1	1241	1189	4	3	399	450
12	5	1598	1608	-10	8	728	705	11	11	257	230	-2	1	379	412	5	3	867	825
13	5	250	226	-8	8	716	690	12	11	257	274	-1	1	1376	1290	6	3	2526	2671
16	5	457	454	-7	8	671	640	-13	12	246	257	1	1	1595	1491	7	3	168	157
19	5	355	426	-6	8	402	413	-12	12	238	313	2	1	208	192	8	3	1140	1133
21	5	252	257	-4	8	672	612	-9	12	533	562	3	1	428	448	9	3	630	701
22	5	349	331	-2	8	386	387	-7	12	420	428	4	1	431	457	10	3	383	346
-20	6	660	679	0	8	959	952	-6	12	231	244	6	1	1045	1063	12	3	685	958
-16	6	280	291	1	8	990	982	-5	12	669	718	7	1	1227	1333	13	3	905	953
-14	6	631	575	2	8	306	317	-4	12	288	322	8	1	1066	1104	14	3	281	273
-13	6	644	683	3	8	268	291	-2	12	471	479	9	1	693	712	15	3	360	319
-12	6	638	622	4	8	828	815	0	12	324	293	10	1	772	764	16	3	445	494
-11	6	319	316	5	8	622	643	2	12	435	473	11	1	433	448	18	3	358	363
-10	6	1877	1832	6	8	507	518	5	12	451	407	12	1	686	709	20	3	408	413
-9	6	1360	1307	7	8	433	420	6	12	240	248	13	1	285	261	22	3	549	542
-8	6	449	428	8	8	497	520	8	12	524	535	14	1	740	734	-23	4	308	338
-7	6	656	655	9	8	392	380	12	12	331	322	16	1	1316	1303	-21	4	310	322
-5	6	201	151	10	8	523	523	-10	13	202	194	17	1	395	398	-20	4	513	478
-4	6	182	184	11	8	615	577	-9	13	299	338	18	1	356	347	-19	4	301	324
-3	6	376	340	12	8	485	463	-8	13	702	715	19	1	310	246	-18	4	482	502
-2	6	1828	1839	13	8	527	553	-7	13	194	211	22	1	457	431	-17	4	355	381
-1	6	158	152	15	8	983	1000	-2	13	352	390	-20	2	855	571	-15	4	1173	1144
0	6	351	360	17	8	346	324	-1	13	331	370	-19	2	540	549	-14	4	488	489
1	6	1097	1095	18	8	503	463	1	13	295	297	-17	2	386	400	-13	4	893	890
2	6	244	251	20	8	273	285	5	13	440	468	-15	2	710	708	-12	4	1104	1065
3	6	445	452	-19	9	295	233	6	13	298	253	-14	2	911	884	-11	4	1038	992
4	6	1030	1054	-17	9	579	568												

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
*** K = 3****				2	6	1069	1047	3	9	261	235	-24	0	324	353	-10	2	507	499
-9	4	939	894	3	6	224	266	4	9	489	495	-23	0	199	145	-9	2	361	360
-8	4	1350	1272	4	6	451	400	5	9	867	858	-22	0	479	500	-8	2	416	413
-7	4	1202	1156	5	6	430	443	6	9	378	353	-21	0	287	340	-7	2	833	803
-6	4	613	575	6	6	604	620	7	9	575	569	-18	0	344	321	-6	2	258	243
-5	4	1960	1883	7	6	567	559	10	9	537	518	-15	0	337	375	-5	2	183	142
-4	4	888	825	8	6	1033	1047	11	9	420	467	-14	0	332	379	-4	2	857	836
-3	4	635	602	9	6	1189	1210	12	9	549	543	-13	C	646	653	-3	2	1866	1741
-2	4	885	870	12	6	689	725	14	9	440	445	-12	0	779	785	-2	2	170	157
-1	4	639	641	13	6	585	570	16	9	419	433	-11	C	800	793	-1	2	655	652
0	4	1815	1818	14	6	242	261	-17	10	304	306	-10	0	218	216	1	2	931	942
1	4	264	237	17	6	442	428	-16	10	368	364	-9	0	344	365	2	2	944	1027
2	4	1063	1067	19	6	253	209	-15	10	424	453	-7	C	970	936	3	2	1400	1480
3	4	1206	1252	20	6	377	348	-14	10	387	420	-5	0	338	344	4	2	547	556
4	4	163	145	21	6	372	349	-13	10	221	272	-4	C	1839	1879	5	2	1365	1415
6	4	804	810	-20	7	356	324	-12	10	326	285	-2	C	1436	1393	6	2	303	315
7	4	419	418	-19	7	376	350	-11	10	616	630	-1	C	255	207	7	2	313	328
8	4	234	243	-18	7	212	225	-10	10	474	510	0	0	556	585	8	2	288	275
9	4	1450	1488	-14	7	678	708	-9	10	226	147	1	0	208	207	10	2	1216	1217
10	4	721	721	-13	7	480	520	-8	10	407	419	2	0	1405	1393	11	2	963	995
11	4	489	453	-12	7	256	254	-7	10	445	441	4	0	1807	1879	12	2	643	664
12	4	267	205	-11	7	215	258	-3	10	420	437	5	0	349	344	13	2	506	506
13	4	301	344	-9	7	869	814	-2	10	547	533	6	0	206	73	14	2	381	384
15	4	347	377	-8	7	408	439	-1	10	671	675	7	0	962	936	15	2	475	491
16	4	330	350	-7	7	698	684	2	10	418	418	9	C	335	365	16	2	312	296
17	4	469	456	-6	7	225	186	3	10	408	395	10	0	181	216	17	2	397	381
18	4	280	315	-5	7	414	417	4	10	606	608	11	0	774	793	18	2	378	404
19	4	280	243	-4	7	675	651	5	10	301	251	12	C	743	785	19	2	334	328
20	4	572	578	-3	7	272	274	7	10	860	821	13	C	627	653	20	2	659	670
23	4	428	410	-2	7	1162	1155	8	10	367	375	14	C	354	379	21	2	234	204
-21	5	257	249	-1	7	630	590	9	10	535	514	15	0	362	375	23	2	260	296
-18	5	540	531	1	7	157	140	10	10	578	571	18	0	367	321	-23	3	211	207
-17	5	396	407	2	7	746	743	13	10	384	401	21	C	334	340	-21	3	356	361
-15	5	494	456	3	7	442	474	16	10	247	210	22	0	482	500	-19	3	625	625
-13	5	630	622	4	7	354	340	-15	11	256	241	24	0	332	354	-18	3	526	506
-12	5	1015	992	5	7	774	792	-14	11	781	832	-24	1	566	570	-17	3	333	339
-11	5	451	414	6	7	822	796	-12	11	244	277	-21	1	431	392	-16	3	626	621
-9	5	663	667	8	7	199	191	-11	11	387	399	-19	1	737	732	-15	3	693	674
-8	5	873	857	9	7	795	775	-10	11	265	247	-17	1	304	329	-13	3	374	371
-7	5	393	414	10	7	292	301	-8	11	557	555	-16	1	490	511	-12	3	439	398
-6	5	642	640	11	7	807	829	-7	11	233	225	-15	1	382	343	-11	3	858	882
-5	5	160	153	12	7	728	725	-6	11	609	661	-14	1	816	798	-10	3	1056	1017
-4	5	2130	1972	14	7	256	251	-5	11	263	250	-12	1	446	411	-9	3	977	948
-3	5	1728	1598	17	7	348	368	-4	11	370	349	-11	1	246	270	-8	3	561	474
-2	5	935	908	19	7	457	413	-3	11	381	390	-10	1	1034	1013	-6	3	1115	1005
-1	5	839	858	20	7	360	343	0	11	954	925	-9	1	1278	1285	-5	3	326	307
1	5	626	611	-20	8	262	337	1	11	831	790	-7	1	748	749	-4	3	793	784
2	5	637	634	-18	8	232	158	2	11	329	294	-6	1	1218	1215	-3	3	223	187
3	5	933	996	-17	8	508	561	4	11	482	522	-5	1	395	412	-1	3	2527	2436
5	5	1215	1232	-15	8	225	240	7	11	500	476	-4	1	869	835	0	3	563	559
6	5	2240	2293	-12	8	223	204	10	11	432	436	-3	1	561	523	1	3	517	517
7	5	195	203	-10	8	940	986	-12	12	481	537	-2	1	374	330	2	3	855	873
8	5	261	283	-9	8	236	185	-11	12	625	657	-1	1	913	820	3	3	453	454
9	5	655	683	-5	8	715	757	-9	12	266	278	0	1	645	640	4	3	1880	1908
10	5	516	509	-2	8	570	545	-8	12	225	196	1	1	1061	1109	5	3	813	852
11	5	456	428	-1	8	928	923	-7	12	209	198	2	1	480	479	6	3	878	899
12	5	491	502	2	8	648	653	-5	12	233	233	3	1	292	317	7	3	580	573
13	5	636	691	5	8	615	615	-3	12	684	712	4	1	807	836	8	3	1100	1153
14	5	338	324	6	8	218	275	-2	12	743	779	5	1	581	596	9	3	374	394
16	5	236	154	8	8	1111	1117	0	12	545	559	6	1	1956	1651	11	3	198	170
17	5	419	399	9	8	1049	1064	2	12	355	278	7	1	780	770	12	3	215	181
18	5	309	328	10	8	331	307	3	12	566	589	8	1	722	739	13	3	499	470
19	5	347	364	12	8	296	277	4	12	356	408	9	1	1194	1220	14	3	1155	1137
20	5	586	587	13	8	489	445	6	12	307	297	10	1	622	648	15	3	386	402
21	5	400	397	14	8	330	322	7	12	503	490	12	1	219	207	19	3	491	490
-22	6	329	338	15	8	225	280	11	12	497	502	14	1	812	816	22	3	345	327
-18	6	503	464	16	8	257	178	-8	13	305	351	15	1	619	626	23	3	219	216
-17	6	409	410	17	8	488	435	-6	13	457	493	16	1	927	942	-22	4	285	322
-15	6	744	753	-19	9	441	487	-4	13	267	247	18	1	375	327	-21	4	364	396
-14	6	248	245	-18	9	304	318	-3	13	468	456	19	1	451	454	-20	4	277	345
-13	6	232	214	-15	9	209	220	-2	13	261	282	20	1	361	411	-19	4	364	319
-12	6	988	963	-14	9	806	849	-1	13	248	286	21	1	753	766	-18	4	703	695
-10	6	613	591	-13	9	621	604	0	13	462	479	22	1	292	251	-17	4	709	702
-8	6	1041	978	-12	9	522	516	1	13	348	334	23	1	486	509	-16	4	703	704
-7	6	392	414	-9	9	357	312	3	13	520	505	-22	2	275	328	-14	4	873	867
-6	6	444	447	-8	9	220	188	5	13	345	366	-18	2	497	517	-13	4	1387	1369
-5	6	919	882	-5	9	358	339	6	13	274	243	-15	2	208	206	-12	4	206	215
-3	6	390	359	-4	9	746	772	-1	14	182	98	-14	2	645	657	-8	4	346	323
-2	6	298	298	-2	9	489	483	0	14	484	484	-13	2	1335	1353	-7	4	1843	1728
-1	6	1121	1141	-1	9	260	255	1	14	246	302	-12	2	980	982	-6	4	919	975
0	6	810	823	1	9	262	285	*** K = 4****				-11	2	683	681	-5	4	618	558
1	6	318	267	2	9	706	736												

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
**K =		4****		17	6	372	382	-4	10	526	546	16	0	523	540	-11	3	350	354
-4	4	1769	1702	18	6	348	279	-3	10	410	405	17	0	275	241	-9	3	576	539
-3	4	998	927	21	6	303	263	0	10	439	417	18	0	235	275	-8	3	393	404
-2	4	961	964	-21	7	540	581	1	10	297	315	19	0	263	206	-7	3	1181	1136
-1	4	662	621	-20	7	251	291	2	10	277	202	20	0	677	721	-6	3	530	507
0	4	240	250	-18	7	307	370	3	10	629	591	-23	1	346	361	-4	3	1107	1047
1	4	1478	1490	-17	7	212	175	5	10	736	762	-22	1	256	272	-3	3	2155	2030
2	4	1908	1855	-14	7	426	480	6	10	541	555	-17	1	678	660	-2	3	845	807
4	4	876	915	-13	7	259	176	7	10	484	489	-16	1	328	315	-1	3	317	288
5	4	500	535	-12	7	515	506	8	10	269	252	-15	1	732	729	0	3	1413	1401
6	4	1507	1535	-11	7	766	738	9	10	288	347	-14	1	475	486	1	3	861	887
7	4	1442	1463	-10	7	442	451	12	10	210	176	-13	1	284	311	3	3	298	326
8	4	215	212	-9	7	253	232	14	10	259	232	-12	1	404	386	4	3	543	624
9	4	251	240	-7	7	289	319	15	10	456	455	-10	1	779	770	5	3	343	342
10	4	619	640	-6	7	609	618	-15	11	364	391	-8	1	1083	1079	6	3	950	976
11	4	1053	1092	-5	7	741	734	-14	11	213	170	-7	1	1140	1153	7	3	287	306
12	4	432	454	-4	7	409	365	-13	11	419	453	-6	1	636	642	8	3	353	384
14	4	388	371	-3	7	534	540	-12	11	638	669	-5	1	937	940	9	3	301	335
15	4	565	586	2	7	661	694	-8	11	270	303	-4	1	947	919	10	3	195	200
16	4	986	981	4	7	858	879	-7	11	323	339	-3	1	1923	1841	11	3	380	353
17	4	442	436	5	7	834	830	-6	11	536	560	-2	1	331	357	12	3	909	929
18	4	464	417	6	7	276	266	-5	11	232	240	0	1	157	91	13	3	274	257
19	4	244	207	7	7	584	556	-4	11	300	328	2	1	1077	1153	14	3	251	211
21	4	218	204	8	7	444	420	-3	11	292	292	3	1	924	1024	15	3	417	424
-20	5	323	371	9	7	605	639	-1	11	609	602	4	1	718	743	16	3	980	966
-19	5	538	527	12	7	340	289	1	11	219	156	6	1	931	950	21	3	320	283
-16	5	358	281	13	7	556	575	2	11	944	946	7	1	538	573	22	3	239	326
-15	5	215	182	17	7	290	329	3	11	279	310	8	1	800	834	-21	4	210	241
-14	5	559	565	19	7	411	378	6	11	364	332	9	1	704	721	-20	4	749	755
-11	5	1119	1075	-18	8	275	286	7	11	581	548	10	1	693	782	-17	4	554	555
-10	5	1362	1310	-17	8	536	554	8	11	611	595	12	1	839	825	-15	4	1235	1226
-9	5	262	262	-15	8	428	493	11	11	243	213	14	1	280	326	-14	4	901	903
-8	5	207	161	-14	8	422	459	13	11	240	190	15	1	331	330	-12	4	401	405
-6	5	868	842	-12	8	383	392	-10	12	530	550	16	1	398	396	-9	4	296	242
-5	5	340	389	-8	8	888	875	-9	12	252	280	17	1	705	751	-7	4	633	596
-4	5	868	838	-7	8	275	294	-5	12	332	389	20	1	286	278	-6	4	1261	1176
-2	5	940	904	-5	8	198	213	-4	12	541	565	22	1	365	307	-5	4	1242	1135
-1	5	2274	2176	-4	8	858	832	-3	12	316	347	23	1	570	557	-4	4	191	153
0	5	347	357	-3	8	421	387	-1	12	509	506	-23	2	311	280	-3	4	431	427
1	5	1440	1451	-1	8	219	202	0	12	111	106	-20	2	452	493	-2	4	871	871
2	5	592	614	1	8	426	460	1	12	294	333	-17	2	323	320	0	4	2092	2032
3	5	1402	1428	2	8	1225	1229	2	12	362	397	-15	2	487	508	1	4	741	713
4	5	1713	1735	6	8	640	626	4	12	737	739	-13	2	843	835	2	4	733	735
8	5	852	842	7	8	1179	1202	5	12	879	867	-12	2	203	175	3	4	1120	1174
9	5	349	346	9	8	268	218	-8	13	260	269	-11	2	459	458	4	4	317	330
11	5	258	271	10	8	462	496	-7	13	314	363	-10	2	224	223	5	4	811	841
12	5	709	735	11	8	286	336	-2	13	433	440	-9	2	226	225	6	4	301	308
13	5	585	583	12	8	324	366	-1	13	562	608	-7	2	171	164	7	4	872	861
14	5	464	465	13	8	250	237	1	13	593	546	-6	2	1336	1303	8	4	1029	1045
15	5	241	133	14	8	318	331	2	13	456	460	-5	2	1485	1420	9	4	233	248
17	5	421	437	15	8	522	498	5	13	289	288	-4	2	986	996	10	4	427	448
18	5	247	269	16	8	240	231	7	13	257	275	-3	2	522	512	12	4	195	158
19	5	639	635	17	8	275	218	**K =		5****		-2	2	758	708	13	4	539	570
21	5	211	202	-14	9	262	269	-23	0	237	274	-1	2	763	736	14	4	512	471
22	5	339	374	-13	9	231	304	-20	0	719	721	0	2	911	902	15	4	865	900
-22	6	278	281	-12	9	849	852	-19	0	248	206	1	2	469	475	17	4	452	444
-17	6	472	458	-11	9	593	587	-18	0	272	275	2	2	504	506	18	4	694	670
-16	6	261	197	-10	9	397	360	-17	0	265	241	3	2	1084	1193	19	4	239	192
-15	6	471	469	-9	9	307	290	-16	0	529	540	4	2	245	242	21	4	304	309
-13	6	1072	1040	-8	9	207	88	-15	0	265	264	5	2	856	919	22	4	204	205
-9	6	620	613	-7	9	229	232	-13	0	796	783	6	2	889	910	-18	5	753	745
-8	6	826	796	-6	9	388	406	-11	0	350	340	7	2	1355	1403	-17	5	726	756
-7	6	842	804	-2	9	277	296	-10	0	531	517	8	2	904	912	-16	5	241	174
-6	6	421	405	-1	9	278	306	-9	0	360	319	9	2	475	491	-13	5	404	372
-5	6	660	653	1	9	207	195	-8	0	392	364	10	2	838	905	-12	5	934	876
-4	6	254	206	2	9	838	815	-7	0	360	402	11	2	216	224	-10	5	364	380
-2	6	344	367	3	9	527	522	-6	0	1813	1829	13	2	379	392	-9	5	932	901
-1	6	714	687	4	9	890	908	-5	0	2028	2114	15	2	497	487	-7	5	193	223
0	6	875	852	5	9	692	682	-3	0	520	517	18	2	584	620	-6	5	463	489
1	6	1074	1070	6	9	433	441	-1	0	667	649	19	2	678	671	-5	5	468	487
2	6	992	987	7	9	221	235	1	0	607	649	20	2	758	782	-4	5	806	781
3	6	485	505	9	9	880	875	3	0	516	517	21	2	307	285	-3	5	1108	1094
	6	226	260	10	9	412	447	5	0	2028	2114	-22	3	275	279	-2	5	724	683
6	6	693	665	11	9	435	456	6	0	1809	1829	-21	3	217	173	-1	5	351	340
7	6	812	871	12	9	595	621	7	0	358	402	-20	3	272	303	0	5	577	586
10	6	552	560	13	9	288	268	8	0	370	364	-19	3	510	487	1	5	403	385
11	6	357	368	-17	10	201	239	9	0	328	319	-18	3	412	474	2	5	715	748
12	6	270	213	-15	10	307	328	10	0	526	517	-17	3	1035	1026	3	5	499	520
13	6	231	252	-12	10	238	253	11	0	352	340	-15	3	478	455	4	5	180	189
14	6	222	225	-11	10	233	276	13	0	796	783	-13	3	236	223	5	5	595	622
15	6	337	270	-10	10	467	435	15	0	228	264	-12	3	422	447	6	5	760	776
16	6	640	647	-9	10	705	703												

Table 31 (continued)

H	L	FOBS	FCAL
K = 5***			
7	5	342	336
9	5	610	633
11	5	779	792
12	5	663	638
14	5	663	686
16	5	559	518
17	5	395	402
18	5	380	351
20	5	656	662
21	5	212	183
-21	6	282	322
-19	6	258	227
-16	6	296	336
-15	6	570	582
-14	6	463	481
-13	6	434	435
-10	6	392	394
-9	6	570	522
-8	6	470	447
-7	6	628	618
-6	6	683	677
-3	6	675	649
-2	6	221	241
-1	6	557	564
0	6	1253	1258
1	6	446	422
3	6	416	397
4	6	446	428
5	6	505	479
6	6	476	444
8	6	915	908
9	6	364	371
10	6	236	228
11	6	312	292
14	6	243	229
15	6	494	510
16	6	278	235
17	6	487	483
18	6	457	420
-20	7	270	260
-18	7	254	263
-17	7	347	343
-16	7	247	273
-15	7	544	570
-12	7	559	526
-10	7	481	414
-8	7	286	279
-6	7	330	281
-5	7	675	692
-4	7	1282	1278
-3	7	501	477
-1	7	230	233
1	7	278	288
2	7	832	853
3	7	304	307
5	7	400	395
6	7	688	698
7	7	387	340
8	7	483	481
9	7	537	507
11	7	717	710
14	7	477	483
17	7	220	171
19	7	227	218
-18	8	295	371
-17	8	297	289
-15	8	217	235
-14	8	531	500
-13	8	563	560
-12	8	314	349
-11	8	267	221
-10	8	335	317
-7	8	1021	1026
-6	8	370	328
-5	8	599	599
-4	8	947	938
-2	8	550	508
-1	8	368	300
0	8	1039	1006
4	8	668	694
5	8	832	823
7	8	539	515
8	8	820	800
9	8	306	277
11	8	475	450
13	8	650	638
14	8	318	330
18	8	449	397
-16	9	362	393
-15	9	369	384
-12	9	434	433
-10	9	664	647
-8	9	639	603
-7	9	261	298
-5	9	580	577
-4	9	845	837
-3	9	481	413
0	9	261	182
2	9	625	640
3	9	672	675
4	9	554	595
5	9	404	417
6	9	325	341
8	9	480	508
9	9	499	487
10	9	456	426
11	9	681	701
12	9	328	338
16	9	337	312
-16	10	241	293
-13	10	434	480
-12	10	426	433
-11	10	431	432
-10	10	337	351
-8	10	344	392
-7	10	377	390
-5	10	580	564
-2	10	899	882
-1	10	499	529
0	10	519	525
1	10	726	685
2	10	226	204
7	10	953	950
8	10	506	508
12	10	241	253
13	10	481	485
14	10	322	307
-14	11	415	442
-13	11	235	194
-9	11	335	317
-8	11	324	313
-7	11	256	245
-6	11	460	474
-5	11	523	518
-4	11	470	452
-3	11	341	326
-1	11	701	713
0	11	721	735
1	11	321	292
2	11	283	294
3	11	235	182
4	11	491	520
5	11	282	279
6	11	283	306
7	11	235	247
8	11	285	288
9	11	259	247
10	11	461	499
11	11	378	387
13	11	663	687
14	11	236	255
15	11	397	435
18	11	444	428
20	11	839	847
-22	12	232	215
-19	12	301	320
-15	12	239	221
-12	12	247	213
-10	12	422	375
-9	12	373	408
-7	12	356	351
-6	12	297	299
-5	12	354	348
K = 6***			
0	0	379	381
-21	0	369	391
-20	0	255	235
-18	0	349	374
-15	0	369	354
-14	0	727	736
-13	0	925	888
-12	0	586	598
-11	0	925	871
-9	0	1142	1140
-8	0	204	160
-7	0	1072	1103
-6	0	370	369
-5	0	612	634
-4	0	693	651
-3	0	847	858
-1	0	704	684
0	0	669	650
1	0	671	684
3	0	814	858
4	0	685	651
5	0	616	634
6	0	360	369
7	0	1066	1103
8	0	217	160
9	0	1124	1140
11	0	878	871
12	0	605	598
13	0	888	888
14	0	722	736
15	0	396	354
18	0	351	374
20	0	230	235
21	0	396	391
22	0	389	381
-22	1	349	345
-19	1	225	213
-18	1	413	407
-14	1	959	963
-13	1	393	378
-12	1	814	809
-11	1	896	879
-9	1	520	524
-8	1	189	135
-7	1	679	671
-6	1	1150	1142
-5	1	281	271
-4	1	994	977
-3	1	296	236
-1	1	682	655
0	1	698	702
1	1	508	529
2	1	991	1069
3	1	352	384
4	1	1467	1550
5	1	316	329
6	1	1924	1941
7	1	368	460
8	1	931	945
9	1	440	444
10	1	731	772
11	1	524	556
13	1	237	191
14	1	706	752
15	1	593	608
18	1	660	623
20	1	326	355
-22	2	356	318
-19	2	256	301
-15	2	755	767
-12	2	515	512
-11	2	718	695
-9	2	373	315
-7	2	716	702
-6	2	277	239
-5	2	217	203
-4	2	641	609
-3	2	1332	1319
-2	2	813	770
-1	2	665	646
1	2	374	360
2	2	886	898
3	2	704	730
4	2	934	948
5	2	976	1036
6	2	200	175
8	2	222	207
9	2	440	482
11	2	433	392
12	2	1009	1066
13	2	992	1021
14	2	260	217
15	2	593	606
16	2	514	538
17	2	676	698
18	2	297	300
20	2	262	286
22	2	283	273
-22	3	332	335
-18	3	420	410
-16	3	818	823
-15	3	248	291
-14	3	613	611
-13	3	425	442
-11	3	464	471
-10	3	481	496
-9	3	890	883
-8	3	259	230
-7	3	460	458
-6	3	185	152
-4	3	1258	1170
-3	3	176	158
-2	3	246	260
-1	3	1630	1539
0	3	978	942
1	3	391	352
2	3	1507	1481
3	3	218	222
4	3	439	448
5	3	502	530
6	3	470	515
7	3	362	350
9	3	339	353
11	3	283	284
12	3	587	613
13	3	838	860
14	3	853	849
15	3	622	660
18	3	242	267
20	3	426	425
-21	4	335	346
-20	4	233	210
-19	4	706	729
-18	4	247	219
-17	4	561	539
-16	4	277	215
-12	4	405	365
-11	4	624	602
-9	4	484	481
-8	4	483	515
-6	4	532	550
-4	4	343	340
-3	4	882	840
-2	4	592	550
-1	4	1617	1568
0	4	519	508
1	4	517	508
2	4	977	976
3	4	259	260
4	4	253	296
5	4	686	713
6	4	248	262
7	4	318	369
8	4	332	362
9	4	345	364
10	4	790	790
11	4	398	424
13	4	826	847
14	4	536	526
16	4	582	546
17	4	1006	971
19	4	565	526
-21	5	261	285
-19	5	275	255
-16	5	741	742
-15	5	428	410
-14	5	760	802
-11	5	1213	1145
-10	5	355	345
-9	5	352	365
-8	5	640	632
-6	5	222	223
-5	5	391	396
-4	5	958	927
-3	5	674	662
-2	5	662	631
-1	5	923	928
1	5	285	289
2	5	703	686
3	5	770	809
4	5	292	296
5	5	472	495
8	5	386	363
9	5	498	492
10	5	241	216
11	5	396	341
12	5	290	240
13	5	562	612
14	5	747	752
15	5	222	134
16	5	1040	1035
17	5	344	279
19	5	212	204
20	5	254	224
-19	6	290	305
-17	6	277	297
-13	6	535	546
-11	6	423	426
-10	6	475	455
-9	6	594	587
-8	6	651	648
-6	6	208	122
-5	6	1225	1213
-4	6	393	406
-1	6	528	524
0	6	409	412
1	6	534	479
2	6	663	676
3	6	597	587
4	6	305	354
5	6	513	544
6	6	624	609
8	6	641	635
12	6	463	447
13	6	719	733
14	6	340	373
15	6	424	391
16	6	284	256
17	6	446	436
19	6	553	562
-19	7	205	230
-18	7	273	323
-17	7	257	265
-16	7	255	258
-14	7	596	592
-13	7	237	245
-9	7	253	253
-8	7	1188	1173

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 6***				-1	11	452	455	-16	2	290	250	-19	5	333	345	-3	8	344	346
-7	7	584	570	0	11	466	473	-15	2	270	207	-16	5	483	489	-2	8	379	406
-6	7	1180	1170	2	11	406	399	-14	2	209	187	-14	5	608	637	-1	8	322	318
-5	7	256	73	3	11	225	218	-10	2	506	511	-12	5	257	277	0	8	431	414
-2	7	848	854	4	11	220	230	-9	2	646	623	-11	5	406	417	1	8	596	588
-1	7	612	635	6	11	439	417	-7	2	762	743	-10	5	438	431	5	8	945	952
0	7	417	402	7	11	391	382	-6	2	337	294	-9	5	414	408	6	8	267	283
1	7	340	366	8	11	289	321	-5	2	950	893	-8	5	783	745	7	8	293	175
2	7	272	295	9	11	270	209	-4	2	791	761	-6	5	714	679	9	8	404	424
3	7	496	527	10	11	315	323	-3	2	1707	1622	-5	5	826	834	10	8	511	459
4	7	418	409	11	11	219	224	-2	2	401	382	-4	5	480	459	11	8	501	514
5	7	401	422	-9	12	241	229	-1	2	811	802	-1	5	374	320	13	8	439	422
6	7	783	803	-7	12	390	380	1	2	584	627	0	5	794	798	-10	9	577	551
7	7	344	357	-5	12	373	334	2	2	476	506	1	5	249	197	-9	9	347	353
8	7	234	198	-4	12	320	341	3	2	364	365	2	5	376	387	-8	9	783	801
10	7	422	393	-3	12	611	640	4	2	425	475	3	5	277	278	-7	9	274	197
12	7	492	501	-2	12	252	200	5	2	183	166	4	5	223	190	-4	9	647	624
14	7	270	276	-1	12	580	584	6	2	527	520	5	5	326	307	-3	9	287	263
15	7	401	389	1	12	236	239	7	2	1174	1176	7	5	383	355	-2	9	764	748
16	7	554	554	4	12	502	471	8	2	209	207	8	5	258	251	1	9	430	381
-17	8	315	287	5	12	303	279	9	2	264	227	10	5	679	667	4	9	644	635
-13	8	249	268	7	12	234	234	10	2	726	750	14	5	530	567	8	9	472	459
-11	8	600	771	**K = 7*****				11	2	337	347	15	5	327	310	10	9	414	366
-10	8	520	516	-21	0	482	534	12	2	302	280	16	5	376	398	11	9	359	350
-9	8	623	600	-17	0	585	592	13	2	508	521	18	5	796	779	12	9	580	577
-8	8	419	410	-15	0	632	683	14	2	373	398	19	5	203	145	13	9	272	273
-7	8	465	432	-14	0	284	303	15	2	1025	1050	-19	6	339	315	14	9	288	262
-6	8	747	719	-13	0	671	648	18	2	304	265	-17	6	414	402	-13	10	372	446
-5	8	853	811	-12	0	324	280	20	2	206	132	-16	6	354	353	-10	10	308	335
-3	8	827	815	-8	0	678	698	21	2	434	379	-15	6	583	560	-9	10	306	312
-2	8	211	62	-7	0	1481	1515	-20	3	476	523	-13	6	481	482	-7	10	346	353
-1	8	347	339	-6	0	256	250	-19	3	246	312	-10	6	228	228	-6	10	216	171
0	8	277	277	-5	0	933	930	-16	3	404	457	-9	6	620	578	-5	10	862	862
2	8	732	718	-4	0	447	452	-15	3	248	234	-8	6	283	138	-3	10	280	264
3	8	541	538	-3	0	378	399	-14	3	714	745	-7	6	822	820	-2	10	431	436
4	8	434	442	-2	0	509	477	-11	3	510	495	-5	6	285	272	1	10	594	603
7	8	457	445	-1	0	1538	1488	-8	3	484	500	-4	6	505	512	5	10	335	286
9	8	688	692	1	0	1455	1468	-7	3	603	567	-3	6	1013	982	7	10	333	351
10	8	340	327	2	0	505	477	-6	3	1281	1235	-2	6	554	548	8	10	251	258
11	8	835	834	3	0	403	399	-5	3	300	223	0	6	302	275	9	10	300	325
15	8	452	448	4	0	425	452	-4	3	962	939	2	6	204	198	11	10	285	285
16	8	412	382	5	0	940	930	-3	3	354	297	3	6	878	857	-8	11	201	210
-14	9	464	448	6	0	271	250	-2	3	374	338	5	6	860	882	-2	11	602	630
-12	9	222	242	7	0	1446	1515	0	3	864	846	6	6	235	241	4	11	397	401
-10	9	333	269	8	0	698	698	1	3	196	182	7	6	328	347	8	11	318	315
-9	9	342	354	12	0	288	280	2	3	305	288	11	6	674	694	9	11	207	233
-8	9	714	720	13	0	639	648	4	3	850	876	12	6	250	250	-5	12	628	677
-6	9	1279	1303	14	0	291	303	6	3	191	137	13	6	255	266	-4	12	400	420
-5	9	527	497	15	0	653	683	7	3	461	455	15	6	643	638	1	12	481	510
-4	9	570	562	17	0	597	592	9	3	293	346	17	6	443	458	3	12	204	152
-2	9	440	431	21	0	486	534	10	3	813	836	-16	7	719	704	**K = 8*****			
0	9	327	364	-20	1	561	590	12	3	443	458	-14	7	483	482	-15	0	1050	1043
3	9	233	231	-19	1	332	257	13	3	246	212	-13	7	378	373	-14	0	260	217
4	9	287	350	-16	1	514	506	16	3	367	386	-12	7	329	353	-13	0	362	354
5	9	459	504	-14	1	577	543	18	3	526	544	-10	7	834	835	-9	0	990	987
6	9	750	732	-13	1	463	474	19	3	237	197	-9	7	240	182	-7	0	203	179
8	9	458	449	-12	1	508	486	-19	4	305	317	-8	7	704	677	-6	0	205	164
12	9	484	485	-10	1	908	898	-17	4	620	621	-7	7	675	701	-5	0	888	905
13	9	401	391	-8	1	672	606	-15	4	628	617	-6	7	747	757	-4	0	483	498
14	9	465	481	-7	1	546	593	-13	4	409	445	-4	7	783	751	-3	0	994	1019
-15	10	272	267	-6	1	725	776	-11	4	256	237	-3	7	316	316	-2	0	551	556
-11	10	252	281	-5	1	524	536	-9	4	716	663	-2	7	618	569	-1	0	851	796
-9	10	392	372	-4	1	1354	1339	-8	4	253	260	-1	7	227	206	1	0	775	796
-8	10	592	591	-2	1	948	942	-6	4	248	264	0	7	653	624	2	0	558	556
-7	10	737	720	-1	1	470	451	-3	4	1011	980	1	7	226	281	3	0	984	1019
-4	10	317	314	0	1	387	391	-2	4	690	645	2	7	393	385	4	0	488	498
-3	10	698	689	2	1	241	225	-1	4	275	287	3	7	324	274	5	0	913	905
0	10	290	334	3	1	214	190	0	4	466	473	4	7	247	251	7	0	213	179
1	10	222	83	4	1	1947	2023	1	4	324	339	8	7	971	978	9	0	954	987
2	10	291	270	5	1	882	952	2	4	318	322	10	7	216	165	13	0	370	354
3	10	656	681	7	1	366	402	3	4	586	585	12	7	309	281	14	0	274	217
4	10	283	295	8	1	416	466	4	4	285	321	13	7	420	390	15	0	1034	1043
5	10	500	542	9	1	696	744	5	4	319	303	14	7	516	497	-16	1	478	510
6	10	374	374	10	1	940	949	6	4	232	223	16	7	282	282	-14	1	227	248
9	10	453	460	12	1	1038	1076	7	4	894	900	17	7	324	286	-12	1	1056	1060
11	10	522	540	13	1	234	184	8	4	373	348	-16	8	295	286	-7	1	576	570
12	10	246	260	16	1	626	604	10	4	345	351	-15	8	237	221	-6	1	1419	1382
13	10	198	197	18	1	284	329	11	4	287	311	-13	8	725	730	-5	1	448	463
-12	11	235	242	19	1	252	288	13	4	533	564	-12	8	285	296	-4	1	725	695
-10	11	276	283	20	1	327	303	15	4	1090	1106	-9	8	335	327	-3	1	238	216
-7	11	323	363	21	1	219	217	16	4	335	376	-7	8	1002	976	-2	1	664	622
-6	11	347	378	-19	2	260	183	19	4	248	234	-6	8	341	341	-1	1	422	371
-5	11	218	250	-18	2	312	317	20	4	278	296	-5	8	936	967	2	1	1215	1259
-4	11	363	394	-17	2	836	861	-20	5	240	202	-4	8	550	560	4	1	240	282
-2	11	474	488																

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 0				8	4	578	625	7	8	252	275	-14	2	297	365	11	5	285	322
5	1	282	232	9	4	683	676	8	8	229	219	-11	2	597	582	-15	6	324	347
6	1	821	837	10	4	312	377	9	8	448	463	-10	2	230	175	-14	6	269	286
7	1	364	411	11	4	275	306	11	8	282	283	-9	2	585	584	-13	6	459	469
8	1	653	647	13	4	735	748	12	8	374	350	-8	2	399	416	-12	6	283	268
10	1	457	505	14	4	320	355	13	8	455	432	-7	2	544	546	-11	6	376	408
12	1	826	864	15	4	396	410	-10	9	320	351	-6	2	384	375	-10	6	415	446
13	1	437	442	16	4	387	360	-9	9	298	327	-5	2	515	519	-9	6	442	423
14	1	392	380	17	4	240	242	-8	9	743	747	-4	2	255	238	-7	6	282	282
17	1	231	212	19	4	201	188	-7	9	295	285	-3	2	731	685	-6	6	255	227
18	1	302	293	-16	5	292	327	-6	9	396	404	0	2	632	658	-4	6	249	205
20	1	285	275	-14	5	493	496	-4	9	337	334	1	2	215	180	-3	6	749	720
-19	2	479	471	-12	5	259	289	-1	9	306	239	3	2	452	478	0	6	420	421
-18	2	396	378	-8	5	909	883	0	9	620	582	5	2	454	468	2	6	378	319
-17	2	488	495	-4	5	513	506	2	9	669	653	7	2	1019	1063	3	6	676	673
-16	2	365	342	-3	5	635	608	5	9	252	225	10	2	455	461	5	6	1185	1165
-15	2	731	736	-1	5	810	781	6	9	730	726	13	2	435	446	6	6	265	174
-11	2	305	324	0	5	219	197	9	9	257	271	15	2	396	373	7	6	384	359
-10	2	250	175	1	5	827	830	11	9	214	192	17	2	225	208	8	6	595	611
-9	2	748	708	2	5	1179	1196	-11	10	268	344	-17	3	432	448	11	6	677	685
-8	2	289	323	3	5	322	320	-10	10	257	228	-16	3	369	390	14	6	246	206
-7	2	552	532	4	5	491	465	-8	10	208	200	-14	3	549	573	15	6	287	323
-4	2	384	370	8	5	785	814	-7	10	639	646	-12	3	259	321	-14	7	203	201
-3	2	722	693	10	5	490	494	-5	10	411	395	-11	3	240	238	-12	7	278	305
-2	2	441	450	12	5	233	282	-3	10	416	460	-10	3	355	328	-10	7	466	423
-1	2	987	914	13	5	224	236	-1	10	303	368	-9	3	273	267	-6	7	718	719
3	2	475	497	15	5	217	235	1	10	336	345	-8	3	452	476	-5	7	310	337
4	2	284	304	16	5	703	687	3	10	519	496	-7	3	550	566	-4	7	220	172
5	2	1049	1111	17	5	252	301	9	10	405	417	-6	3	1265	1211	-1	7	312	285
7	2	223	261	18	5	315	252	-8	11	289	301	-5	3	446	388	0	7	295	341
9	2	771	815	-17	6	322	265	-4	11	458	498	-4	3	293	255	2	7	688	684
10	2	345	311	-12	6	660	660	-1	11	231	117	-3	3	839	800	3	7	467	482
12	2	385	402	-11	6	769	799	0	11	234	163	-2	3	530	515	4	7	537	471
13	2	625	653	-5	6	586	582	4	11	293	257	0	3	383	382	5	7	326	308
14	2	215	91	-4	6	578	582	6	11	720	706	1	3	266	270	6	7	477	459
15	2	356	362	-3	6	292	223	K = 0				2	3	670	669	8	7	645	660
17	2	269	271	-2	6	532	536	-17	0	740	753	4	3	826	838	11	7	391	377
-16	3	465	484	-1	6	617	605	-14	0	279	295	5	3	529	539	13	7	205	221
-15	3	345	390	0	6	274	236	-13	0	790	802	6	3	341	283	14	7	479	492
-14	3	757	739	2	6	286	315	-11	0	414	385	7	3	221	219	-13	8	605	663
-13	3	336	273	3	6	1059	1085	-10	0	406	363	10	3	513	508	-5	8	545	514
-12	3	609	567	5	6	962	968	-9	0	265	293	12	3	511	543	-3	8	671	675
-10	3	221	195	7	6	839	828	-7	0	558	951	13	3	312	289	-1	8	341	340
-9	3	271	245	9	6	441	453	-6	0	433	459	15	3	237	274	1	8	866	829
-8	3	684	648	10	6	278	303	-5	0	281	319	-14	4	379	396	5	8	729	747
-6	3	497	481	12	6	425	406	-3	0	656	663	-12	4	494	453	6	8	261	230
-5	3	295	304	13	6	767	775	-1	0	859	854	-11	4	546	544	8	8	384	413
-4	3	916	884	-16	7	378	410	1	0	796	854	-9	4	613	588	11	8	428	413
-3	3	325	347	-14	7	781	812	3	0	646	663	-8	4	269	279	-8	9	253	261
-2	3	292	299	-8	7	951	965	5	0	287	319	-6	4	699	703	-6	9	231	255
-1	3	548	512	-6	7	323	307	6	0	456	459	-4	4	424	444	-2	9	501	508
0	3	1035	1022	-5	7	367	400	7	0	932	951	-3	4	876	875	3	9	228	244
1	3	391	421	-4	7	326	378	8	0	209	107	-2	4	285	275	4	9	581	603
2	3	1029	1018	-2	7	607	579	10	0	375	363	-1	4	393	376	8	9	311	329
6	3	381	365	0	7	730	732	11	0	406	385	0	4	1160	1150	-5	10	422	417
8	3	473	512	2	7	541	520	13	0	790	802	1	4	333	370	-2	10	251	250
10	3	313	382	3	7	345	362	14	0	306	295	2	4	625	672	1	10	383	348
12	3	582	623	4	7	583	567	17	0	748	753	5	4	568	537	3	10	329	276
14	3	535	534	5	7	482	458	-17	1	373	401	7	4	981	996	5	10	318	331
16	3	412	399	6	7	1088	1064	-14	1	881	886	8	4	444	419	K = 10			
17	3	233	238	7	7	450	482	-12	1	308	312	11	4	396	394	-17	0	271	286
18	3	300	277	8	7	302	294	-10	1	309	323	14	4	261	224	-15	0	724	749
-19	4	296	274	9	7	362	372	-8	1	404	366	15	4	298	272	-14	0	462	455
-18	4	382	415	10	7	297	322	-7	1	464	456	17	4	233	216	-13	0	311	339
-17	4	420	429	14	7	344	358	-6	1	525	513	-17	5	404	396	-12	0	614	633
-16	4	279	292	15	7	303	333	-5	1	251	201	-16	5	328	358	-5	0	463	450
-15	4	229	291	16	7	762	737	-4	1	1314	1261	-14	5	601	577	-3	0	692	683
-12	4	216	137	-15	8	496	505	-3	1	378	365	-13	5	226	162	-2	0	341	334
-11	4	555	575	-14	8	225	174	-2	1	487	426	-12	5	515	527	2	0	305	334
-9	4	482	467	-12	8	286	290	0	1	490	516	-9	5	299	272	3	0	664	703
-8	4	262	215	-11	8	712	708	2	1	418	483	-6	5	755	721	5	0	445	450
-5	4	277	231	-8	8	350	353	3	1	312	351	-4	5	235	169	6	0	228	231
-4	4	278	283	-7	8	364	393	4	1	1248	1297	-3	5	541	522	12	0	644	633
-2	4	473	518	-6	8	465	471	7	1	437	425	0	5	462	480	13	0	363	339
-1	4	552	588	-5	8	867	843	10	1	632	631	2	5	575	560	14	0	449	455
0	4	516	536	-3	8	720	714	14	1	406	373	3	5	443	456	15	0	714	749
1	4	688	698	-2	8	257	249	16	1	341	338	4	5	388	373	17	0	280	286
2	4	622	667	0	8	291	238	17	1	319	277	5	5	761	762	-16	1	425	434
3	4	624	658	2	8	457	448	18	1	477	453	6	5	840	850	-15	1	333	354
4	4	359	387	3	8	1395	1384	-19	2	200	251	8	5	615	615	-12	1	539	554
5	4	687	691	4	8	286	316	-17	2	687	716	10	5	450	469	-11	1	402	417
6	4	691	705	8	8	361	391	-15	2	281	271								

TABLE 32: ATOM COORDINATES

AND ISOTROPIC TEMPERATURE FACTORS

ATOM	x	y	z	B
Nb	0.58136(2)	0.21418(5)	0.19528(4)	2.47*
As	0.20939(3)	0.15780(7)	0.26735(6)	3.31*
S1	0.52186(8)	0.1130(1)	0.0746(1)	3.26*
S2	0.57210(8)	0.3413(2)	0.0567(1)	3.60*
S3	0.51630(8)	0.1329(2)	0.3169(1)	3.75*
S4	0.56193(8)	0.3659(1)	0.3010(1)	3.54*
S5	0.63390(8)	0.0503(1)	0.2242(1)	3.54*
S6	0.68163(7)	0.2798(2)	0.1989(1)	3.51*
C11	0.4876(3)	0.2027(6)	-0.0067(5)	2.82*
C12	0.4412(3)	0.1741(6)	-0.0731(5)	3.43*
C13	0.4164(3)	0.2420(7)	-0.1411(6)	4.21*
C14	0.4364(3)	0.3455(7)	-0.1445(6)	4.09*
C15	0.4824(3)	0.3765(6)	-0.0820(6)	3.69*
C16	0.5091(3)	0.3074(6)	-0.0132(5)	3.06*
C21	0.5210(3)	0.2120(7)	0.4254(5)	3.81*
C22	0.4989(4)	0.1770(7)	0.5182(7)	4.93*
C23	0.4971(4)	0.2458(9)	0.6005(7)	6.19*
C24	0.5165(4)	0.3452(9)	0.5921(7)	6.09*
C25	0.5395(3)	0.3818(7)	0.5039(7)	4.70*
C26	0.5405(3)	0.3143(6)	0.4180(6)	3.41*
C36	0.7256(3)	0.1716(6)	0.1733(5)	3.19*

Table 32 (continued)

ATOM	x	y	z	B
C35	0.7837(3)	0.1875(6)	0.1505(6)	3.86*
C34	0.8198(3)	0.1032(8)	0.1328(6)	4.97*
C33	0.7983(4)	0.0024(7)	0.1415(6)	5.04*
C32	0.7418(4)	0.0137(6)	0.1648(6)	4.66*
C31	0.7040(3)	0.0717(6)	0.1835(5)	3.17*

RIGID BODIES

(a) Phenyl Carbon Atoms

C41	0.1589(2)	0.0435(3)	0.2397(4)	3.4(2)
C42	0.1656(3)	-0.0184(4)	0.1533(3)	4.1(2)
C43	0.1319(3)	-0.1087(4)	0.1387(4)	4.5(2)
C44	0.0915(2)	-0.1371(3)	0.2105(4)	4.7(2)
C45	0.0847(3)	-0.0752(4)	0.2968(3)	4.9(2)
C46	0.1184(3)	0.0151(4)	0.3114(4)	4.3(2)
D	3.710(3) [a]			
E	0.982(4)			
F	4.924(4)			
C51	0.1688(2)	0.2697(3)	0.3259(4)	3.4(2)
C52	0.1118(2)	0.2914(4)	0.2916(4)	4.4(2)
C53	0.0845(1)	0.3833(4)	0.3226(3)	4.9(2)
C54	0.1140(2)	0.4533(3)	0.3877(4)	4.9(2)
C55	0.1710(2)	0.4315(4)	0.4220(4)	4.7(2)
C56	0.1984(1)	0.3397(4)	0.3910(3)	4.0(2)

Table 32 (continued)

ATOM	x	y	z	B
D	5.779(3)			
E	2.731(4)			
F	4.418(3)			
C61	0.2679(4)	0.1098(4)	0.3600(10)	3.6(2)
C62	0.3211(5)	0.0725(4)	0.3265(5)	5.1(2)
C63	0.3613(3)	0.0279(4)	0.3961(7)	5.7(2)
C64	0.3482(4)	0.0207(4)	0.4990(10)	5.1(2)
C65	0.2950(5)	0.0580(4)	0.5318(5)	4.9(2)
C66	0.2548(3)	0.1026(4)	0.4622(7)	4.3(2)
D	2.023(3)			
E	1.217(8)			
F	5.084(8)			
C71	0.2370(5)	0.2098(4)	0.1429(8)	3.3(1)
C72	0.1963(5)	0.2212(4)	0.0622(4)	4.4(2)
C73	0.2126(7)	0.2680(5)	-0.0285(7)	5.5(2)
C74	0.2696(5)	0.3034(4)	-0.0134(8)	5.4(2)
C75	0.3103(5)	0.2920(4)	0.0423(4)	6.3(2)
C76	0.2940(7)	0.2452(5)	0.1330(7)	5.2(2)
D	1.109(4)			
E	2.521(8)			
F	4.425(8)			

Table 32 (continued)

ATOM	x	y	z	B
(b) Phenyl Hydrogen Atoms				
H1	0.7990	0.2619	0.1446	4.5
H2	0.8613	0.1152	0.1151	5.0
H3	0.8243	-0.0598	0.1281	5.0
H4	0.7250	-0.0880	0.1705	4.5
D	3.159			
E	0.277			
F	5.085			
H5	0.4840	0.1029	0.5229	5.4
H6	0.4809	0.2184	0.6663	6.0
H7	0.5158	0.3948	0.6530	6.0
H8	0.5537	0.4557	0.4962	5.4
D	3.448			
E	1.285			
F	1.748			
H9	0.4267	0.0982	-0.0685	4.1
H10	0.3826	0.2199	-0.1869	4.7
H11	0.4182	0.3963	-0.1949	4.7
H12	0.4978	0.4509	-0.0846	4.1
D	0.281			
E	2.406			
F	4.529			
H13	0.1945	0.0016	0.1020	4.6

Table 32 (continued)

ATOM	x	y	z	B
H14	0.1369	-0.1535	0.0773	5.1
H15	0.0674	-0.2020	0.2004	5.0
H16	0.0556	-0.0953	0.3482	5.5
H17	0.1132	0.0597	0.3730	5.1
D	3.707			
E	0.981			
F	5.973			
H18	0.0905	0.2414	0.2452	5.0
H19	0.0436	0.3989	0.2983	5.9
H20	0.0944	0.5191	0.4100	5.5
H21	0.1922	0.4816	0.4685	5.1
H22	0.2391	0.3241	0.4154	4.7
D	5.779			
E	2.732			
F	5.465			
H23	0.3305	0.0773	0.2529	5.1
H24	0.3994	0.0013	0.3725	6.1
H25	0.3770	-0.0107	0.5486	5.8
H26	0.2856	0.0531	0.6052	5.3
H27	0.2166	0.1290	0.4856	4.7
D	2.020			
E	1.219			
F	6.134			

Table 32 (continued)

ATOM	x	y	z	B
H28	0.1555	0.1957	0.0691	5.1
H29	0.1836	0.2756	-0.0864	5.6
H30	0.2814	0.3364	-0.1034	6.2
H31	0.3511	0.3173	0.0352	6.8
H32	0.3230	0.2374	0.1909	5.6
D	1.111			
E	2.515			
F	5.467			

*These values are equivalent isotropic temperature factors[81] corresponding to the anisotropic thermal parameters shown in Table 33.

[a]D, E, and F are the angles by which the coordinates of the rigid body are rotated with respect to a set of axes X, Y, Z. The origin of these axes is placed at the centre of the ring with the X axis parallel to a^*, the Z axis parallel to c, and the Y axis parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c.

TABLE 33: ANISOTROPIC THERMAL PARAMETERS ($Å^2$)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	0.0324(3)	0.0310(4)	0.0302(3)	-0.0003(3)	0.0007(2)	-0.0025(3)
As	0.0385(5)	0.0502(6)	0.0370(5)	-0.0037(4)	0.0025(4)	-0.0057(5)
S1	0.0510(12)	0.0340(11)	0.0383(11)	-0.0004(9)	-0.0071(9)	-0.0022(9)
S2	0.0515(12)	0.0430(12)	0.0420(11)	-0.0098(11)	-0.0024(9)	0.0051(10)
S3	0.0547(12)	0.0407(13)	0.0475(12)	-0.0054(10)	0.0120(10)	-0.0034(10)
S4	0.0413(11)	0.0397(12)	0.0535(12)	-0.0008(9)	0.0059(9)	-0.0093(10)
S5	0.0457(12)	0.0388(12)	0.0496(13)	0.0048(9)	-0.0042(10)	0.0083(10)
S6	0.0385(10)	0.0394(12)	0.0556(12)	-0.0022(10)	0.0009(9)	-0.0093(11)
C11	0.036(4)	0.036(5)	0.036(4)	-0.005(4)	-0.000(3)	-0.001(4)
C12	0.045(5)	0.048(5)	0.037(4)	-0.007(4)	-0.006(4)	0.000(4)
C13	0.049(5)	0.069(7)	0.041(5)	0.004(5)	-0.004(4)	0.004(5)
C14	0.054(5)	0.062(6)	0.039(5)	0.011(5)	-0.007(4)	0.008(5)
C15	0.053(5)	0.041(5)	0.046(5)	0.006(4)	0.002(4)	0.006(4)
C16	0.036(4)	0.049(5)	0.031(4)	0.006(4)	0.005(3)	-0.005(4)
C21	0.040(4)	0.066(6)	0.039(5)	0.006(5)	0.007(4)	-0.008(5)

Table 33 (continued)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C22	0.063(6)	0.067(7)	0.058(6)	0.008(5)	0.011(5)	0.010(5)
C23	0.079(7)	0.111(9)	0.045(6)	0.022(7)	0.011(5)	0.005(6)
C24	0.081(7)	0.109(9)	0.041(6)	0.032(7)	-0.006(5)	-0.021(6)
C25	0.045(5)	0.076(7)	0.057(6)	0.014(5)	-0.011(4)	-0.025(5)
C26	0.040(4)	0.044(5)	0.046(5)	0.006(4)	0.000(4)	-0.007(4)
C31	0.038(4)	0.048(5)	0.034(4)	0.010(4)	-0.002(4)	0.001(4)
C32	0.061(6)	0.053(6)	0.063(6)	0.010(5)	-0.004(5)	0.011(5)
C33	0.061(6)	0.067(7)	0.064(6)	0.029(5)	0.010(5)	0.012(5)
C34	0.043(5)	0.086(7)	0.061(6)	0.020(5)	0.005(4)	0.019(6)
C35	0.040(5)	0.066(6)	0.040(5)	0.003(4)	-0.004(4)	0.007(4)
C36	0.045(5)	0.042(5)	0.034(4)	0.007(4)	-0.002(4)	0.002(4)

TABLE 34: INTRA-IONIC CONTACTS (Å)

ATOMS	DISTANCE	ATOMS	DISTANCE
Nb-S1	2.428(2)	S2-S6	3.178(3)
Nb-S2	2.442(2)	S4-S6	3.294(3)
Nb-S3	2.458(2)	S1-C11	1.736(7)
Nb-S4	2.433(2)	S2-C16	1.740(7)
Nb-S5	2.436(2)	S3-C21	1.747(7)
Nb-S6	2.451(2)	S4-C26	1.760(8)
As-C41	1.891(4)	S5-C31	1.739(7)
As-C51	1.883(4)	S6-C36	1.750(7)
As-C61	1.880(4)	C11-C12	1.402(9)
As-C71	1.896(4)	C12-C13	1.356(10)
S1-S2	3.143(3)	C13-C14	1.398(10)
S3-S4	3.160(3)	C14-C15	1.374(10)
S5-S6	3.147(3)	C15-C16	1.392(9)
S1-S3	3.204(3)	C16-C11	1.424(9)
S1-S5	3.282(3)	C21-C22	1.410(10)
S3-S5	3.184(3)	C22-C23	1.396(12)
S2-S4	3.245(3)	C23-C24	1.349(13)
C24-C25	1.374(12)	C33-C34	1.383(12)
C25-C26	1.422(10)	C34-C35	1.382(11)
C26-C21	1.385(10)	C35-C36	1.395(9)
C31-C32	1.419(10)	C36-C31	1.375(10)
C32-C33	1.363(11)		

TABLE 35: INTRA-IONIC ANGLES (DEGREES)

ATOMS	ANGLES	ATOMS	ANGLES
S1-Nb-S2	80.40(7)	Nb-S3-C21	105.5(3)
S3-Nb-S4	80.47(7)	Nb-S4-C26	105.4(3)
S5-Nb-S6	80.18(7)	Nb-S5-C31	106.1(3)
S1-Nb-S5	84.87(7)	Nb-S6-C36	106.0(3)
S1-Nb-S3	81.94(7)	S1-C11-C16	120.2(6)
S3-Nb-S5	81.18(7)	S2-C16-C11	119.0(5)
S2-Nb-S4	83.46(7)	S3-C21-C26	119.7(6)
S2-Nb-S6	81.03(7)	S4-C26-C21	121.1(6)
S4-Nb-S6	84.81(7)	S5-C31-C36	121.1(6)
S1-Nb-S4	133.25(7)	S6-C36-C31	119.9(6)
S1-Nb-S6	134.51(7)	C41-As-C51	110.6(2)
S3-Nb-S2	136.61(7)	C41-As-C61	107.1(2)
S3-Nb-S6	136.50(7)	C41-As-C71	109.0(2)
S5-Nb-S2	135.63(7)	C51-As-C61	109.6(2)
S5-Nb-S4	133.86(7)	C51-As-C71	105.9(2)
Nb-S1-C11	106.5(2)	C61-As-C71	114.6(2)
Nb-S2-C16	106.1(3)	C11-C12-C13	122.4(7)
C12-C13-C14	119.5(7)	C25-C26-C21	120.0(8)
C13-C14-C15	120.0(7)	C26-C21-C22	119.1(8)
C14-C15-C16	121.2(7)	C31-C32-C33	121.1(8)
C15-C16-C11	120.0(7)	C32-C33-C34	120.3(8)
C16-C11-C12	117.8(6)	C33-C34-C35	119.5(8)

Table 35 (continued)

ATOMS	ANGLES	ATOMS	ANGLES
C21-C22-C23	119.6(8)	C34-C35-C36	120.4(8)
C22-C23-C24	120.5(9)	C35-C36-C31	120.5(7)
C23-C24-C25	121.8(10)	C36-C31-C32	118.0(7)
C24-C25-C26	119.9(9)	S3-S1-S5	58.80(6)
S6-S2-S4	61.69(6)	S5-S3-S1	61.83(6)
S2-S4-S6	58.16(6)	S3-S5-S1	59.37(6)
S2-S6-S4	60.15(6)		

TABLE 36: INTER-IONIC CONTACTS (Å)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
S1	H9	$\bar{x}$+1, $\bar{y}$, $\bar{z}$	2.942
S1	H20	1/2-x, 1/2+y-1, 1/2-z	2.942
S1	C54	1/2+x, 1/2-y, 1/2+z-1	3.409(6)
S1	S1	$\bar{x}$+1, $\bar{y}$, $\bar{z}$	3.607(4)
S1	C53	1/2+x, 1/2-y, 1/2+z-1	3.661(6)
S2	H17	1/2+x, 1/2-y, 1/2+z-1	2.913
S3	H15	1/2-x, 1/2+y, 1/2-z	2.855
S4	H3	1/2-x+1, 1/2+y, 1/2-z	2.901
S4	C44	1/2-x, 1/2+y, 1/2-z	3.523(5)
S4	C45	1/2-x, 1/2+y, 1/2-z	3.640(5)
S5	H25	$\bar{x}$+1, y, $\bar{z}$+1	3.048
S6	H29	1/2+x, 1/2-y, 1/2+z	2.908
S6	C33	1/2-x+1, 1/2+y, 1/2-z	3.549(9)
S6	C32	1/2-x+1, 1/2+y, 1/2-z	3.606(8)
S6	C73	1/2+x, 1/2-y, 1/2+z	3.680(5)
C35	C65	1/2+x, 1/2-y, 1/2+z-1	3.612(10)
C35	C66	1/2+x, 1/2-y, 1/2+z-1	3.688(9)
C34	H14	$\bar{x}$+1, $\bar{y}$, $\bar{z}$	3.038
C32	H21	1/2+x, 1/2-y, 1/2+z-1	2.811
C32	C55	1/2+x, 1/2-y, 1/2+z-1	3.682(9)
C31	H21	1/2+x, 1/2-y, 1/2+z-1	2.909
C31	C55	1/2+x, 1/2-y, 1/2+z-1	3.495(8)

Table 36 (continued)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
C21	C44	1/2-x, 1/2+y, 1/2-z	3.638(9)
C23	H18	1/2+x, 1/2-y, 1/2+z	2.821
C23	C52	1/2+x, 1/2-y, 1/2+z	3.606(11)
C25	H28	1/2+x, 1/2-y, 1/2+z	2.942
C25	H8	$\bar{x}$+1, $\bar{y}$+1, $\bar{z}$+1	2.980
C25	C25	$\bar{x}$+1, $\bar{y}$+1, $\bar{z}$+1	3.517(17)
C26	H15	1/2-x, 1/2+y, 1/2-z	2.886
C26	C44	1/2-x, 1/2+y, 1/2-z	3.472(8)
C11	C53	1/2+x, 1/2-y, 1/2+z-1	3.400(9)
C12	H20	1/2-x, 1/2+y-1, 1/2-z	3.049
C12	C53	1/2+x, 1/2-y, 1/2+z-1	3.685(9)
C13	H6	x, y, z-1	2.996
C13	C75	x, y, z	3.549(10)
[illegible]3	H31	x, y, z	2.966
C[illegible]5	H16	1/2-x, 1/2+y, 1/2-z	2.947
C[illegible]2	C56	1/2-x, 1/2+y-1, 1/2-z	3.676(7)
[illegible]4	H32	1/2-x, 1/2+y-1, 1/2-z	2.811
[illegible]44	C76	1/2-x, 1/2+y-1, 1/2-z	3.609(7)
C45	H31	1/2-x, 1/2+y-1, 1/2-z	2.947
C45	H12	1/2+x-1, 1/2-y, 1/2+z	3.023
C45	C75	1/2-x, 1/2+y-1, 1/2-z	3.577(8)
C45	C76	1/2-x, 1/2+y-1, 1/2-z	3.699(7)
C53	C63	1/2-x, 1/2+y, 1/2-z	3.672(7)

Table 36 (continued)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
C54	H23	1/2-x, 1/2+y, 1/2-z	2.778
C54	C62	1/2-x, 1/2+y, 1/2-z	3.574(7)
C55	H23	1/2-x, 1/2+y, 1/2-z	2.956
C64	C73	1/2-x, 1/2+y-1, 1/2-z	3.537(8)
C65	H1	1/2+x-1, 1/2-y, 1/2+z	2.731
C65	C74	1/2-x, 1/2+y-1, 1/2-z	3.571(8)
C66	H1	1/2+x-1, 1/2-y, 1/2+z	3.095
H9	H20	1/2-x, 1/2+y-1, 1/2-z	2.380

TABLE 37: LEAST SQUARES PLANE CALCULATIONS

(A) ATOMS FORMING PLANE: Nb, S1, S2

EQUATION OF PLANE: $-0.8413X + 0.3686Y + 0.3953Z + 9.1444 = 0.0$ [a]

(B) ATOMS FORMING PLANE: Nb, S3, S4

EQUATION OF PLANE: $0.7683X - 0.2315Y + 0.5967Z - 11.0967 = 0.0$

(C) ATOMS FORMING PLANE: Nb, S5, S6

EQUATION OF PLANE: $-0.0706X + 0.1393Y + 0.9877Z - 1.9792 = 0.0$

(D) ATOMS FORMING PLANE: S1, S2, C11, C12, C13, C14 C15, C16

EQUATION OF PLANE: $-0.6239X + 0.3044Y + 0.7198Z + 6.3172 = 0.0$

DISTANCES OF ATOMS FROM PLANE (Å):

S1	-0.001(2)	S2	0.009(2)
C11	-0.048(7)	C12	0.041(7)
C13	0.078(8)	C14	0.010(8)
C15	-0.071(8)	C16	-0.086(7)
Nb	-0.7144(6)		

(E) ATOMS FORMING PLANE: S3, S4, C21, C22, C23, C24, C25, C26

Table 37 (continued)

EQUATION OF PLANE: 0.9191X - 0.3096Y + 0.2438Z - 11.2653 = 0.0

DISTANCES OF ATOMS FROM PLANE (Å):

S3	0.004(2)	S4	0.004(2)
C21	-0.090(7)	C22	-0.012(9)
C23	-0.067(9)	C24	0.060(9)
C25	-0.023(8)	C26	-0.067(7)
Nb	-0.7099(6)		

(F) ATOMS FORMING PLANE: S5, S6, C31, C32, C33, C34, C35, C36.

EQUATION OF PLANE: 0.2788X + 0.0011Y + 0.9603Z - 6.8577 = 0.0

DISTANCES OF ATOMS FROM PLANE (Å):

S5	-0.006(2)	S6	0.001(2)
C31	0.036(7)	C32	-0.042(8)
C33	-0.052(9)	C34	-0.004(9)
C35	0.057(8)	C36	0.055(7)
Nb	0.6869(6)		

(G) ATOMS FORMING PLANE: S1, S3, S5

EQUATION OF PLANE: -0.3396X - 0.9393Y + 0.0484Z + 5.3688 = 0.0

DISTANCES OF ATOMS FROM PLANE (Å):

Nb	1.5787(6)

(H) ATOMS FORMING PLANE: S2, S4, S6

Table 37 (continued)

EQUATION OF PLANE: -0.3423X - 0.9380Y + 0.0545Z + 8.5348 = 0.0

DISTANCES OF ATOMS FROM PLANE (Å):

Nb	-1.5699(6)

[a] X, Y and Z are in Å and refer to the orthogonal coordinates along *a*, *b*, *c**.

TABLE 38: DIHEDRAL ANGLES BETWEEN SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE
Nb, S1, S2	Nb, S3, S4	119.7°
Nb, S1, S2	Nb, S5, S6	120.1°
Nb, S3, S4	Nb, S5, S6	120.2°
Nb, S1, S2	S1, S2, C11, C12, C13, C14, C15, C16	22.8°
Nb, S3, S4	S3, S4, C21, C22, C23, C24, C25, C26	22.6°
Nb, S5, S6	S5, S6, C31, C32, C33, C34, C35, C36	21.8°
S1, S3, S5	S2, S4, S6	0.6°

DESCRIPTION OF STRUCTURE

The portion of the molecule of major interest, i.e. the $Nb(bdt)_3^-$ anion, is shown in the three dimensional representation in Fig. 14. The metal is surrounded approximately equidistantly by six sulfur atoms in the form of a trigonal prism, thus it has approximate C_{3h} symmetry. The dithiolene ligands radiate from the metal in a "paddle-wheel" arrangement as was the case for $Mo(bdt)_3$ and the other trigonal prismatic dithiolenes.[129,130,132] The prism is not however as regular as that in $Mo(bdt)_3$, with a significant range in niobium-sulfur distances from 2.428(2) Å to 2.458(2) Å. The mean Nb-S distance (2.441 Å) is also significantly longer than the Mo-S distance (2.367 Å) in $Mo(bdt)_3$ and thus is the longest metal-sulfur distance observed in any of the trigonal prismatic molecules (Table 48).

It is interesting that in the previous trigonal prismatic structures the metal-sulfur bond lengths had been amazingly constant, considering that the covalent and ionic radii[133] of vanadium differed, by approximately 0.07 Å, from those of molybdenum and rhenium. $Nb(bdt)_3^-$ is therefore the first example of a prism in which this is no longer true; the Nb-S distance being approximately 0.11 Å longer than

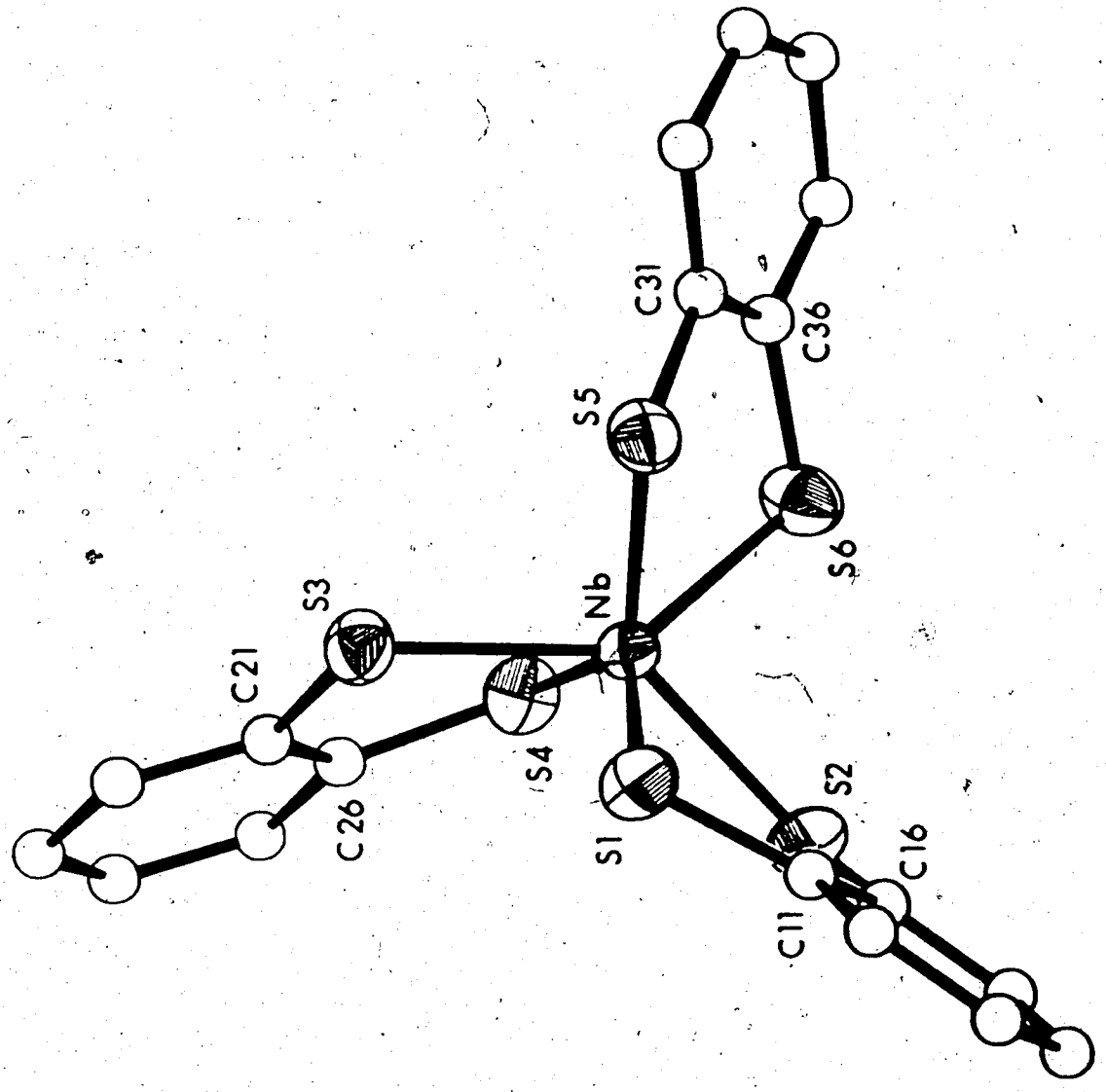


Fig. 14: A PERSPECTIVE VIEW OF THE $Nb(S_2C_6H_4)_3^-$ ANION.

the metal-sulfur distances in the three other prisms and also 0.074 Å longer than in $Mo(bdt)_3$ (to which this comparison is most useful). The increase in metal-sulfur distances progressing from the molybdenum to the niobium complex is approximately consistent with the corresponding increase in the metal covalent radii.[133] Although the values for the metal covalent radii are ambiguous (especially for $Nb(bdt)_3^-$ since the extra electron will expand the niobium orbitals increasing its radius from that of the neutral species), a very rough comparison is obtained using Pauling's values. This yields a predicted increase in metal-sulfur bonds of about 0.05 Å when calculated using the neutral atom radii.

The constancies of the metal-sulfur distances in the previous trigonal prisms, in spite of differing metal radii, had been attributed as a consequence of proposed interligand S-S bonding.[124] Thus the difference in Nb-S distances compared with Mo-S distances tends to indicate a possible breakdown in S-S bonding and an expected increase in S-S distances. Because of the relatively fixed ligand bite this should manifest itself in longer interligand S-S distances compared to intraligand S-S distances. This is in fact what is observed with the

mean interligand S-S distance (3.231 Å) being significantly longer than the intraligand S-S distance (3.150 Å). Here again slight distortions are obvious with a range in interligand S-S distances from 3.178(3) Å to 3.294(3) Å.

The sulfur-carbon distances (1.745 Å), although similar to the other *tris* dithiolenes, are longer than any observed previously and more significantly are longer than those in $Mo(bdt)_3$ (1.727 Å) where the same ligand is involved. Thus the sulfur-carbon bonds have less double bond character in the niobium complex and the ligands are therefore more dithiolate and less dithioketonic in character than for $Mo(bdt)_3$. The mean carbon-carbon distance within the ligands is again consistent with those observed in benzene[158] and in several disubstituted benzene derivatives,[159] as mentioned in Chapter VI. Again, as was the case for $Mo(bdt)_3$, there is a wide range in C-C distances (Fig. 15). From the diagram showing the average C-C bond lengths one sees that the C2-C3, C3-C4, and C4-C5 distances are significantly shorter than the other three. This may be interpreted as indicating some contribution from the dithioketonic formulation but this simple interpretation should not be made in the absence of a full analysis of the thermal

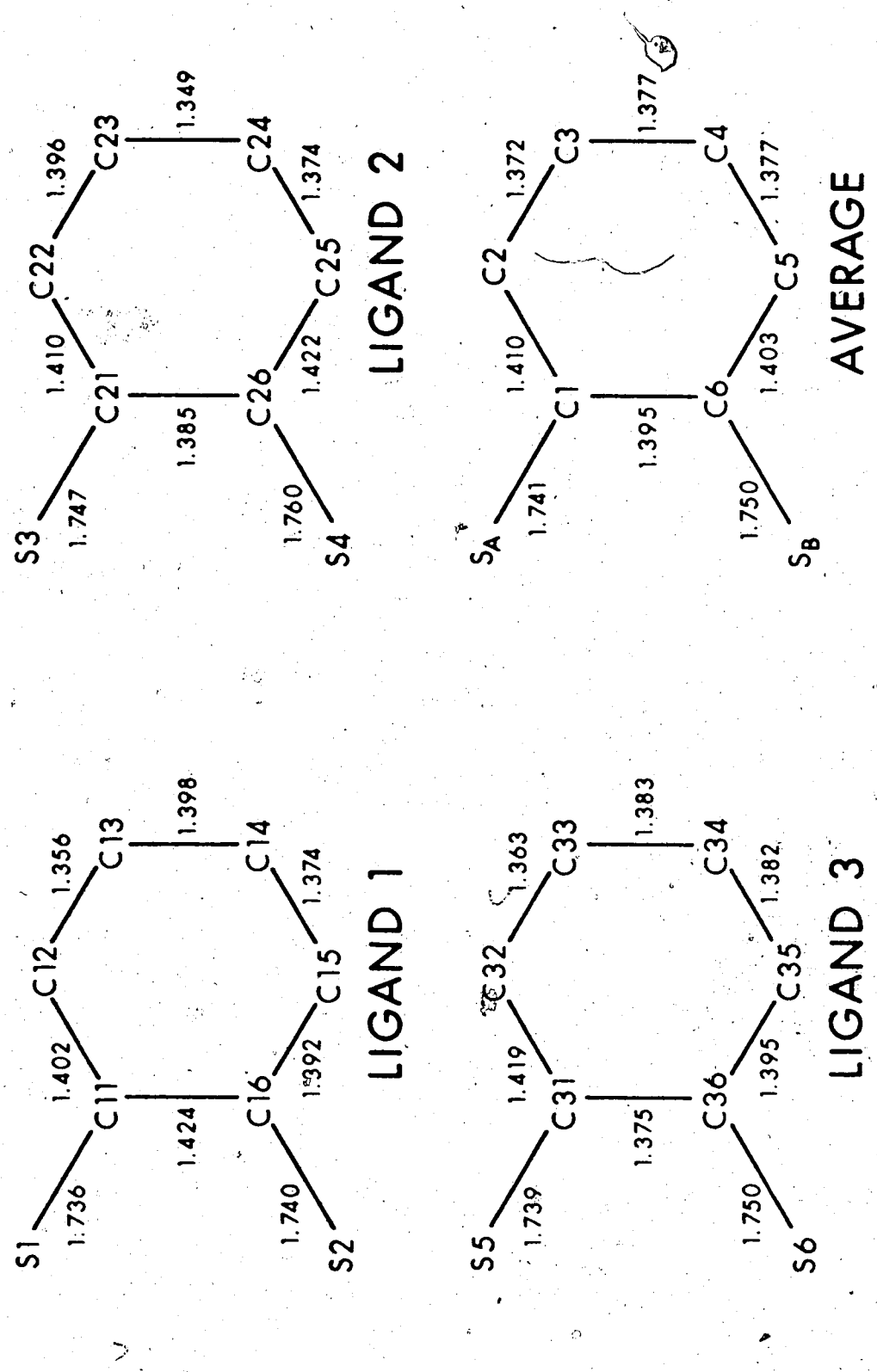


Fig. 15: DIMENSIONS WITHIN THE DITHIOLENE LIGANDS.

parameters and an assessment of their effect on the observed uncorrected bond distances.

The intra- and interligand S-Nb-S angles average 80.35° and 82.88° respectively and are therefore an indication of the slight distortion from trigonal prismatic coordination. Possibly a more significant indication of the distortion, however, is the *range* in the interligand S-Nb-S angles, from 84.87(7)° to 81.03(7)°. The S-Nb-S angles, involving sulfur atoms approximately *trans* to each other, average 135.06° and is again similar to the value of 136(1)° found in the other prisms.

The two triangular faces of the prism deviate slightly from being parallel, the angle between their normals being 0.6°. In addition the angles between the NbS_2 planes, as shown in Table 38, are all close to the expected 120°. The Nb-S-C angles average 105.9° and are all in close agreement with each other.

The S-C-C angles (S_A-C_1-C_6 and S_B-C_6-C_1 in Fig. 15) average 120.1° and are close to the expected value of 120°. This good internal agreement of the Nb-S-C and S-C-C angles adds further proof that the deviations in the interligand S-Nb-S angles are indeed significant.

As was observed in $Mo(bdt)_3$, $Mo(S_2C_2H_2)_3$,[130]

and $Mo[Se_2C_2(CF_3)_2]_3$,[152] the ligand planes again deviate considerably from the corresponding MS_2 planes. These deviations are more regular in $Nb(bdt)_3^-$ than in $Mo(bdt)_3$ (see Table 49). Their mean values, 22.4° and 21.4°, respectively are however in good agreement and both are larger than the values of 18° and 18.6° observed in $Mo(S_2C_2H_2)_3$ and $Mo[Se_2C_2(CF_3)_2]_3$ respectively. That these dihedral angles are irregular in $Mo(bdt)_3$ yet regular in $Nb(bdt)_3^-$ is probably a consequence of packing forces. The flexibility, afforded by the rotational freedom of the phenyl groups of the tetraphenylarsonium cation, allows effective packing without major deformation of the ligand planes. It is probable then that the structure, observed in the crystal, closely approximates the structure in solution. It is interesting that this bend of the ligand plane from the MS_2 plane has been observed in the trigonal prismatic molybdenum dithiolenes and also in the molybdenum diselenato complex, and now has been observed in $Nb(bdt)_3^-$, which is isoelectronic with the molybdenum analogue. In contrast, the ligand planes were found to be coplanar with the MS_2 planes in both $Re(S_2C_2Ph_2)_3$[129] and $V(S_2C_2Ph_2)_3$.[132]

A three dimensional representation of the

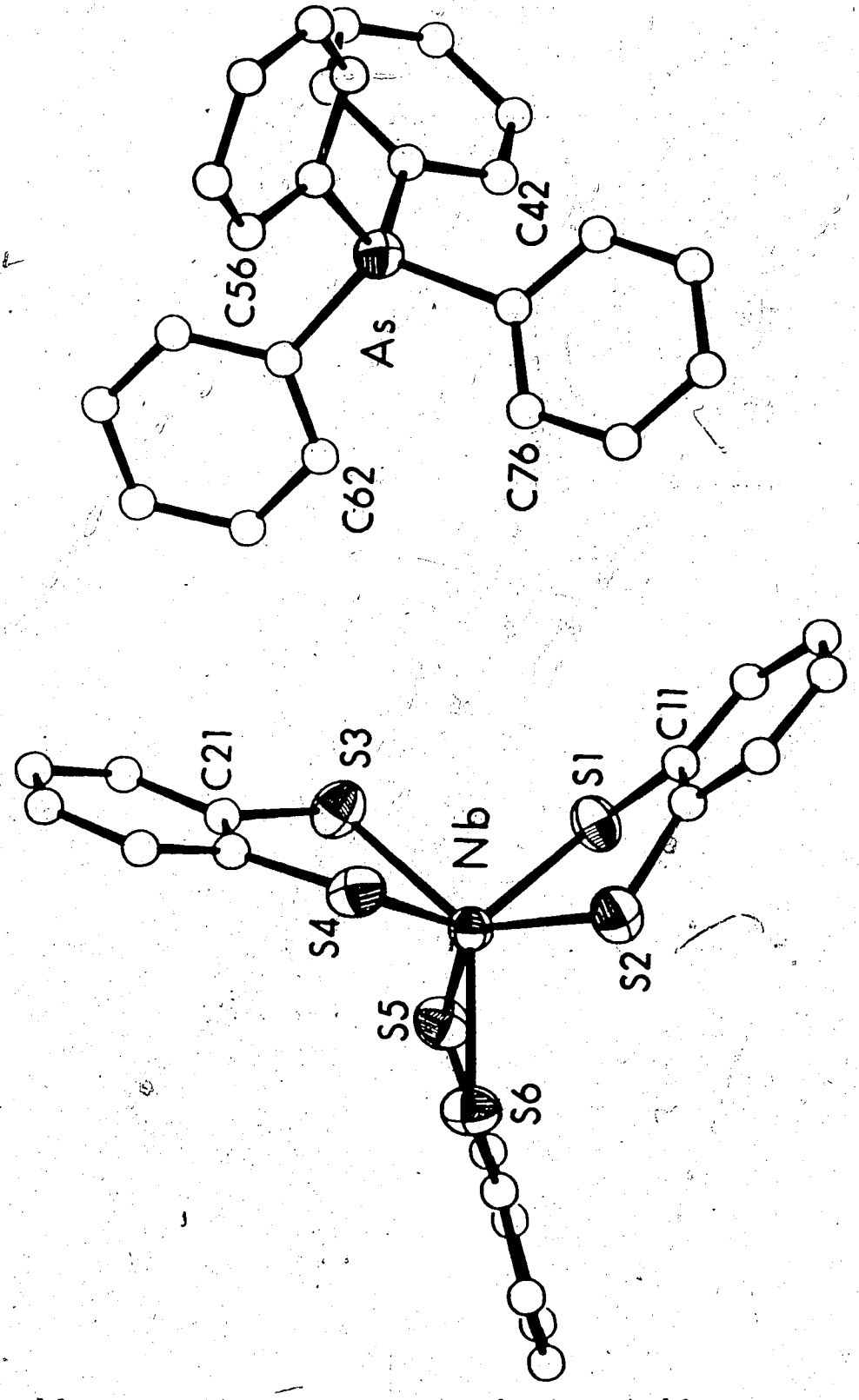


Fig. 16: A PERSPECTIVE VIEW OF $[As(C_6H_5)_4][Nb(S_2C_6H_4)_3]$, VIEWED DOWN THE CRYSTALLOGRAPHIC *b* AXIS.

$Nb(bdt)_3^-$ anion and the tetraphenylarsonium cation, viewed down the crystallographic *b* axis, is shown in Fig. 16. The geometry of the cation is quite normal with no unusual features. The arsenic atom is surrounded in almost perfect tetrahedral coordination with the C-As-C angles being close to the predicted 109.5°, and all deviations from this value are easily explained by intermolecular interactions. The arsenic-carbon bonds are similar and the mean (1.888 Å) approximates the value predicted from the sums of the covalent radii[133,162] (1.94 Å), assuming an arsenic-carbon single bond involving sp^2 hybridized carbon atoms. These observed bond lengths agree favourably with other determinations[163,164] where the tetraphenylarsonium cation was involved.

CHAPTER VIII: THE CRYSTAL AND MOLECULAR STRUCTURE OF *BIS* (TETRAMETHYLAMMONIUM) *TRIS* (BENZENE-1,2-DITHIOLATO) ZIRCONIUM, $([(CH_3)_4N]_2[Zr(S_2C_6H_4)_3])$.

EXPERIMENTAL

Bright red crystals of $[(CH_3)_4N]_2[Zr(bdt)_3]$, suitable for single crystal X-ray diffraction studies, were kindly supplied by Dr. Takats and Mr. Martin. These crystals were prepared[143] by the reaction of sodium cyclopentadienide and benzene dithiol and the subsequent reaction with $Zr[N(C_2H_5)_2]_4$, and crystallization with tetramethylammonium chloride. Preliminary photography showed mmm Laué symmetry indicating an orthorhombic space group. Systematic absences determined by Weissenberg (0kℓ, 1kℓ; CuK_α X-radiation) and Precession photography (h0ℓ, h1ℓ, hk0, hkl; MoK_α X-radiation) are h00: h = 2n + 1, and 0k0: k = 2n + 1 consistent with the space group $P2_12_12$. Precise lattice parameters were obtained at 22° from a least squares analysis performed on the setting angles of 12 high angle reflections, accurately centred on a Picker automatic four circle diffractometer, using CuK_{α_1} X-radiation. The resulting

cell parameters and estimated standard deviations are: a = 9.931(2) Å, b = 14.368(2) Å, c = 11.098(2) Å The observed density [1.38(2) g cm^{-3}], obtained by floatation in a mixture of chloro- and bromobenzene is consistent with the theoretical value of 1.381 g cm^{-3}, calculated assuming two molecules with formula weight 660.19 a.m.u. occupy the unit cell of volume 1587.9 $Å^3$. Since the space group $P2_12_12$ has four general equivalent positions, the $Zr(bdt)_3^{2-}$ dianion is therefore restricted to having 2-fold symmetry and must sit on the crystallographic 2-fold axis. The two tetramethylammonium cations can either be related by the two-fold or sit on the two-fold axis.

Intensity data were collected on the Picker automatic diffractometer using CuK_α X-radiation filtered with a 0.0005" thick nickel foil and using a 2° take-off angle. The crystal was mounted in a general orientation but with the a^* axis approximately coincident with the ϕ axis of the diffractometer. A coupled $2\theta/\omega$ scan technique, with a scan speed of 1° min^{-1}, was employed for data collection with all unique reflections with $2\theta \leq 125°$ being collected. The two theta scan range for each reflection was $2° + \Delta 2\theta$ where $\Delta 2\theta$ corresponded to $[2\theta(K_{\alpha_1}) - 2\theta(K_{\alpha_2})]$.

Forty second stationary background counts on each side of the peak were recorded and assuming linearity of background, intensities and standard deviations in the intensities were calculated as shown in Chapter II using a "p factor" of 0.03. A scintillation counter was used in conjunction with a pulse height analyzer, tuned to accept 95% of the CuK_α peak. Three standard reflections were collected automatically every 100 data reflections. In addition several additional reflections were collected manually to assess decomposition. No significant decomposition was observed so no correction was necessary.

Of the 1403 unique reflections collected, 1054 were significantly above background using the criterion $I/\sigma(I) \geq 3.0$. The significant data were then reduced to structure factor amplitudes by correction for Lorentz, polarization and absorption effects. Standard deviations in the structure factors were again calculated as in Chapter II.

The crystal faces were identified and their perpendicular distances to an arbitrarily chosen origin measured as: (0,1,0), 3.268×10^{-3} cm; $(0,\bar{1},0)$, 10.836×10^{-3} cm; $(\bar{1},0,0)$, 20.640×10^{-3} cm; (0,0,1), 3.09×10^{-3} cm; (1,1,0), 0.0 cm; $(1,\bar{1},0)$, 0.0 cm; and $(1,0,\bar{12})$, 0.0 cm. The face $(1,0,\bar{12})$ is acknow-

ledged as a very unusual choice, but its position is most consistent with the indices chosen, since it is opposite to the (0,0,1) face but inclined to it by about 5°. The absorption coefficient[86] for CuK_α X-radiation is 66.63 cm^{-1}, leading to a range in transmission factors from 0.756 to 0.423.

In the original data collection several irregularities were observed. The reflections occurred as "pulses" in the counter and their exact cause was unknown, but was probably due to some electronic device connected to the diffractometer power line. The reflections where this was actually observed were rejected. However it was believed (on the basis that several $|F_o|$ values were extremely high) that these pulses had occurred throughout the data collection. For this reason the $hk\ell$ data were recollected along with the $h\bar{k}\ell$ data so all three data sets could be compared and faulty reflections could be excluded. The second $hk\ell$ data set was merged with the $h\bar{k}\ell$ data to obtain improved standard deviations. In this merged data set the number of statistically reliable reflections increased to 1126. The same data collection techniques were used for the second $hk\ell$ data and the $h\bar{k}\ell$ data as was used for the original $hk\ell$ data. Terms used in the Zachariasen extinction correction were calculated at this stage.

STRUCTURE SOLUTION AND REFINEMENT

A sharpened Patterson map[146] was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, $0 \leq w \leq 0.5$. Since the zirconium atom is restricted to lie on the two-fold axis, the Harker vectors are located at 1/2, 1/2, 2z; and 1/2, 1/2, -2z, so the solution is trivial yielding the coordinates for the zirconium as (0.0, 0.0, 0.189) from the largest vector at (0.5, 0.5, 0.378). The next six most intense vectors could be interpreted as Zr-S vectors about either the origin or the Zr-Zr Harker vector. From initial inspection of the placement of these vectors, it was evident that the zirconium coordination was close to octahedral and was definitely not trigonal prismatic. Due to the extra symmetry of the Patterson, care had to be taken in choosing the vectors to represent the three independent sulfur atoms, in order for the model to phase correctly. Several arbitrary choices can be made initially. The S1 position was calculated from the vector at (0.05, 0.168, 0.0) yielding the coordinates (0.05, 0.168, 0.189). From the vector at (0.16, 0.0, 0.18) the S2 position was calculated as (0.16, 0.0, 0.009). The position of S3, however, must be chosen in such a way to be consistent with the choice of S1 and S2. There are two

possible choices for the S3 position yielding the positions (0.185, -0.048, 0.315) or (0.185, 0.048, 0.315). A choice between the two was made on the basis of sulfur-sulfur vectors which showed the first position was correct.

In the first refinements, involving only the zirconium and sulfur positions, the y coordinate of S2 was not refined, since it was possible that it could refine in the wrong direction and hamper the phasing. A brief resumé of the refinement is shown in Table 39.

TABLE 39: REFINEMENT OUTLINE

	MODEL	R_1	R_2
(1)	Zr and S atoms	0.297	0.384
(2)	Complete anion (isotropic B's)	0.152	0.243
(3)	Anion and Cation (isotropic B's)	0.088	0.106
(4)	Anisotropic Zr and S	0.074	0.097
(5)	Anisotropic Zr, S, N and C atoms of tetramethyl ammonium	0.069	0.088
(6)	Absorption Correction	0.050	0.063
(7)	Change of Hand	0.057	0.073
(8)	Carbon atoms of dithiolene ligands anisotropic	0.042	0.061
(9)	Hydrogen atoms of dithiolene ligands	0.039	0.059
(10)	Extinction correction[147]	0.039	0.059
(11)	Merged Data	0.034	0.053
(12)	Methyl Hydrogens included as rotors	0.029	0.035

Structure factors were calculated using the atomic scattering factors for the neutral atoms for zirconium, sulfur, carbon and nitrogen by Cromer and Mann.[75] The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.[149] Anomalous dispersion corrections by Cromer[76] were applied to the zirconium and sulfur scattering factors ($^{\Delta}f'_{Zr} = -0.62$, $^{\Delta}f''_{Zr} = 2.42$, $^{\Delta}f'_{S} = 0.31$, $^{\Delta}f''_{S} = 0.58$).

A refinement was performed with a change of hand for model (6) and the original model was judged significantly better on the basis of a Hamilton's R test[79] (at the 0.005 significance level). Hydrogen positions on the dithiolene ligands were calculated from the known geometry and orientation of the benzene rings, using a C-H distance of 1.0 Å. The hydrogen parameters were not refined. The hydrogen atoms were given thermal parameters approximately 10 - 15% greater than their attached carbon atom. An electron density difference map, phased on model (11), failed to locate any of the methyl hydrogen atoms, instead only smears of electron density were observed in the predicted regions. In addition the tetramethylammonium carbon atoms had anomalous thermal parameters, so the difference map was inspected for obvious signs of

disorder involving these carbon atoms. No signs of disorder, however, were obvious. Although the methyl hydrogens were not located, they were added to the structure factor calculations in the form of free rotating rigid bodies.[165] The ideal tetrahedral coordination of the carbon atoms was assumed and the centres of gravity and angles defining the orientation of the "hydrogen triangles" were calculated using the assumed geometry, and the direction cosines of the nitrogen-carbon bonds.

Model (11), which is the refinement of the merged data, contains all the corrections performed on the previous models.

RESULTS

Observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 40. The final fractional coordinates and isotropic temperature factors of all atoms are shown in Table 41. Standard deviations were obtained from the inverse matrix of the final least squares analysis. Table 42 shows the anisotropic thermal parameters (U_{ij}'s)[80] of all anisotropic atoms. Relevant bond lengths and angles are shown in Tables 43 and 44, and were obtained with

their standard deviations from ORFFE. Several inter-ionic contacts which are comparable to the predicted van der Waals contacts[151] are shown in Table 45. Selected least squares planes are shown in Table 46. In addition Table 47 lists the dihedral angles between selected planes.

The numbering scheme for all non-hydrogen atoms is shown in Figures 17 and 18. The hydrogen atoms H1 through H6 are attached sequentially to the carbon atoms (C2 through C9) which are not bonded to sulfur atoms. The hydrogen atoms H7 through H18 are bonded sequentially in groups of three to carbon atoms C10 through C13. Since the hydrogen atoms of the methyl groups were included as hindered rotors, no individual temperature factors are given, rather the temperature factors for the groups are shown in Table 41.

TABLE 40: OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (ELECTRONS X 10)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 0**				7	1	148	148	1	1	538	514	7	6	262	256	1	6	414	421
0	1	507	503	7	2	495	493	1	2	962	955	7	7	151	150	1	7	150	145
0	2	797	721	7	3	312	307	1	3	533	537	7	8	159	140	1	9	399	393
0	3	114	111	7	4	427	429	1	5	635	628	7	10	183	195	1	10	259	255
0	4	217	214	7	5	177	167	1	6	566	562	7	11	[illegible]	165	1	11	186	175
0	5	784	806	7	6	569	570	1	7	343	358	8	[illegible]		144	1	12	113	110
0	6	967	1008	7	7	216	216	1	8	264	254	8	[illegible]		209	2	0	93	31
0	7	402	407	7	8	135	144	1	9	205	204	8	3	[illegible]	157	2	1	236	228
0	8	106	167	7	9	137	148	1	10	265	262	8	4	[illegible]	381	2	2	260	256
0	9	554	545	7	10	167	185	1	11	164	168	8	5	[illegible]	148	2	3	1075	1047
0	10	190	189	7	11	214	230	2	1	314	265	8	6	[illegible]	146	2	4	393	390
0	11	117	106	8	0	388	381	2	2	939	936	8	7	261	261	2	5	374	384
1	F	1146	1184	8	1	632	642	2	3	399	400	8	8	193	209	2	7	138	147
1	2	345	319	8	3	206	204	2	4	581	595	8	9	206	214	2	8	290	278
1	3	400	402	8	4	197	198	2	5	246	259	8	10	163	166	2	9	271	272
1	4	216	225	8	5	419	417	2	6	265	261	9	0	343	344	2	10	165	172
1	5	167	167	8	6	147	132	2	7	408	417	9	1	207	214	2	11	2[illegible]3	250
1	6	718	727	8	7	191	179	2	8	222	228	9	3	107	114	3	0	146	152
1	7	712	709	8	10	202	202	2	9	192	197	9	5	143	153	3	1	258	263
1	9	201	214	9	1	106	107	2	10	213	203	9	6	248	245	3	2	158	163
1	11	178	184	9	2	285	291	2	11	106	[illegible]8	9	8	141	154	3	4	601	604
1	12	240	239	9	4	258	256	2	12	234	2[illegible]	9	10	114	124	3	5	151	150
2	0	420	427	9	7	317	304	3	0	1585	1617	10	1	137	135	3	6	205	190
2	1	726	686	9	8	231	242	3	1	542	532	10	2	224	223	3	7	192	178
2	2	296	311	9	9	144	138	3	2	240	242	10	3	167	160	3	8	94	88
2	3	658	671	9	10	144	155	3	4	278	261	10	4	233	222	3	9	306	307
2	4	266	279	10	0	414	397	3	5	330	325	10	6	243	227	3	10	391	389
2	5	680	657	10	1	337	331	3	6	523	526	10	7	218	215	3	12	165	177
2	6	589	582	10	3	347	345	3	7	145	143	10	8	108	112	4	0	118	60
2	8	217	211	10	4	151	128	3	8	173	150	10	9	149	155	4	1	477	479
2	9	188	181	10	5	305	300	3	10	83	99	11	0	441	444	4	2	515	520
2	10	223	209	10	6	214	213	3	11	248	249	11	1	265	262	4	3	595	614
2	11	223	222	11	1	156	143	3	12	98	88	11	2	205	202	4	4	471	465
2	12	158	143	11	2	397	405	4	0	335	319	11	3	335	335	4	5	168	164
3	F	376	377	11	3	166	156	4	1	271	280	11	4	177	173	4	6	209	212
3	2	154	111	11	4	478	469	4	2	307	292	11	5	409	396	4	7	141	150
3	3	221	233	11	5	144	141	4	3	387	403	11	7	111	100	4	8	379	361
3	5	235	253	11	6	281	288	4	4	210	198	11	8	119	122	4	9	174	162
3	6	214	218	11	7	94	112	4	5	151	149	12	0	143	160	4	10	183	177
3	7	662	675	11	8	96	98	4	6	445	440	12	1	282	279	4	11	177	181
3	8	214	210	11	9	147	167	4	7	521	517	12	2	258	266	5	0	125	130
3	9	221	213	12	0	395	390	4	8	154	141	12	3	189	202	5	1	554	564
3	10	174	169	12	1	279	295	4	9	279	279	12	4	355	353	5	2	635	630
3	12	300	309	12	2	163	164	4	10	151	156	12	6	278	275	5	3	491	487
4	0	1678	1630	12	3	287	281	4	11	130	150	12	7	132	139	5	4	645	642
4	1	754	734	12	4	159	160	4	12	209	218	13	0	328	332	5	5	217	210
4	2	213	208	12	5	397	393	5	0	1368	1371	13	1	169	167	5	6	295	303
4	3	178	188	12	7	85	95	5	1	613	615	13	2	152	149	5	7	323	312
4	4	131	126	13	1	106	107	5	2	560	561	13	3	176	189	5	8	168	172
4	5	253	262	13	2	128	124	5	3	379	370	13	5	171	171	5	9	391	387
4	6	734	736	13	3	97	107	5	4	383	378	13	6	111	128	5	10	136	137
4	8	160	157	13	4	183	173	5	5	692	692	14	0	121	119	5	11	125	138
4	9	142	147	13	6	192	206	5	6	299	310	14	4	97	111	6	0	764	785
4	10	186	199	13	7	121	121	5	7	283	285	15	1	90	73	6	1	266	269
4	11	159	170	14	0	180	184	5	8	320	333	16	0	73	77	6	2	799	806
4	12	79	83	14	1	128	122	5	9	135	150	16	1	84	82	6	3	551	541
5	1	566	590	14	3	112	101	5	10	311	303	***H = 2*****				6	4	175	174
5	2	426	432	14	5	90	113	5	11	162	160	0	0	1160	1162	6	5	382	378
5	3	177	185	14	6	84	103	6	0	293	287	0	1	919	978	6	6	179	179
5	4	567	576	15	2	132	118	6	1	743	725	0	2	1375	1394	6	7	333	332
5	6	361	386	15	4	96	91	6	2	478	487	0	3	783	793	6	8	307	311
5	7	487	485	16	0	181	179	6	3	351	335	0	4	139	147	6	10	162	157
5	8	88	87	16	1	93	108	6	4	738	740	0	5	620	631	6	11	129	134
5	9	263	255	***H = 1*****				6	5	163	160	0	6	101	63	7	1	528	520
5	11	216	218	0	1	682	709	6	6	567	561	0	7	287	288	7	2	180	177
6	0	1670	1703	0	2	659	672	6	7	322	339	0	8	349	336	7	3	372	370
6	1	373	380	0	3	514	534	6	8	192	198	0	10	239	230	7	4	581	572
6	2	343	351	0	4	623	610	6	9	282	288	0	11	105	90	7	5	220	214
6	3	266	270	0	5	115	94	6	10	154	149	0	12	124	127	7	6	352	344
6	4	430	430	0	6	808	794	6	11	182	196	1	0	385	369	7	7	238	235
6	5	865	846	0	7	643	625	7	0	671	677	1	1	676	675	7	9	264	261
6	6	298	305	0	8	282	281	7	1	443	435	1	2	972	967	7	10	180	173
6	7	244	241	0	9	397	404	7	2	432	441	1	3	767	765	8	0	345	340
6	9	202	192	0	11	192	190	7	3	503	503	1	4	1042	1060	8	1	107	110
6	10	269	266	0	12	206	208	7	4	171	173	1	5	269	267	8	2	229	226
6	11	166	171	1	0	1585	1547	7	5	500	490								

Table 40 (continued)

K	L	FOBS	FCAL
**H =	2****		
8	3	261	258
8	4	163	173
8	5	199	191
8	6	225	211
8	7	127	138
8	8	252	259
8	9	112	92
8	10	84	90
9	1	316	307
9	3	92	98
9	4	110	121
9	5	299	297
9	6	133	131
9	7	259	254
9	8	91	109
9	9	186	187
9	10	117	127
10	0	386	381
10	1	155	147
10	2	375	370
10	3	220	223
10	4	293	292
10	5	122	112
10	6	233	236
10	7	140	129
10	8	242	235
11	1	363	356
11	2	215	208
11	3	213	223
11	4	306	309
11	5	106	93
11	6	182	180
11	7	186	187
11	8	131	133
12	0	335	338
12	2	293	294
12	3	237	235
12	5	160	151
12	6	157	139
12	7	180	189
13	0	206	217
13	1	223	221
13	2	93	82
13	3	126	134
13	4	152	154
13	5	126	98
13	6	148	140
13	7	144	148
14	0	133	133
14	2	89	114
14	3	90	92
14	4	98	77
15	1	85	88
15	2	85	80
15	3	94	92
15	4	82	92
**H =	3****		
0	1	329	334
0	2	893	894
0	3	705	725
0	4	890	902
0	6	332	314
0	8	150	142
0	9	519	521
0	10	248	244
0	11	136	132
1	0	459	470
1	1	317	317
1	2	632	631
1	3	1339	1356
1	4	341	349
1	5	403	389
1	6	199	197
1	7	224	221
1	8	495	501
1	9	289	282
1	10	202	202
1	11	171	168
2	0	535	533
2	1	124	114
2	2	594	592
2	3	355	326
2	4	889	887
2	5	247	234
2	6	164	155
2	7	137	151
2	9	367	363
2	10	344	339
2	11	88	96
3	1	131	138
3	2	548	565
3	3	718	711
3	4	540	526
3	5	240	240
3	7	171	169
3	8	244	242
3	9	365	359
3	10	88	92
3	11	189	188
4	0	115	126
4	1	587	600
4	2	403	402
4	3	300	299
4	4	641	636
4	5	294	287
4	6	257	256
4	7	142	144
4	9	321	317
4	10	236	236
5	0	117	113
5	1	210	206
5	2	673	668
5	3	746	743
5	4	164	164
5	5	211	217
5	6	134	136
5	7	332	350
5	8	439	450
5	9	133	120
5	10	159	157
5	11	108	105
6	0	99	99
6	1	461	461
6	2	261	267
6	3	513	518
6	4	521	522
6	5	143	143
6	6	334	326
6	7	233	223
6	8	247	247
6	9	367	371
6	10	117	117
6	11	73	36
7	0	282	286
7	1	279	281
7	2	516	526
7	3	611	607
7	4	346	341
7	5	88	131
7	6	166	165
7	7	241	234
7	8	375	380
7	9	103	87
7	10	88	89
8	0	352	347
8	1	427	429
8	2	245	251
8	3	109	101
8	4	270	256
8	5	319	315
8	7	190	206
8	8	131	115
8	9	217	215
8	10	131	146
9	0	223	228
9	1	182	177
9	2	377	380
9	3	92	77
9	4	352	349
9	6	213	212
9	7	187	191
9	8	242	238
9	9	100	82
10	0	153	148
10	1	369	371
10	2	170	158
10	3	153	154
10	4	179	182
10	5	136	160
10	6	213	188
10	7	214	211
10	8	148	160
10	9	192	192
11	0	296	288
11	1	128	120
11	2	357	354
11	3	255	265
11	5	117	119
11	6	158	166
11	7	219	205
11	8	231	235
12	0	87	89
12	1	369	364
12	2	175	175
12	3	175	170
12	4	215	212
12	5	132	130
12	6	132	135
12	7	143	155
13	0	217	215
13	2	228	228
13	3	184	186
13	4	123	120
13	6	132	129
14	1	119	120
14	4	93	113
14	5	94	105
15	2	84	94
15	3	89	93
**H =	4*****		
0	0	435	439
0	2	532	524
0	3	735	734
0	4	124	117
0	5	209	196
0	6	268	249
0	7	271	270
0	8	417	422
0	9	147	134
0	10	178	159
0	11	95	93
1	0	199	203
1	1	710	717
1	2	490	486
1	3	335	312
1	4	630	622
1	5	233	230
1	6	219	216
1	7	341	334
1	9	320	318
1	10	109	112
2	0	67	90
2	1	495	489
2	2	564	581
2	3	537	526
2	4	286	275
2	5	301	295
2	6	288	284
2	7	203	199
2	8	444	442
2	9	186	190
2	10	162	157
2	11	125	129
3	0	410	400
3	1	372	368
3	2	267	263
3	3	446	434
3	4	358	362
3	5	276	282
3	6	342	343
3	7	189	191
3	8	136	123
3	9	280	280
3	10	211	199
3	11	90	87
4	0	130	119
4	1	306	297
4	2	460	473
4	3	550	554
4	4	376	386
4	5	297	289
4	6	286	291
4	7	256	251
4	8	382	383
4	9	150	158
4	10	119	123
4	11	193	191
5	0	69	52
5	1	616	610
5	2	449	443
5	3	323	344
5	4	549	549
5	5	305	300
5	6	204	196
5	7	223	229
5	9	233	246
5	10	142	151
6	0	404	400
6	1	285	288
6	2	457	465
6	3	546	536
6	4	123	127
6	5	224	230
6	6	167	185
6	7	217	217
6	8	342	338
6	9	95	100
6	10	112	119
7	0	414	420
7	1	370	380
7	2	391	398
7	3	210	213
7	4	320	317
7	6	272	258
7	7	284	285
7	8	97	121
7	9	235	255
7	10	85	91
8	1	293	293
8	2	347	343
8	3	262	251
8	5	259	254
8	6	144	149
8	7	192	197
8	8	280	288
8	9	116	138
9	1	360	364
9	2	180	178
9	3	142	130
9	4	304	301
9	5	178	170
9	6	151	159
9	7	136	148
9	9	99	127
10	0	303	315
10	1	180	199
10	2	174	180
10	3	382	382
10	4	139	134
10	5	127	130
10	6	183	182
10	7	103	98
10	8	189	190
11	0	181	177
11	1	217	215
11	2	205	204
11	3	135	140
11	4	226	226
11	5	131	140
11	6	155	142
11	7	109	112
12	2	214	216
12	3	183	178
12	5	172	162
12	7	109	108
12	1	162	170
13	2	151	154
13	3	157	159
13	4	161	163
14	0	105	116
14	2	105	122
14	3	163	155
14	4	117	101
15	0	93	99
15	1	127	130
**H =	5*****		
0	1	672	675
0	2	101	98
0	4	107	96
0	5	273	288
0	6	294	284
0	7	475	489
0	8	118	114
0	9	173	168
0	11	82	88
1	0	652	664
1	1	330	331
1	2	331	323
1	3	184	189
1	4	228	240
1	5	396	382
1	6	509	514
1	7	196	203
1	8	330	341
1	10	157	159
1	11	149	153
2	0	366	368
2	1	720	721
2	2	393	390
2	3	179	172
2	4	160	140
2	5	285	265
2	6	293	281
2	7	507	498
2	9	140	157
2	11	81	65
3	0	883	890
3	1	335	336
3	2	416	418
3	3	201	204
3	4	121	128
3	5	336	329
3	6	420	415
3	7	147	155
3	8	268	272
3	10	134	133
4	0	223	221
4	1	620	627

Table 40 (continued)

K	L	FOBS	FCAL
H = 5**			
4	2	347	339
4	3	178	172
4	4	295	301
4	5	261	247
4	6	263	263
4	7	333	327
4	8	114	112
4	9	134	143
4	10	110	102
5	0	252	263
5	1	244	255
5	2	155	165
5	3	149	153
5	4	254	238
5	5	464	462
5	6	228	235
5	7	134	130
5	8	250	250
5	10	166	171
6	0	86	107
6	1	297	300
6	2	229	228
6	3	102	102
6	4	292	299
6	6	251	257
6	7	290	283
6	9	150	143
6	10	86	94
7	0	348	354
7	1	319	337
7	2	107	115
7	3	390	384
7	5	338	342
7	6	254	254
7	8	201	211
7	9	96	115
8	0	209	214
8	1	278	281
8	2	470	465
8	4	304	291
8	6	140	150
8	7	208	202
8	8	85	82
8	9	115	126
9	0	137	143
9	1	185	184
9	2	130	124
9	3	277	271
9	4	195	186
9	5	309	310
9	8	130	130
10	0	230	237
10	1	115	108
10	2	243	242
10	4	284	279
10	5	187	175
10	6	181	177
10	7	103	119
11	0	119	108
11	1	241	242
11	3	220	220
11	4	121	105
11	5	261	254
12	1	150	168
12	2	219	229
12	4	190	195
13	0	126	131
13	1	136	127
13	3	193	193
13	4	121	111
14	1	102	93
14	2	128	137
H = 6**			
0	0	765	769
0	1	381	389
0	2	103	100
0	3	141	133
0	5	481	490
0	6	480	468
0	8	119	113
0	10	128	133
1	1	601	605
1	2	174	175
1	3	192	179
1	4	156	149
1	5	333	329
1	6	335	341
1	7	370	367
2	0	808	823
2	1	197	197
2	2	160	174
2	3	111	125
2	4	339	343
2	5	461	460
2	6	465	469
2	7	147	160
2	8	229	223
2	9	124	128
2	10	168	167
3	1	477	494
3	2	181	182
3	3	192	193
3	4	219	218
3	6	275	275
3	7	388	384
3	8	95	98
3	9	162	157
3	10	71	64
4	0	486	496
4	1	462	473
4	2	176	166
4	3	161	150
4	4	193	200
4	5	473	483
4	6	335	338
4	7	106	93
4	8	212	221
4	10	184	187
5	0	326	320
5	1	364	366
5	2	375	384
5	4	182	185
5	5	183	188
5	6	229	214
5	7	224	226
5	8	124	128
5	9	116	134
6	0	436	436
6	1	258	256
6	4	220	216
6	5	394	394
6	6	271	268
6	7	103	95
6	8	107	112
7	1	233	222
7	2	206	217
7	3	223	223
7	4	205	196
7	5	185	173
7	6	217	211
7	7	218	219
7	9	107	112
8	0	333	325
8	1	249	251
8	2	123	118
8	3	212	222
8	4	319	320
8	5	391	386
8	6	150	153
8	8	130	131
9	1	228	224
9	2	371	373
9	3	108	99
9	4	280	279
9	6	149	154
9	7	127	126
10	0	149	154
10	1	328	331
10	3	235	218
10	4	155	148
10	5	282	284
10	6	102	84
11	2	178	168
11	4	145	158
11	5	81	44
12	0	164	151
12	1	132	136
12	4	80	93
13	0	120	118
13	1	101	94
13	2	160	163
H = 7**			
0	2	119	127
0	4	274	274
0	6	181	173
0	7	146	148
0	8	88	92
0	9	129	136
1	0	255	260
1	1	202	209
1	2	158	134
1	3	213	208
1	4	262	268
1	5	446	448
1		214	213
1	9	86	79
2	1	473	471
2	2	391	385
2	3	214	202
2	4	360	364
2	5	174	164
2	6	230	206
2	7	193	197
2	9	121	120
3	0	574	582
3	1	337	337
3	2	278	278
3	3	310	319
3	4	258	249
3	5	471	470
3	6	163	152
3	7	96	107
3	8	154	174
3	9	89	79
4	0	282	294
4	1	271	263
4	2	339	336
4	3	168	169
4	4	286	278
4	6	247	253
4	7	218	203
4	9	179	184
5	0	239	239
5	1	255	253
5	3	121	108
5	4	159	160
5	5	326	340
5	6	186	183
5	8	185	173
6	1	215	222
6	2	161	166
6	3	145	135
6	4	153	162
6	5	176	189
6	6	104	111
6	7	199	208
7	0	310	320
7	1	173	169
7	2	232	238
7	3	183	156
7	4	149	155
7	5	275	281
7	6	231	228
7	8	141	134
8	1	320	317
8	2	164	175
8	3	124	122
8	4	249	241
8	5	98	103
8	6	121	127
8	7	157	168
9	0	281	285
9	1	118	135
9	2	169	177
9	3	149	157
9	4	175	172
9	5	269	273
9	6	113	105
10	1	191	191
10	2	175	170
10	3	98	95
10	4	105	120
11	0	228	224
12	0	120	117
12	1	120	137
H = 8**			
0	1	140	127
0	3	522	531
0	5	139	149
0	7	85	91
0	8	104	120
1	2	327	320
1	3	134	138
1	4	375	362
2	2	332	334
2	3	323	328
2	4	131	135
2	5	333	327
2	7	160	170
2	8	187	184
3	1	278	275
3	2	267	267
3	3	236	246
3	4	424	425
3	6	204	201
3	8	84	85
4	0	220	218
4	1	130	106
4	2	242	245
4	3	419	416
4	5	220	230
4	7	132	125
4	8	145	140
5	1	165	160
5	2	159	168
5	4	253	240
5	5	164	155
5	7	101	110
6	2	120	120
6	3	129	133
6	5	99	85
6	6	98	124
7	1	192	206
7	3	125	118
7	4	145	147
7	5	161	167
7	6	85	84
8	0	310	307
8	2	273	282
8	3	137	141
8	5	174	178
8	6	98	105
9	1	314	313
9	2	105	100
9	3	136	129
9	4	196	196
10	0	221	215
10	2	176	186
10	3	126	123
11	1	174	171
H = 9**			
0	2	151	145
0	4	245	238
1	0	86	79
1	2	221	217
1	3	351	347
2	1	314	331
2	2	242	250
2	3	153	145
2	4	308	301
2	5	111	112
2	6	90	110
3	0	252	251
3	1	123	112
3	2	378	371
3	3	397	398
3	5	191	185
3	7	204	191
4	0	100	87
4	1	198	203
4	2	147	142
4	3	189	190
4	4	291	278
4	6	138	149
5	1	106	89
5	2	222	219
5	3	219	206
5	4	124	117
5	5	106	85
6	0	102	104
6	2	127	120
6	3	93	91
6	4	102	117
6	5	153	134
7	0	84	85
7	2	212	201
7	3	164	186
7	4	93	92
8	0	92	89
8	1	261	262
8	2	91	80
8	3	116	106
8	4	196	201
9	0	195	191
9	2	230	228
H = 10**			
0	2	161	157
0	3	131	149
0	4	150	124
1	1	191	192
1	5	97	111
2	0	262	262
2	2	274	276
2	3	170	157
2	5	120	116
3	1	309	313
3	2	94	107
3	3	163	161
3	4	190	201
4	0	182	173
4	2	226	224
4	3	211	211
5	0	97	95
5	1	116	122
5	2	140	138
6	1	87	65
6	2	104	101
7	1	111	122
H = 11**			
0	1	117	118
1	0	233	236
2	1	264	278

TABLE 41: ATOM COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	B
Zr	0.0	0.0	-0.18983(6)	3.01*
S1	-0.1645(2)	-0.0080(2)	-0.0132(1)	4.56*
S2	0.0535(2)	0.1716(1)	-0.2142(2)	4.15*
S3	-0.1851(2)	0.0474(1)	-0.3350(1)	4.33*
C1	-0.0697(7)	-0.0046(7)	0.1207(5)	4.55*
C2	-0.1364(10)	-0.0100(8)	0.2326(6)	7.08*
C3	-0.0686(11)	-0.0036(10)	0.3391(5)	8.76*
C4	-0.0580(7)	0.2186(4)	-0.3220(5)	3.71*
C5	-0.0480(8)	0.3120(5)	-0.3527(6)	5.13*
C6	-0.1351(10)	0.3523(6)	-0.4355(7)	6.07*
C7	-0.2330(10)	0.2999(8)	-0.4869(8)	6.57*
C8	-0.2475(8)	0.2068(6)	-0.4570(6)	5.08*
C9	-0.1597(7)	0.1658(5)	-0.3737(5)	3.93*
N	-0.4980(8)	-0.2008(3)	-0.1384(5)	4.45*
C10	-0.3933(9)	-0.2662(8)	-0.1198(14)	10.92*
C11	-0.5023(15)	-0.1388(7)	-0.0264(8)	10.01*
C12	-0.4761(11)	-0.1372(7)	-0.2393(8)	9.07*
C13	-0.6332(9)	-0.2452(6)	-0.1408(10)	7.08*
		RIGID BODIES		
H1	-0.2398	-0.0170	0.2308	7.90
H2	-0.1198	-0.0085	0.4177	9.60

Table 41 (continued)

Atom	x	y	z	B
D	4.610[a]			
E	1.571			
F	1.571			
H3	0.0269	0.3512	-0.3143	6.20
H4	-0.1241	0.4203	-0.4566	7.00
H5	-0.2981	0.3283	-0.5469	7.90
H6	-0.3209	0.1671	-0.4949	6.30
D	3.391			
E	2.447			
F	3.747			
		HINDERED ROTORS		
H7	-0.3503	-0.2810	-0.1985	
H8	-0.3250	-0.2381	-0.0636	11.00
H9	-0.4316	-0.3238	-0.0827	
BARRIER	0.02[b]			
RADIUS	0.946			
D	0.721			
E	1.373			
F	0.0			
H10	-0.5980	-0.1260	-0.0060	
H11	-0.4537	-0.0797	-0.0446	11.00
H12	-0.4571	-0.1722	0.0416	
BARRIER	0.02			

Table 41 (continued)

ATOM	x	y	z	B
RADIUS	0.946			
D	0.625			
E	3.106			
F	0.0			
H13	-0.[illegible]75	-0.1230	-0.2447	
H14	-0.5275	-0.0785	-0.2238	9.5
H15	-0.5078	-0.1674	-0.3144	
BARRIER	0.02			
RADIUS	0.946			
D	0.676			
E	6.091			
F	0.0			
H16	-0.6652	-0.2550	-0.0568	
H17	-0.6972	-0.2034	-0.1853	8.0
H18	-0.6265	-0.3065	-0.1838	
BARRIER	0.02			
RADIUS	0.946			
D	0.444			
E	4.689			
F	0.0			

*Equivalent isotropic temperature factors-corresponding to the anisotropic thermal parameters shown in Table 42.

[a]D, E, and F are as described for Table 32.

[b]BARRIER (Bd) is the relative barrier to rotation of the hindered rotor group. $Bd = V_o/2kT$, where V_o = potential barrier to rotation (kcal mol^{-1}).

TABLE 42: ANISOTROPIC THERMAL PARAMETERS ($\AA^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	0.0369(4)	0.0467(4)	0.0309(3)	0.0033(5)	0.0	0.0
S1	0.0519(10)	0.0724(12)	0.0491(8)	-0.0014(13)	0.0142(8)	-0.0058(13)
S2	0.0503(10)	0.0535(9)	0.0536(10)	-0.0022(8)	-0.0099(8)	0.0043(8)
S3	0.0479(10)	0.0663(10)	0.0502(10)	0.0035(9)	-0.0149(9)	-0.0029(8)
C1	0.093(5)	0.042(3)	0.038(3)	-0.021(6)	0.013(3)	-0.003(5)
C2	0.134(8)	0.080(6)	0.055(4)	-0.051(6)	0.042(5)	-0.029(5)
C3	0.200(12)	0.096(5)	0.036(3)	-0.065(11)	0.021(4)	-0.015(7)
C4	0.049(4)	0.055(4)	0.038(3)	0.009(3)	0.004(3)	0.005(3)
C5	0.074(6)	0.061(4)	0.060(4)	0.011(4)	0.012(4)	0.009(4)
C6	0.080(6)	0.080(6)	0.071(5)	0.033(5)	0.011(5)	0.024(5)
C7	0.081(7)	0.116(7)	0.052(5)	0.044(6)	-0.004(5)	0.026(6)
C8	0.058(5)	0.088(6)	0.047(4)	0.022(4)	-0.012(4)	0.014(5)
C9	0.049(4)	0.070(4)	0.030(3)	0.018(4)	0.005(3)	0.002(3)
N	0.042(3)	0.054(3)	0.073(3)	-0.005(4)	-0.000(5)	0.017(3)

Table 42 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C10	0.048(6)	0.110(8)	0.257(16)	0.028(5)	0.031(8)	0.081(10)
C11	0.153(10)	0.113(7)	0.114(7)	-0.049(9)	-0.003(11)	-0.018(6)
C12	0.083(8)	0.137(8)	0.124(7)	-0.012(6)	0.006(6)	0.075(7)
C13	0.063(6)	0.095(7)	0.111(8)	-0.018(5)	-0.009(6)	0.032(6)

TABLE 43: INTRA-IONIC CONTACTS (Å)

ATOMS	DISTANCE (Å)	ATOMS	DISTANCE (Å)
Zr-S1	2.555(2)	Zr-S2	2.537(2)
Zr-S3	2.538(2)	S2-S3	3.255(2)
S1-S1'	3.275(3)	S1-S2'	3.424(3)
S2-S3'	3.662(2)	S1-S3	3.665(2)
S1-C1	1.759(6)	S2-C4	1.764(6)
S3-C9	1.772(7)	C1-C1'	1.391(14)
	1.410(8)	C2-C3	1.364(11)
	1.366(22)	C4-C5	1.388(9)
	1.389(10)	C6-C7	1.355(13)
	1.386(11)	C8-C9	1.400(9)
	1.388(9)	N-C10	1.416(10)
N-C11	1.530(10)	N-C12	1.462(9)
N-C13	1.487(10)		

TABLE 44: INTRA-IONIC ANGLES (DEGREES)

ATOMS	ANGLE	ATOMS	ANGLE
S1-Zr-S1'	79.74(8)	S2-Zr-S3	79.80(6)
S1-Zr-S3	92.06(6)	S1-Zr-S2'	84.51(7)
S3-Zr-S2'	92.40(6)	S3-Zr-S3'	101.19(8)
S1-Zr-S2	105.03(7)	S2-Zr-S2'	167.76(8)
S1-Zr-S3'	159.80(7)	Zr-S1-C1	107.7(2)
Zr-S2-C4	108.2(2)	Zr-S3-C9	108.0(2)
S1-C1-C1'	122.4(2)	S2-C4-C9	121.9(5)
S3-C9-C4	121.8(5)	C1'-C1-C2	118.2(5)
C1-C2-C3	121.8(9)	C2-C3-C3'	119.9(6)
C9-C4-C5	118.6(6)	C4-C5-C6	121.4(7)
C5-C6-C7	119.6(8)	C6-C7-C8	120.7(8)
C7-C8-C9	119.9(8)	C8-C9-C4	119.8(6)
C10-N-C11	106.8(10)	C10-N-C12	114.7(8)
C10-N-C13	112.4(6)	C11-N-C12	105.1(6)
C11-N-C13	103.8(8)	C12-N-C13	112.9(7)
S2'-S1-S3	62.10(5)	S2'-S3-S1	55.71(5)
S1'-S2-S3'	62.19(5)		

TABLE 45: INTER-IONIC CONTACTS (Å)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE (Å)
S2	H5	1/2+x, 1/2-y, $\bar{z}$-1	3.031
S2	C10	$\bar{x}$, $\bar{y}$, z	3.786(9)
S3	H2	x, y, z-1	2.930
S3	C12	$\bar{x}$-1, $\bar{y}$, z-1	3.756(11)
C1	C10	1/2-x-1, 1/2+y, $\bar{z}$	3.446(15)
C1	C13	1/2+x, 1/2-y-1, $\bar{z}$	3.657(13)
C1	C10	1/2+x, 1/2-y-1, $\bar{z}$	3.730(15)
C2	C13	1/2+x, 1/2-y-1, $\bar{z}$	3.662(14)
C2	C10	1/2-x-1, 1/2+y, $\bar{z}$	3.733(17)
C3	C6	1/2-x-1, 1/2+y-1, $\bar{z}$	3.754(12)
C4	H5	1/2+x, 1/2-y, $\bar{z}$-1	3.036
C4	C13	$\bar{x}$-1, $\bar{y}$, z	3.687(12)
C5	H6	1/2+x, 1/2-y, $\bar{z}$-1	2.832
C5	C8	1/2+x, 1/2-y, $\bar{z}$-1	3.666(10)
C8	C13	$\bar{x}$-1, $\bar{y}$, z	3.745(13)
	C12	$\bar{x}$-1, $\bar{y}$, z	3.792(13)
C9	C13	$\bar{x}$-1, $\bar{y}$, z	3.494(12)

TABLE 46: LEAST SQUARES PLANE CALCULATIONS

(A) ATOMS FORMING PLANE: Zr, S1, S3

EQUATION OF PLANE: 0.5985X - 0.2147Y - 0.7718Z = -1.6254 [a]

(B) ATOMS FORMING PLANE: Zr, S1, S1'

EQUATION OF PLANE: -0.0622X + 0.9978Y = 0.0

(C) ATOMS FORMING PLANE: S2, S3, C4, C5, C6, C7, C8, C9.

EQUATION OF PLANE: 0.6201X - 0.2685Y - 0.7372Z = -1.4221

DISTANCES OF ATOMS FROM PLANE (Å);

S2	0.000(3)	C6	0.014(12)
S3	0.002(3)	C7	-0.013(14)
C4	-0.032(10)	C8	-0.016(15)
C5	-0.015(11)	C9	0.044(15)
Zr	-0.1303(8)		

(D) ATOMS FORMING PLANE: S2, S2', C1, C1', C2, C2', C3, C3'

EQUATION OF PLANE: -0.0717X + 0.9974Y = 0.0

DISTANCES OF ATOMS FROM PLANE (Å):

S1	0.003(3)	C2	-0.046(13)
S1'	-0.003(3)	C2'	0.046(13)
C1	-0.016(10)	C3	0.044(15)
C1'	0.016(10)	C3'	-0.044(15)

(E) ATOMS FORMING PLANE: S1, S3', S2'

EQUATION OF PLANE: 0.9176X + 0.3961Y - 0.03372Z = -1.5424

Table 46 (continued)

[a] X, Y, and Z are in Å and refer to the orthogonal coordinates along a, b and c^*.

TABLE 47: DIHEDRAL ANGLES BETWEEN SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE (DEGREES)
(1) Zr, S2, S3	Zr, S2', S3'	101.1
(2) Zr, S2, S3	Zr, S1, S1'	104.7
(3) Zr, S2, S3	S2, S3, C4, C5, C6, C7, C8, C9	3.9
(4) Zr, S1, S1'	S1, S1', C1, C1', C2, C2', C3, C3'	0.5
(5) S2, S3, C4, C5, C6, C7, C8, C9	S2', S3,', C4', C5', C6', C7', C8', C9'	95.0
(5) S2, S3, C4, C5, C6, C7, C8, C9	S1, S1', C1, C1', C2, C2', C3, C3'	108.2

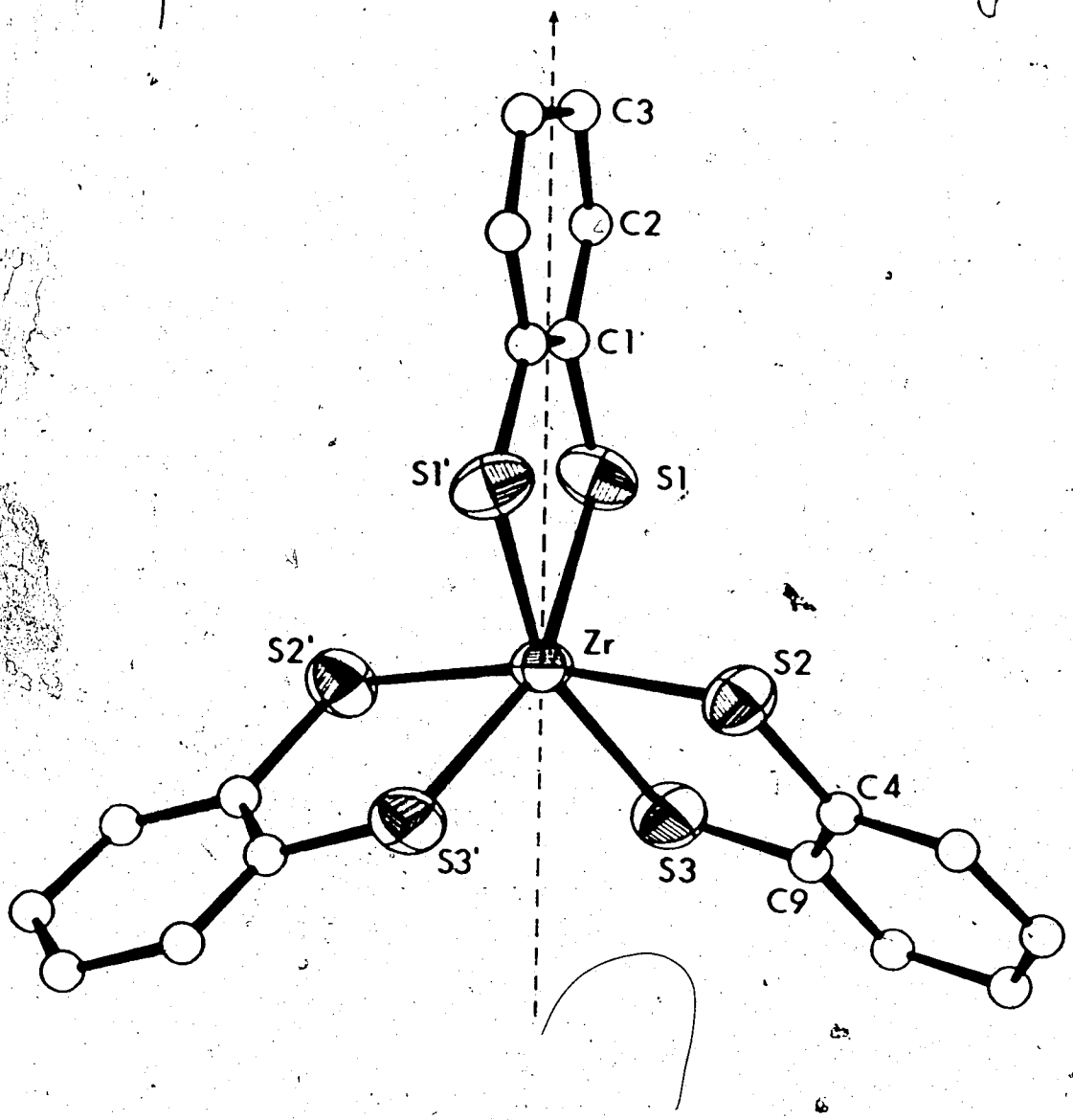


Fig. 17: A Perspective View of the $Zr(S_2C_6H_4)_3^{2-}$ Dianion, Viewed Down the Approximate Molecular 3-Fold Axis.

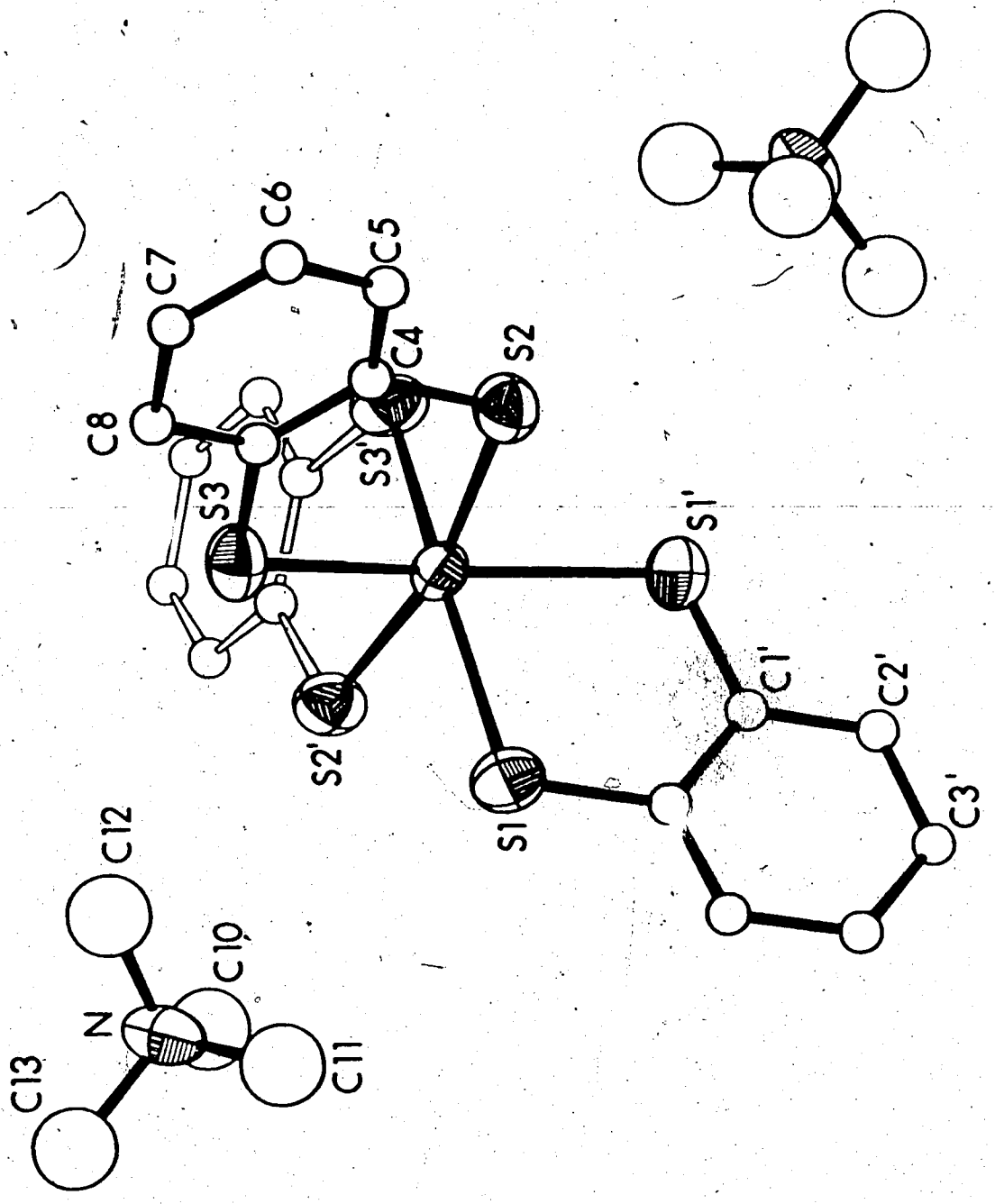


Fig. 18: A Perspective View of $[N(CH_3)_4]_2[Zr(S_2C_6H_4)_3]$

DESCRIPTION OF STRUCTURE

The $Zr(bdt)_3^{2-}$ dianion, viewed down its approximate three-fold axis, is shown in Fig. 17, and the dianion and the two tetramethylammonium cations are shown in Fig. 18. The dianion is located on the crystallographic two-fold axis whereas the tetramethylammonium cations sit in general positions.

In the dianion, the six sulfur atoms are approximately equidistant from the zirconium atom and form a coordination polyhedron which is intermediate between an octahedron and a trigonal prism. Since the $ZrS_2C_6H_4$ fragments are approximately planar, the symmetry of $Zr(bdt)_3^{2-}$ approximates D_3. The dithiolene ligands radiate from the zirconium atom in a "propeller-like" arrangement as opposed to the "paddle-wheel" arrangement in the trigonal prisms.

In describing the degree of distortion of the metal coordination from either of the trigonal prismatic or octahedral limits, two parameters are especially useful; the S-M-S angles involving sulfur atoms which are almost *trans* to each other, and the projection angle between the two triangular faces of the prism (trigonal twist angle).

In a regular trigonal prism the S-M-S angle between pseudo *'trans'* sulfur atoms is approximately

136°. In an octahedron this angle is 180°. These two extremes are shown in Fig. 19, the S2-M-S4 angle being the angle of interest. However, for an

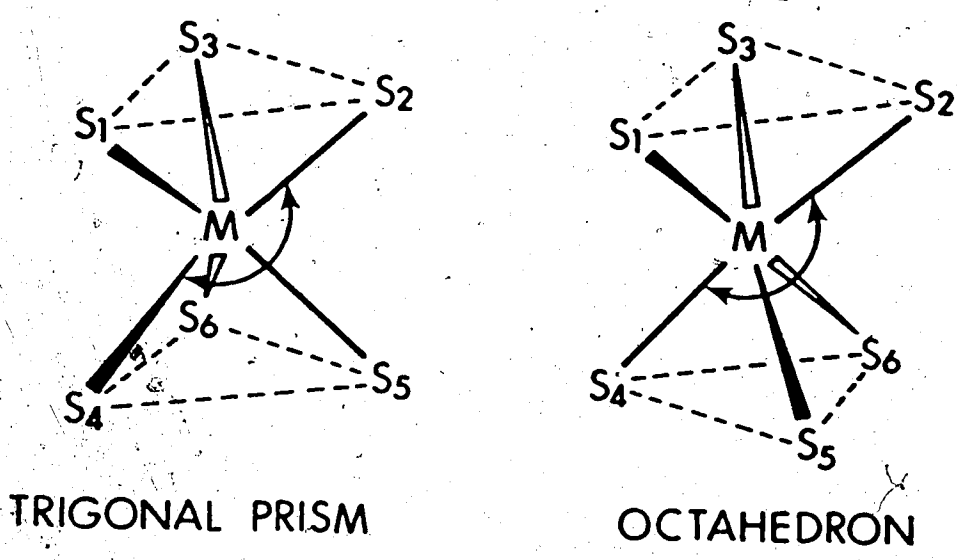


Fig. 19. *Trans* S-M-S Angles in the Trigonal Prism and the Octahedron.

intraligand S-Zr-S angle of ~ 80°, considering only the geometric constraints of the ligand, a *trans* S-Zr-S angle of 170° is obtained as the corrected octahedral limit.[161] The values observed for the $Zr(bdt)_3^{2-}$ dianion [167.76(8)° and 159.80(7)°] are thus closer to the octahedral limit and on this basis the zirconium coordination can be described as distorted octahedral. The non-equivalence of these two independent values indicates that the distortion is not regular and that one ligand (containing S1 and S1') is

rotated more towards the trigonal prismatic structure than the other two ligands.

The other indication of the degree of distortion from the prismatic or octahedral limits is the trigonal twist or projection angle shown in Fig. 20. In the trigonal prism where the two triangular faces are eclipsed, this angle equals 0°, whereas in the ideal octahedron this angle is 60°. Again however, because of the constraint of ligand bite in these bidentate ligands, the octahedral limit is not attained. Rather, this angle will be limited by the ratio of intra-

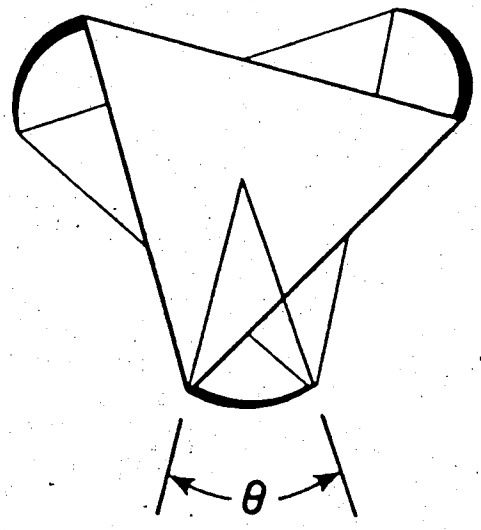


Fig. 20. Trigonal Twist Angle Projected Perpendicular to the Molecular 3-Fold Axis.

ligand S-S distances to the M-S distances. For the Zr(tdt)$_3^{2-}$ dianion, this ratio (1.284) predicts[166] (on the basis of minimizing interligand repulsions) a twist angle of approximately 48° for the corrected octahedral limit. An average twist angle in this structure is calculated at 37° using equilateral triangles that correspond to a best fit with the observed individual atom coordinates. Thus the twist angle differs from the corrected octahedral limit by only 11°. By comparison, in the structure[167] of $Al(O_2C_7H_5)_3$, the observed trigonal twist angle (48.1°) is essentially that calculated using the constraints of ligand bite and this appears typical of structures where the only factor favouring the prism is minimization of the interligand repulsions. Thus the deviation of 11° from the corrected octahedral limit is significant and indicates a genuine tendency towards trigonal prismatic coordination in this structure.

The Zr-S distances (av. 2.543 Å) are longer than those observed in the molybdenum and niobium *tris* (benzene dithiol) complexes (see Table 48) and thus complete a trend through this series with the metal-sulfur distances increasing approximately as predicted by their covalent radii.[133] As with the niobium complex, the metal-sulfur distances again

contain irregularities of statistical significance. The Zr-S distance within the ligand bisected by the two-fold axis [2.555(2) Å] is longer than the other two independent Zr-S distances [2.537(2) Å and 2.538(2) Å].

Although this complex is of considerable interest in relation to the other *tris* dithiolenes, it is also interesting in its own right. The number of structurally characterized six coordinate zirconium complexes is small[168] and indeed $[N(CH_3)_4]_2[Zr(bdt)_3]$ is believed to be the first example of a six coordinate zirconium-sulfur complex. The observed Zr-S distances lie midway between the values 2.49 Å and 2.58 Å, corresponding to the sums of the covalent and ionic (Zr^{4+} and S^{2-}) radii[133,169] respectively.

The intraligand S-Zr-S angles (av. 79.77°) are slightly less than those observed in $Mo(bdt)_3$ and $Nb(bdt)_3^-$ (82.12° and 80.35° respectively) and complete a trend through the series. This trend is due to the relatively fixed ligand bite which does not increase as rapidly as the metal-sulfur distances.

The S-C distances seem to be an excellent indication of the tendency of the ligand towards either the oxidized or reduced formulations. In $Zr(bdt)_3^{2-}$ the average S-C distance (1.765 Å) is very close to

that predicted for a single bonded sulfur-carbon distance (1.77 Å).[84,133] Thus the ligand geometry approximates that corresponding to the dithiolato formulation and the formal oxidation state of (IV) appears to be a reasonable description for the zirconium atom in this structure. This structure is important in demonstrating that the ligand can attain the dithiolato limit. The carbon-carbon distances within the ligands (av. 1.384 Å) are close to those observed in benzene.[158] However, as in the molybdenum and niobium complexes, shortening of the C_C-C_D bond is observed (see Fig. 21), probably due to thermal motion of the rings. In addition, in ligand 1, which is bisected by the crystallographic two-fold axis, the bond lengths vary significantly throughout the ring. One worrying feature of this ring is the presence of anomalously high thermal parameters (U_{11}'s) of the carbon atoms. This seems to indicate either a disorder or a systematic error is present. The disorder could correspond to the non-equivalence of Zr-S1 and Zr-S1' distances for a particular model. However, this problem is unlikely to affect the general conclusions of this study. The C-C bond lengths within the rings are therefore unreliable and no chemical significance should be placed on their

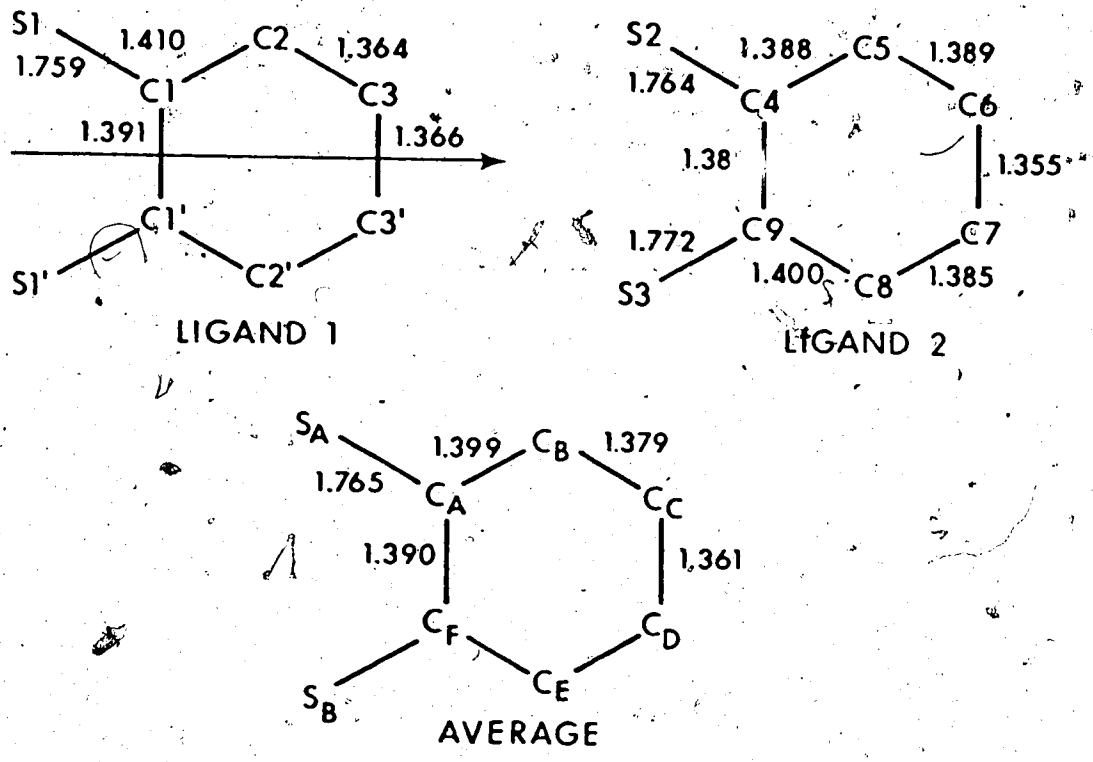


Fig. 21: Dimensions Within the Dithiolene Ligands.

differences.

The interligand S-S distances are, as expected, much longer than the intraligand distances, this due merely to the distortion towards the octahedron which maximizes the interligand separations. In addition the intraligand S-S distances in $Zr(bdt)_3^{2-}$ are longer than those in $Mo(bdt)_3$ and $Nb(bdt)_3^-$, and are due to increasing S-C distances through the series. The

TABLE 48: SELECTED DISTANCES (Å) FOR FOR *TRIS*(1,2-DITHIOLENE) COMPLEXES

COMPOUND	M-S	S-S (INTRA)	S-S (INTER)	S-C	REFERENCE
$Re(S_2C_2Ph_2)_3$	2.325(4)	3.032(10)	3.050(8)	1.69[a]	129
$Mo(S_2C_2H_2)_3$	2.33(1)	3.10	3.11	1.70(3)	130
$V(S_2C_2Ph_2)_3$	2.338(4)	3.060(6)	3.065	1.69(1)	132
$V[S_2C_2(CN)_2)_3^{2-}$	2.36(1)	3.13(2)	3.20	1.72(2)	140
$Mo[S_2C_2(CN)_2]_3^{2-}$	2.373(4)	3.113	3.188	1.74(1)	141,170
$W[S_2C_2(CN)_2]_3^{2-}$	2.371(5)	3.112	3.193	1.73(2)	170
$Fe[S_2C_2(CN)_2]_3^{2-}$	2.261(2)	3.147(2)	3.19	1.731(4)	142
$In[S_2C_2(CN)_2]_3^{3-}$	2.604(8)	3.40(1)	3.89(1)	1.72(3)	171
$Mo(S_2C_6H_4)_3$	2.367(2)	3.110(3)	3.091(2)	1.727(6)	THIS WORK
$Nb(S_2C_6H_4)_3^-$	2.441(2)	3.150(3)	3.232(3)	1.744(7)	"
$Zr(S_2C_6H_4)_3^{2-}$	2.543(2)	3.265(3)	3.584(2)	1.765(6)	"

[a]Where standard deviations are not shown, they were not given in the original paper. In $Re(S_2C_2Ph_2)_3$ the standard deviations are not shown due to a wide ra n S-C distances.

TABLE 49: SELECTED ANGLES FOR *TRIS* (1,2-DITHIOLENE) COMPLEXES (DEGREES)

COMPOUND[d]	S-M-S (INTRA)	S-M-S (TRANS)	PROJECTION ANGLE[c]	DIHEDRAL MS_2/LIGAND ANGLE	COORDINATION
$Re(S_2C_2Ph_2)_3$	81.4(4)	-136	<1	--	TRIGONAL PRISM
$Mo(S_2C_2H_2)_3$	82.5	-136	0	18	"
$V(S_2C_2Ph_2)_3$	81.7(2)	-136	8.5 [a]	--	"
$V[S_2C_2(CN)_2]_3^{2-}$	--	158.6	TWISTED [b]	--	DISTORTED OCTAHEDRON
$Mo[S_2C_2(CN)_2]_3^{2-}$	82.3(2)	156	28	-2	"
$W[S_2C_2(CN)_2]_3^{2-}$	82.1(2)	156	28	-2	"
$Fe[S_2C_2(CN)_2]_3^{2-}$	88.0(1)	--	-60	--	OCTAHEDRON
$In[S_2C_2(CN)_2]_3^{3-}$	81.5(8)	169.3(3)	--	--	DISTORTED OCTAHEDRON
$Mo(S_2C_6H_4)_3$	82.18(8)	135.70(7)	0	13.1,21.1, 30,0	TRIGONAL PRISM
$Nb(S_2C_6H_4)_3^-$	80.35(7)	135.06(7)	0.7	22.4	TRIGONAL PRISM
$Zr(S_2C_6H_4)_3^{2-}$	79.77(7)	163.78(8)	37.0	3.9,0.5	DISTORTED OCTAHEDRON

[a] Calculated in ref. 172 from atomic coordinates given in original paper.

[b] No coordinates or twist angle given.

[c] Trigonal twist angle projected perpendicular to molecular 3-fold axis.

[d] References shown in Table 48.

S-C-C and C-C-C angles within the ligands are all close to the expected value of 120°.

An interesting feature observed in $Mo(bdt)_3$ and isoelectronic $Nb(bdt)_3^-$ is the large bend of the MS_2 planes from the ligand S_2C_6 planes (21.4° and 22.4° respectively). This had also been observed in $Mo(S_2C_2H_2)_3$[150] and $Mo[Se_2C_2(CF_3)_2]_3$[152] but was not observed in $Re(S_2C_2Ph_2)_3$[129] or $V(S_2C_2Ph_2)_3$.[132] In $Zr(bdt)_3^{2-}$ these planes are approximately coplanar, the dihedral angles between ZrS_2 and S_2C_6 planes being 3.9° and 0.5°. Although Schrauzer had attributed[138] the bend observed in $Mo(S_2C_2H_2)_3$ as due to hybridization of the sulfur atoms between sp^2 and sp^3, it is then difficult to account for the near planarity of the ligands in the zirconium, rhenium and vanadium complexes.

Comparison of the angular parameters in Table 49 allows the complexes to be placed in order of increasing tendency toward the trigonal prismatic structure. Consideration must be given to the general criticism of X-ray crystallographic studies, that one cannot guarantee that the observed geometry corresponds to the ground state. Thus the differences between $V(mnt)_3^{2-}$ and $Mo(mnt)_3^{2-}$ [or $W(mnt)_3^{2-}$] may not be significant. The order for the dianionic species is then:

corrected octahedral limit $\simeq$ $Fe(mnt)_3^{2-}$ < $Zr(bdt)_3^{2-}$ <

$V(mnt)_3^{2-}$
$Mo(mnt)_3^{2-}$ << trigonal prismatic limit
$W(mnt)_3^{2-}$

The corresponding order for the isoelectronic series, as described in this thesis is:

corrected octahedral limit < $Zr(bdt)_3^{2-}$ << $Nb(bdt)_3^{-}$ $\leq$ $Mo(bdt)_3$

= trigonal prismatic limit.

Chapter IX presents a general rationalization for these trends.

A perspective view of the dianion and the tetramethylammonium cations is shown in Fig. 18. As expected the cations are close to tetrahedral, with the small distortions present being due to packing effects. The average N-C distance (1.474 Å) agrees quite well with that predicted (1.47 Å) assuming single bonded covalent radii.[133] This value is also in good agreement with previous structural determinations in which the tetramethylammonium cation was involved.[173,174]

CHAPTER IX: TRIGONAL PRISMATIC *vs.* OCTAHEDRAL COORDINATION IN *TRIS* (1,2-DITHIOLATO) COMPLEXES

The isoelectronic series of *tris* (1,2-dithiolato) complexes, described in the latter part of this thesis, show dramatic changes in the coordination polyhedron. These changes, from an almost perfect trigonal prism in the neutral molybdenum complex, to a very slightly distorted trigonal prism in the niobium complex anion, to a distorted octahedron in the zirconium complex dianion, are accompanied by smooth increases in metal-sulfur distances, sulfur-carbon distances, and interligand sulfur-sulfur distances (see Table 48). These changes correspond to the increasing importance of the dithiolato formulation for the ligand, that is, $S_2C_6H_4^{2-}$. The increase in interligand sulfur-sulfur distances would lead to a reduction in direct sulfur-sulfur bonding, which has been postulated as a factor in stabilizing the prism.[137,138,170] In this chapter the structural trends are correlated with molecular orbital energy level diagrams.

Two energy level schemes have been presented to account for the stability of the prism in certain *tris* (1,2-dithiolato) complexes. One of these schemes, due to Schrauzer and Mayweg[138] (which will be referred to as scheme 1) is presented for an unspecified first

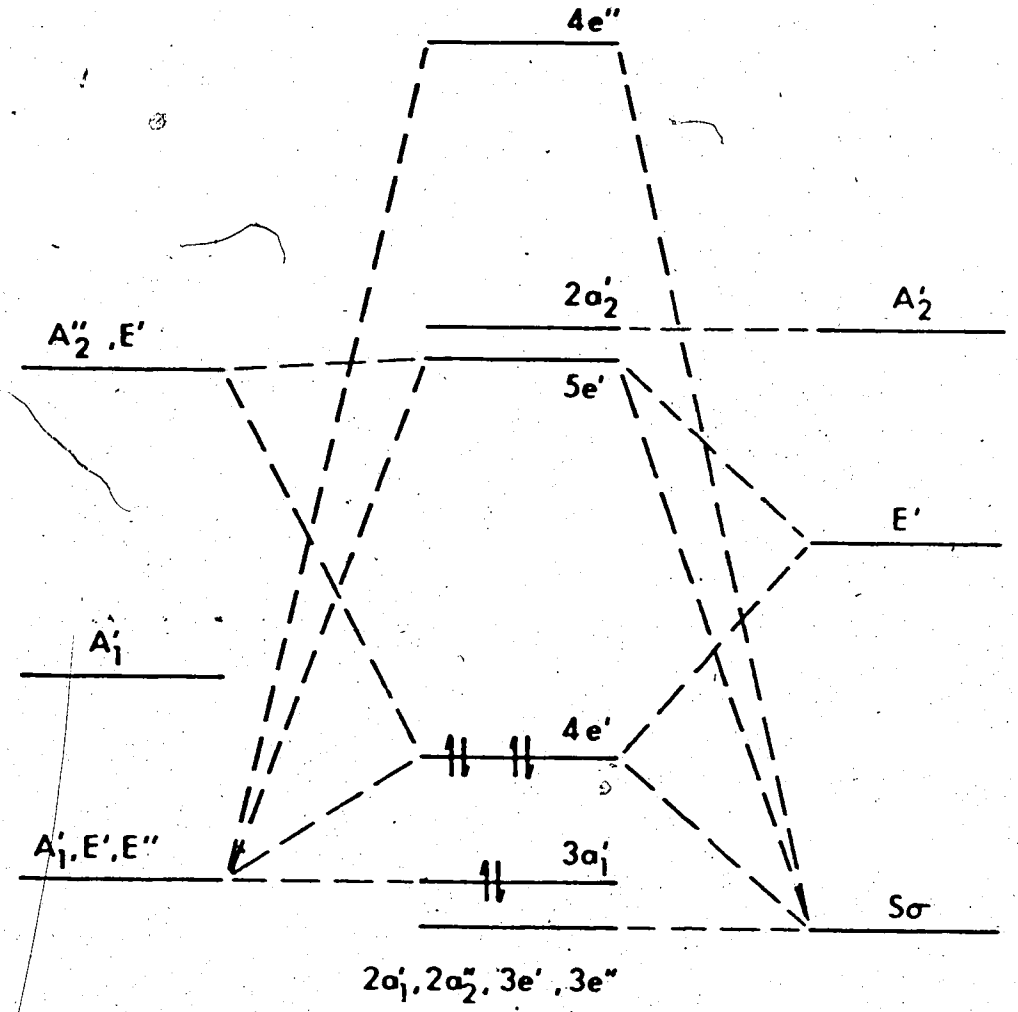


FIG. 22: MOLECULAR ORBITAL ENERGY LEVELS OF INTEREST FOR TRIGONAL PRISMATIC DITHIOLENES, BY G. N. SCHRAUZER AND V. P. MAYWEG

transition series element. The important levels of this scheme are shown in Fig. 22. The alternative scheme, due to Gray *et. al.*[137] (which will be referred to as scheme 2), is shown in Fig. 23. The differences between the two schemes arise, in part, from the relative positions of the metal and ligand orbitals.[132] Both schemes agree on the importance of the interaction of the metal $d_{x^2-y^2}$ and d_{xy} orbitals with appropriate combinations of ligand π orbitals (symmetry b_1 for an isolated ligand) to give bonding 4e' and antibonding 5e' levels. Scheme 2, however, proposes an additional significant interaction between the metal d_{z^2} orbital and ligand non-bonding sigma orbitals, giving one bonding ($2a_1'$) and one antibonding ($3a_1'$) level. Scheme 1 has also been challenged on the basis of electron spin resonance studies,[132,175] and can be shown to be inconsistent with the electronic spectra in this series of compounds. Specifically it predicts an increase in the frequency that would correspond to the transitions $3a_1' \rightarrow 5e''$ and $3a_1' \rightarrow 2a_2'$ when comparing the niobium complex with the molybdenum complex, which is the opposite of the experimental results (Table 18). Scheme 2 correctly predicts the experimental observations, as Gray *et. al.*[137] attribute the transitions as due to $2a_2''(\pi_h)$, $3e'(\pi_h) \rightarrow 3a_1'(d_{z^2})$.

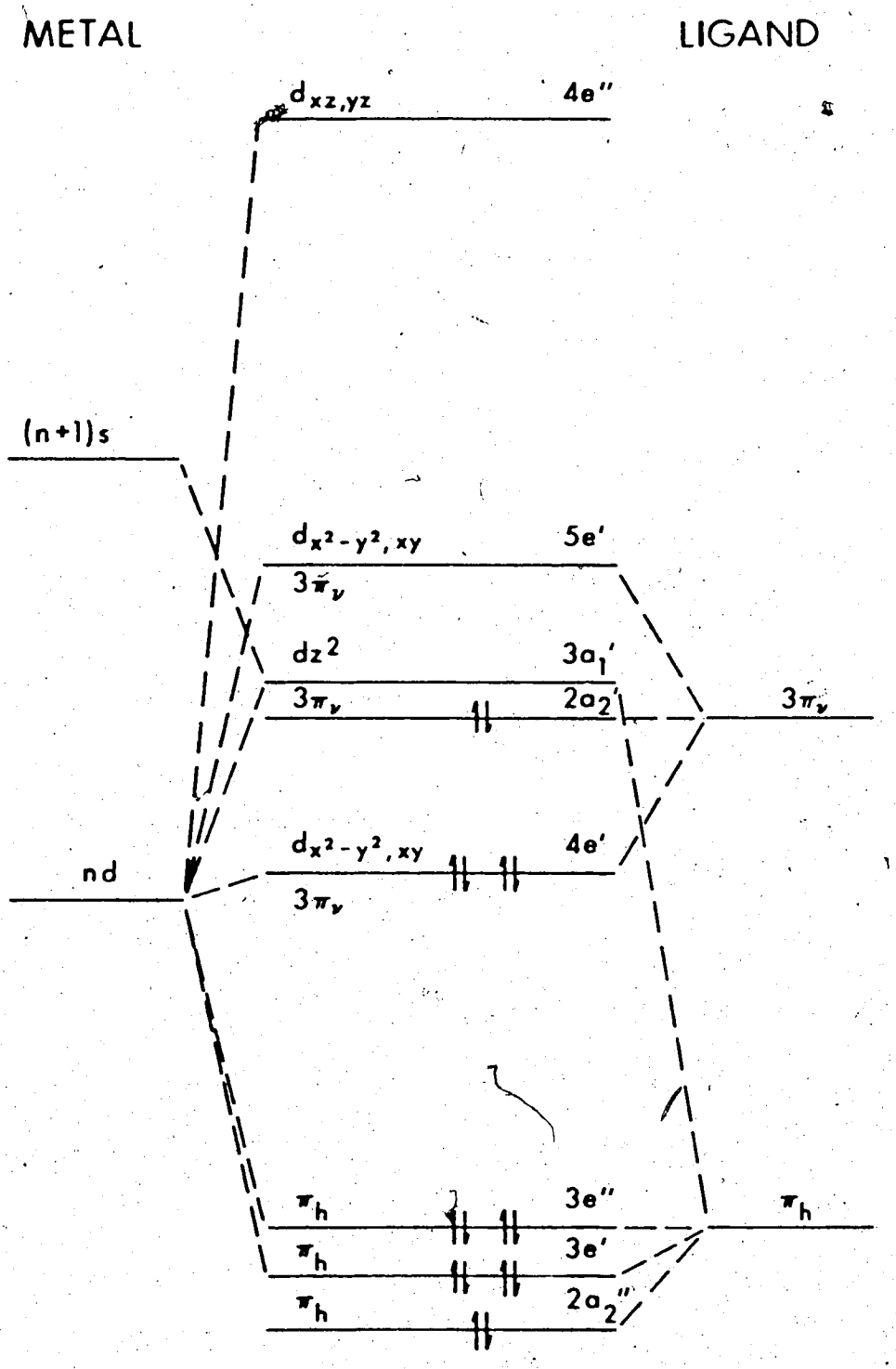


FIG. 23: MOLECULAR ORBITAL ENERGY LEVELS OF INTEREST FOR TRIGONAL PRISMATIC DITHIOLENES, BY H. B. GRAY *et. al.*

Since scheme 2 seems more consistent with the experimental results, it is favoured over scheme 1, and therefore will be used in all subsequent discussions. In this M.O. description (Fig. 23), the levels $2a_2''$, 3e' and 3e" consist mainly of sulfur sp^2 hybrid orbitals (π_h) at 120° to the σ orbitals pointing at the metal. The $2a_2'$ orbital is non-bonding and the $3a_1'$ is principally metal in character, having symmetry d_{z2}. The 4e' and 5e' are both metal (d_{x2-y2},d_{xy}) and ligand ($3\pi_v$) in character and both are strongly delocalized over the metal and ligands. Stability of the prism was postulated, by Gray *et. al.* as due to interaction of the sulfur π_h orbitals with the metal d_{z2} orbital producing the stable bonding orbital $2a_1'$, which is always filled; also the interaction of the metal d_{x2-y2} and d_{xy} orbitals with the $3\pi_v$ ligand orbitals produces the stable 4e' orbitals which are also filled in these complexes.

In order to use the M.O. scheme by Gray *et. al.* it must be shown that it will apply to the series of interest in this thesis. Considering the ligand and metal orbitals separately, it can first be shown that the energy levels of the molybdenum 4d and rhenium 5d orbitals are similar.[176] Therefore use of the molybdenum atom instead of rhenium in scheme 2 is justified.

The energy levels of the ligands $S_2C_2H_2$ and $S_2C_6H_4$ can be compared using the calculations of Birss and Das Gupta.[160] The π orbitals for these ligands, the calculated orbital energies and geometries are presented in Figs. 24, 25 and 26. Each ligand is shown in the reduced form (corresponding to the dithiolato limit) and in the neutral or oxidized form (2 π electrons less). The π orbitals of particular interest are the $2b_1$ for $S_2C_2H_2$ and $3b_1$ for $S_2C_6H_4$. Comparing the oxidized forms of the ligands, the energies of the $2b_1$ ($S_2C_6H_2$) and $3b_1$ ($S_2C_6H_4$) levels are -16.4 e.v. and -15.3 e.v. respectively. A comparison of the reduced forms of the ligands shows the energies are -10.2 e.v. and -10.0 e.v. for the same levels. The probable error in these energy levels is of the order of 0.3 e.v.. Thus it is clear that the molecular orbital scheme proposed for $Re(S_2C_2H_2)_3$ should closely approximate that used for $Mo(S_2C_6H_4)_3$, because of the near equality of both metal and ligand orbital energies.

As postulated by Gray *et. al.*,[137] the stability of the prism is due, in part, to the interaction of the ligand $3\pi_v$ and metal $d_{x^2-y^2}$ and d_{xy} orbitals, producing the 4e' orbital. The series, $Mo(bdt)_3$, $Nb(bdt)_3^-$ and $Zr(bdt)_3^{2-}$, permits examination of this

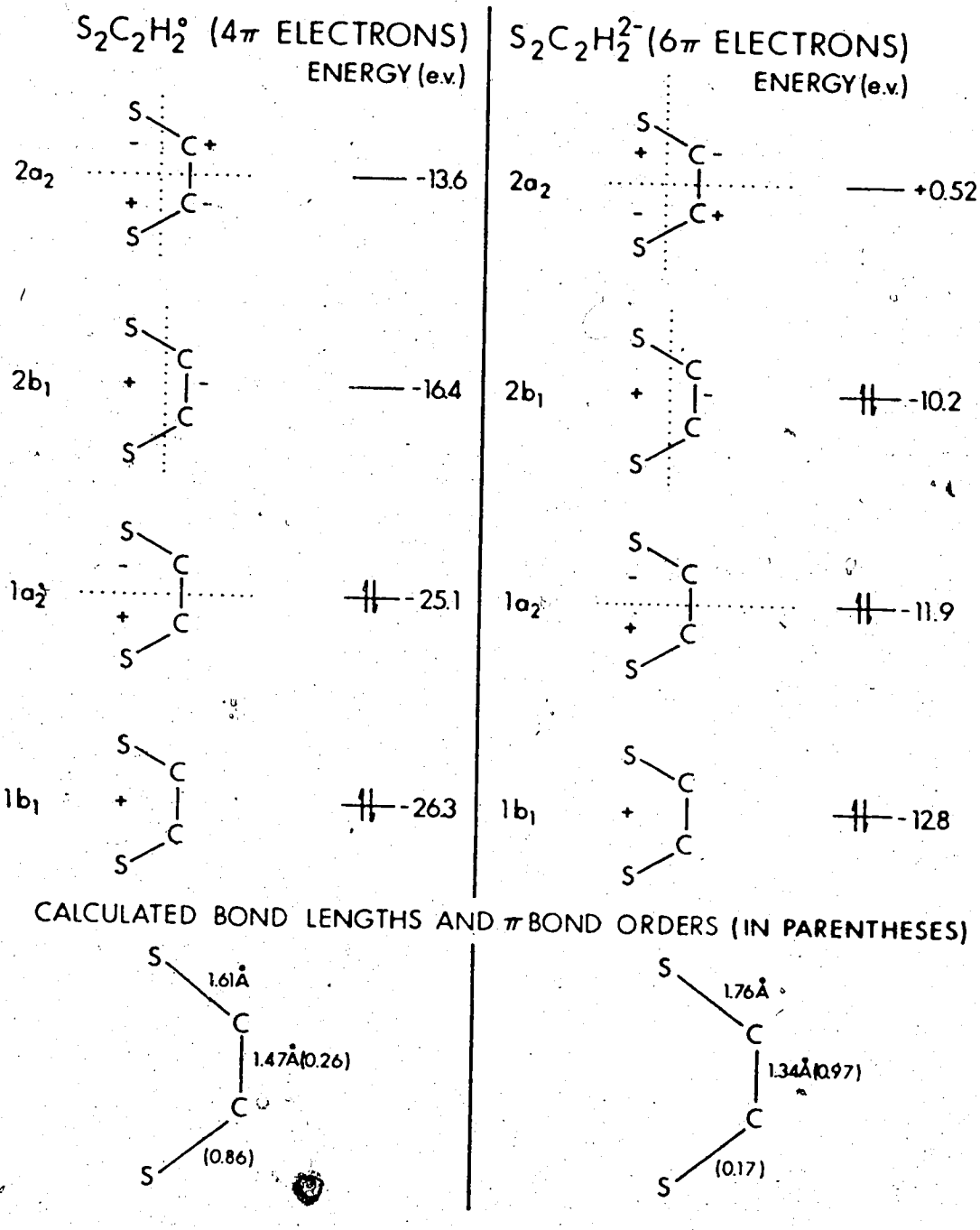


FIG. 24: REPRESENTATIONS OF THE MOLECULAR ORBITALS AND ENERGY LEVELS FOR $S_2C_2H_2$ AND $S_2C_2H_2^{2-}$

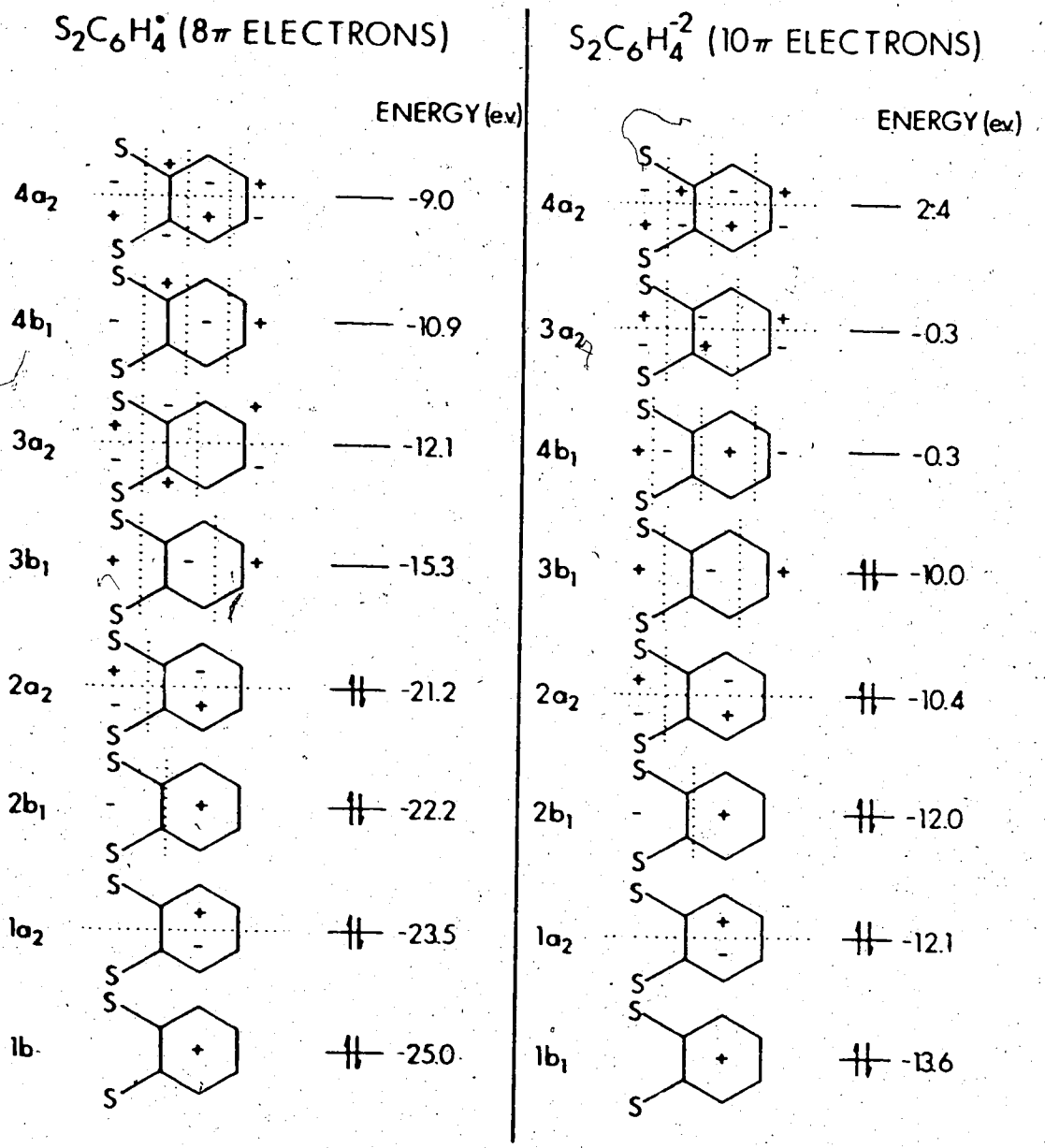


FIG. 25: REPRESENTATIONS OF THE MOLECULAR ORBITALS AND ENERGY LEVELS FOR $S_2C_6H_4$ AND $S_2C_6H_4^{2-}$.

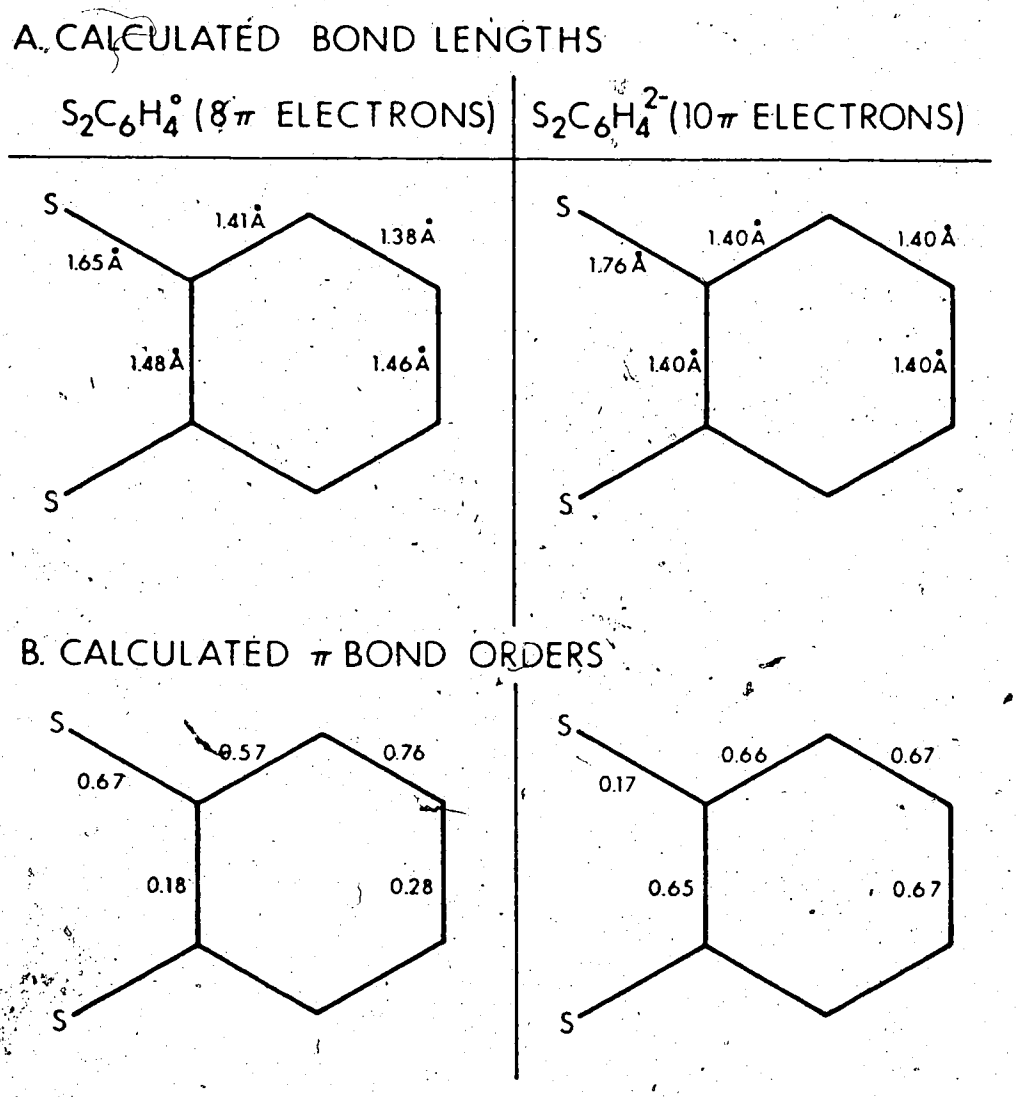


FIG. 26: PREDICTED BOND LENGTHS AND π BOND ORDERS FOR $S_2C_6H_4$ AND $S_2C_6H_4^{2-}$

postulate, since in this isoelectronic series no change in the geometry of the coordination polyhedra can be attributed to the occupation of the antibonding orbitals, as has been postulated[141,170] for the destabilization of the prisms in $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$.

The 4e' level should be extremely sensitive to the metal orbital energies due to the near-equivalence in energy of the d orbitals and the 4e' level. The $2a_1'$ level will also be affected but not as much, due to the greater energy separation of it from the metal d orbitals. As the d orbital energies increase, the 4e' level should be destabilized and should become more ligand ($3\pi_v$) in character. This increase in the ligand character of the 4e' level should be paralleled by a structural change, corresponding to an increase in the contribution of the reduced form structure. The molecular orbital description of the ligands is used in preference to the oversimplified valence bond descriptions, that is, the dithiolato and dithioketonic structures, shown in Fig. 11, since the discussion concerns energy levels and not just geometric changes.

The ligand undergoes extensive geometric changes upon the reduction:

$S_2C_6H_4^{\circ}$ (8 π electrons) + 2e $\rightarrow$ $S_2C_6H_4^{2-}$ (10 π electrons)

as is shown in Fig. 26. In principle, both sulfur-carbon and carbon-carbon distances could be used in assessing the relative importance of the reduced and oxidized structures in a particular case. In practice, the high uncertainty in the carbon-carbon bond lengths (due to naturally higher standard deviations and large effects due to thermal motion) makes them unsuitable for a semi-quantitative discussion and the more reliable sulfur-carbon distances provide the only useful guide. Sulfur-carbon bond lengths for the *tris* (benzene-1,2-dithiolato) complexes, described in this thesis, and the theoretical geometries of the oxidized and reduced formulations can be ordered as follows: $S_2C_6H_4^{\circ}$, (1.648 Å) < $Mo(bdt)_3$, (1.727 Å) < $Nb(bdt)_3^-$, (1.744 Å) < $Zr(bdt)_3^{2-}$, (1.765 Å) ≈ $S_2C_6H_4^{2-}$, (1.763 Å). This series indicates that the ligand tends toward the reduced geometry as the energy of the d orbital increases.

In assessing the ligand and metal orbital character of the 4e' level, it should be noted that appropriate extremes do not correspond to $[S_6C_{18}H_{12}]^{\circ}$ and $[S_6C_{18}H_{12}]^{6-}$ (equivalent to three ligands in the oxidized and reduced forms), since the ligand $3\pi_v$ orbitals give rise to the $2a_2'$ level as well as the 4e' level (see Fig. 23). This $2a_2'$ level is non-bonding,

entirely located on the ligand and is always occupied by two electrons. Hence the discussion of the 4e' levels must utilize limiting geometries defined by $[S_6C_{18}H_{12}]^{2-}$ and $[S_6C_{18}H_{12}]^{6-}$, that is, allowing for the $2a_2'$ occupancy.

Fig. 27 shows the plots of S-C bond length *vs.* S-C π bond order for the ethylene and benzene dithiol ligands, as calculated by Birss and Das Gupta.[160] The limiting extremes, $S_2C_2H_2$ and $S_2C_2H_2^{2-}$, also $S_2C_6H_4$ and $S_2C_6H_4^{2-}$, are shown on the respective plots. For the ligand system $S_6C_{18}H_{12}^{2-}$, the π bond order and bond length can be calculated assuming one contribution of $S_2C_6H_4^{2-}$ for two contributions of $S_2C_6H_4$ This yields a S-C π bond order of 0.50 and a corresponding S-C bond length of 1.69 Å. If the 4e' levels are completely ligand in character, the ligand $3\pi_v$ orbitals would contain 6 electrons and would be described as $S_6C_{18}H_{12}^{6-}$. The S-C π bond order and S-C bond length for this extreme are 0.17 and 1.76 Å respectively. These two limits, $S_6C_{18}H_{12}^{2-}$ and $S_6C_{18}H_{12}^{6-}$, then correspond to the extremes that the 4e' orbital is completely metal and completely ligand in character, respectively.

In $Mo(bdt)_3$ the average S-C bond length (1.727 Å) corresponds to a π bond order of 0.32 and thus lies

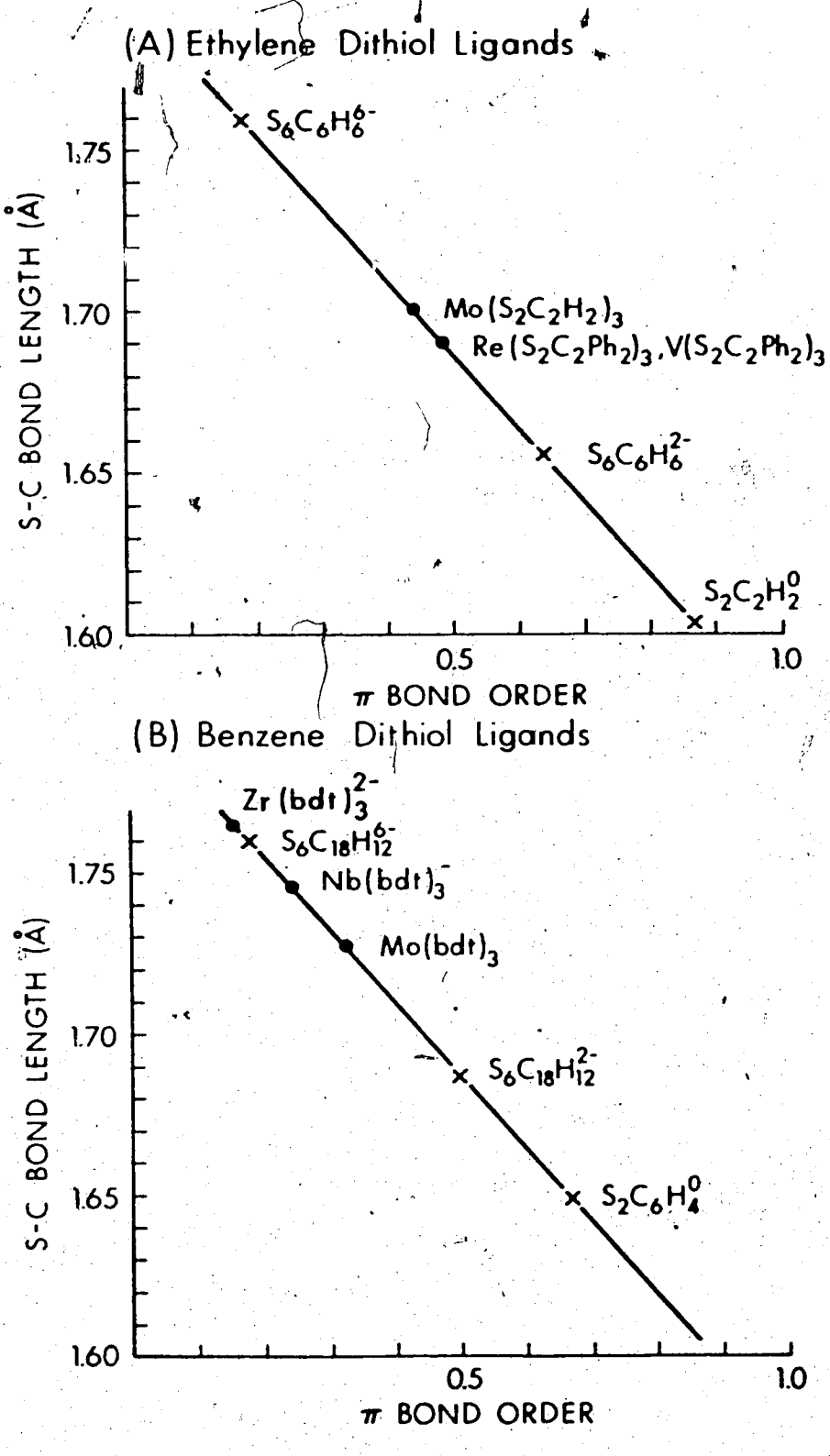


FIG. 27: S-C BOND LENGTH *vs.* π BOND ORDER FOR ETHYLENE AND BENZENE DITHIOL LIGANDS

approximately midway between the $S_6C_{18}H_{12}^{6-}$ and $S_6C_{18}H_{12}^{2-}$ extremes. The 4e' level therefore has approximately equal contributions from the metal and ligand orbitals. Ir $Nb(bdt)_3^-$ the S-C bond length of 1.744 Å and π bond order of 0.24 corresponds to three quarters of the electron density of 4e' being on the ligand and only one quarter of the electron density being on the metal. The S-C bond length of 1.765 Å in $Zr(bdt)_3^{2-}$ indicates that the ligand has reached the limiting reduced formulation. It is to be noted, however, that there is a tendency in the zirconium coordination toward the trigonal prism, indicating possibly that the 4e' level still has a small amount of metal contribution. It is also possible that the tendency toward the prism is favoured by the overlap of the ligand π_h and metal d_{z^2} orbitals, which may still be operative.

In Chapter V it was mentioned that any comparison in bond lengths between ethylene and benzene dithiol ligands should be made with extreme care. This can now be demonstrated with the aid of the calculations by Birss and Das Gupta,[160] shown in Fig. 27. In the ethylene dithiol ligands, employing similar arguments as used for the benzene dithiol ligands, the S-C bond lengths and π bond orders can be calculated for

the $S_6C_6H_6^{2-}$ and $S_6C_6H_6^{6-}$ extremes. These bond lengths and π bond orders are 1.66 Å and 0.64 for $S_6C_6H_6^{2-}$ and 1.76 Å and 0.17 for $S_6C_6H_6^{6-}$. Thus although $Mo(S_2C_2H_2)_3$ has S-C distances (av. 1.70 Å) which are shorter than in $Mo(bdt)_3$, a comparison on Fig. 27 shows that in the two complexes the 4e' level has a similar make-up. It is therefore apparent that for different ligands, even in similar bonding situations, differences in bond lengths are to be expected.

The series of complexes, $Mo(bdt)_3$, $Nb(bdt)_3^-$ and $Zr(bdt)_3^{2-}$ therefore shows the importance of the interaction of the metal $d_{x^2-y^2}$ and d_{xy} with the ligand π_v orbitals in stabilizing the trigonal prism. In addition, the prism stability in this series is maximized in $Mo(bdt)_3$, where the 4e' orbital contains approximately equal contributions from metal and ligand and thus the electrons are completely delocalized over the metal-ligand framework. In the 1,1-dithiolato complexes[177-184] the ligands do not have orbitals of the proper symmetry and energy to overlap with the $d_{x^2-y^2}$ and d_{xy} orbitals of the metal.[157] Therefore this delocalization is not possible and all 1,1-dithiolato complexes have distorted octahedral coordinations.

Interligand sulfur-sulfur bonding has also been

presented as a reason for prism stability,[137,138,170] and the trends observed in the benzene dithiol series can also be explained by assuming that a breakdown in S-S bonding occurs, progressing from the molybdenum complex through to the zirconium complex. As the d energies increase, so also do the metal radii. Therefore, as the metal radii increase from Mo to Nb to Zr, the interligand S-S distances increase and the slight distortion observed in $Nb(bdt)_3^-$ can be explained as a partial breakdown in this S-S bonding. At $Zr(bdt)_3$ presumably the sulfur atoms have been forced far enough apart to result in a distorted octahedral coordination, due to an almost complete breakdown in S-S bonding. A significant argument, however, against sulfur-sulfur bonding as a major stabilizing force in the prism can be seen in a comparison of $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$ with $Nb(bdt)_3^-$. In the niobium complex the interligand sulfur-sulfur distances are greater than those in the molybdenum or the tungsten dianions (see Table 48), yet the niobium complex is trigonal prismatic, whereas the dianions are distorted octahedrons.

The major argument for sulfur-sulfur bonding has been the short sulfur-sulfur contacts observed in the prisms, as compared with the predicted van der Waals

contacts[151] (3.70 Å). However these contacts probably arise as a consequence of other factors which stabilize the prism, and are probably not themselves the reason for this geometry. It is believed that the forces between the sulfur atoms are repulsive in nature rather than attractive, as proposed.[137,138,170] This can offer a possible explanation for the geometry observed[132] in $V(S_2C_2Ph_2)_3$, which is distorted slightly from the prism by a trigonal twist of 8.5°. If, as suspected, the prism dimensions in the rhenium and molybdenum complexes[129,130] have reached their minimum, due to increasing S-S repulsions, then in the vanadium complex the smaller size of the metal could result in poor overlap of the metal and ligand orbitals (possibly ligand π_h with metal d_{z^2}). It is then possible that in order to attain the maximum stability, the prism distorts slightly by the observed trigonal twist. In this respect a complete structural determination of $Cr(S_2C_2Ph_2)_3$ is desirable, since X-ray power photographs indicated[128,129] it is isomorphous with $V(S_2C_2Ph_2)_3$. However, since the chromium radius is smaller than that of vanadium,[133] if the above arguments apply, the coordination of the chromium complex should be more distorted from the prism than the vanadium complex.

Any proposed sulfur-sulfur bonding can occur by two mechanisms: overlap of the sulfur p orbitals perpendicular to the ligand plane (π_v orbitals), or overlap of the non-bonding sulfur lone pair (π_h orbitals). It is not believed, however, that either mechanism has a significant effect in stabilizing the prism, since both types of overlap are possible in the 1,1-dithiolato systems, yet these systems invariably have geometries which are close to the "corrected" octahedral limit.

In conclusion, the importance of the 4e' molecular orbital in stabilizing the trigonal prism is evidenced in the series: $Mo(bdt)_3$, $Nb(bdt)_3^-$ and $Zr(bdt)_3^{2-}$. The increasing energies of the metal d orbitals, progressing from the molybdenum to the zirconium complex, destabilizes the 4e' level, which in turn results in destabilization of the prism. Interligand sulfur-sulfur bonding is not believed to be a significant factor in stabilizing the prism.

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APPENDIX 1: MOLECULAR DISORDER IN TETRACARBONYL RHENIUM *BIS* (μ-DIPHENYLSILICON) RHENIUM TETRACARBONYL, $[Re_2(CO)_8[Si(C_6H_5)_2]_2]$.

The crystal and molecular structure of $Re_2(CO)_8[Si(C_6H_5)_2]_2$ was solved by X-ray diffraction techniques by Bennett and Haas.[64] The compound crystallizes in the monoclinic space group C2/m with two discrete molecules per unit cell, thus imposing site symmetry 2/m on the molecule. The unit cell dimensions are: a = 13.976(3) Å, b = 10.549(1) Å, c = 12.025(3) Å, β = 117.57(6)°, giving an observed density 1.98(2) g cm^{-3}, which agrees well with the calculated value of 2.03 g cm^{-3}. A three dimensional representation of the molecule is shown in Fig. 28. The molecule bears a strong resemblance to the related hydrides $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$, having an almost identical Re_2Si_2 framework. As in the hydrides, two mutually *trans* carbonyl groups on each rhenium atom are perpendicular to the Re_2Si_2 plane. The other carbonyl groups are approximately *trans* to the Re-Si bonds.

The crystals contain discrete and disordered molecules, the disorder involving the phenyl groups attached to each silicon atom. One phenyl ring is located approximately in the crystallographic mirror and the other lies approximately perpendicular

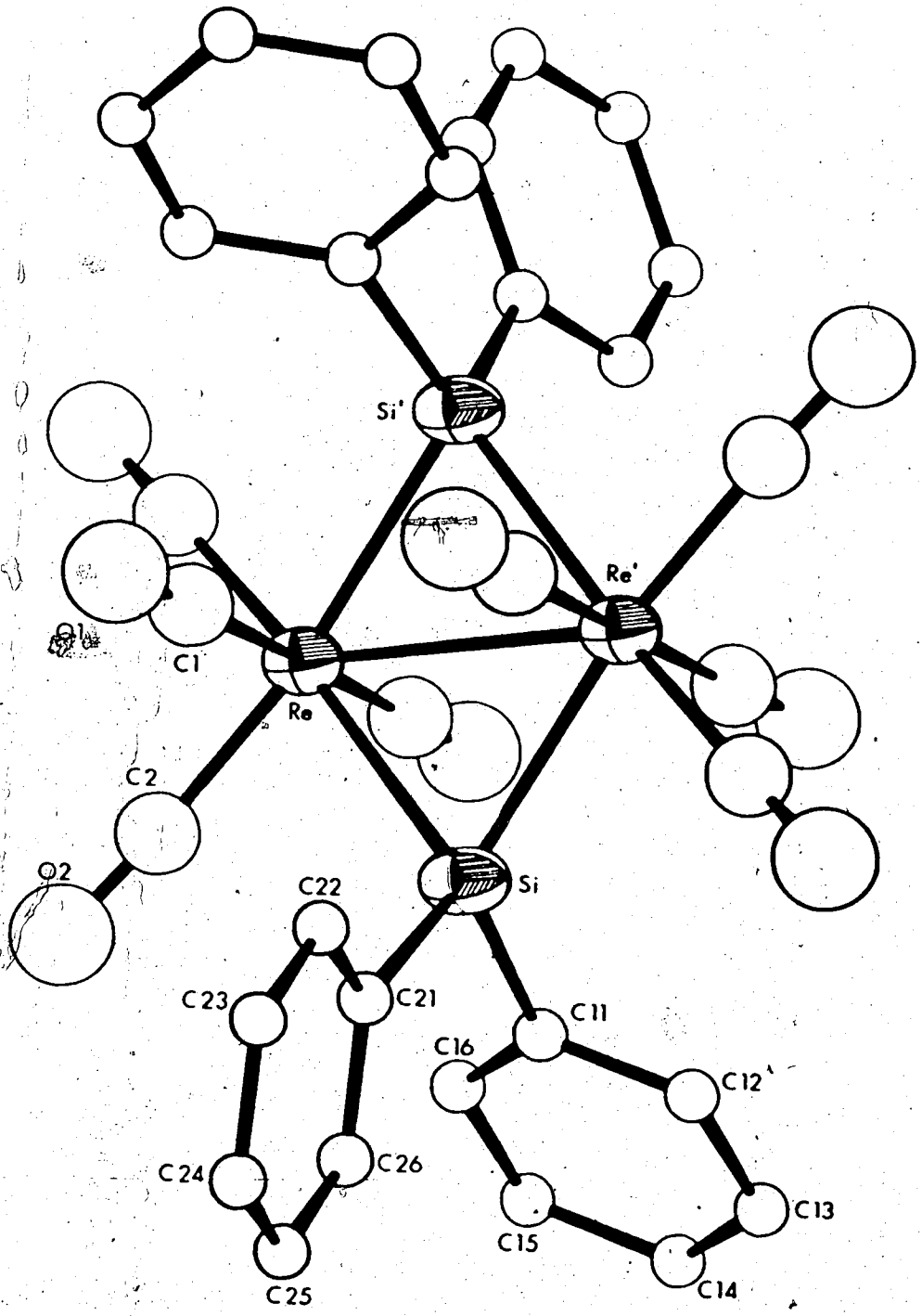

FIG. 28: A PERSPECTIVE VIEW OF $Re_2(CO)_8[Si(C_6H_5)_2]_2$

to it. Final refinement of this disordered model yielded $R_1 = 0.036$ and $R_2 = 0.057$ for 1153 independent reflections refining 52 parameters in the least squares refinement.

The final anisotropic thermal parameters (U_{ij}'s) for Re and Si are shown in Table 50, and the final positional parameters and the isotropic B's are shown in Table 51. Bond lengths and angles along with their standard deviations are shown in Table 52. In the representation of the molecule (Fig. 28) only one pair of disordered phenyl groups are shown for clarity. In addition the ring carbon atoms are given artificially low thermal parameters, also for clarity of the drawing.

The anomalously large values of U_{22} for both Re and Si were initially interpreted as due to residual absorption effects or other possible systematic errors in the data. However the structural determination[185] of the isomorphous $Mn_2(CO)_8[Si(C_6H_5)_2]_2$ shed new light on this problem. The manganese compound crystallizes in the space group A2/m with cell dimensions, $a = 11.788(2)$ Å, $b = 10.480(2)$ Å, $c = 13.744(2)$ Å and $\beta = 117.367(6)°$. (This is identical to C2/m with the a and c axes interchanged). Here again the phenyl rings are disordered in the same

TABLE 50: ANISOTROPIC THERMAL PARAMETERS FOR ORDERED MODEL

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.0291(3)	0.0534(3)	0.0357(3)	0	0.0167(2)	0
Si	0.0314(13)	0.0660(17)	0.0364(13)	0	0.0157(11)	0

TABLE 51: POSITIONAL PARAMETERS AND ISOTROPIC B'S FOR ORDERED MODEL

Atom	x	y	z	B
Re	0	0.14224(3)	0	3.06*
Si	0.1388(2)	0	0.1678(2)	3.53*
C1	0.0724(8)	0.1448(6)	-0.1054(9)	4.04(15)
C2	0.1041(5)	0.2649(7)	0.1069(6)	3.99(12)
O1	0.1162(7)	0.1518(5)	-0.1686(8)	6.09(16)
O2	0.1682(7)	0.3414(6)	0.1658(7)	6.03(15)
C11	0.1424(8)	0.0146(13)	0.3289(6)	3.1(2)
C12	0.1265(10)	0.1262(10)	0.3807(10)	3.9(3)
C13	0.1301(10)	0.1237(10)	0.4987(10)	4.9(4)
C14	0.1496(8)	0.0097(13)	0.5649(6)	5.2(3)
C15	0.1655(10)	-0.1018(10)	0.5130(10)	5.1(3)
C16	0.1620(10)	-0.0994(10)	0.3950(10)	4.5(3)
C21	0.2854(15)	0.0165(13)	0.2008(34)	3.5(2)
C22	0.3172(22)	-0.0106(15)	0.1090(19)	3.9(2)
C23	0.4261(29)	-0.0043(14)	0.1382(21)	4.7(2)
C24	0.5033(15)	0.0292(13)	0.2591(34)	4.5(3)

Table 51 (con't)

Atom	x	y	z	B
C25	0.4715(22)	0.0563(15)	0.3509(19)	6.9(4)
C26	0.3626(29)	0.0500(14)	0.3218(21)	4.6(3)

*Equivalent isotropic temperature factor corresponding to the anisotropic thermal parameters shown in Table 50.

TABLE 52: SELECTED BOND LENGTHS AND ANGLES

(A) BOND LENGTHS (Å)

Re-Re	3.001(1)	Re-Si	2.542(3)
Re-Cl	1.95(1)	Re-C2	1.93(1)
Si-C11	1.92(1)	Si-C21	1.91(1)
Cl-O1	1.18(1)	C2-O2	1.17(1)

(B) ANGLES (DEGREES)

Re-Si-Re'[a]	72.3(1)	Si-Re-Si'	107.7(1)
Cl-Re-Cl'	178.4(4)	C2-Re-C2'	95.6(4)
Cl-Re-C2	88.0(3)	Cl-Re-Si	95.1(2)
C2-Re-Si	78.7(2)	C11-Si-C21	105.0(4)
C11-Si-Re	114.1(3)	C11-Si-Re	117.6(4)
Re-Cl-O1	177.2(6)	Re-C2-O2	176.0(7)

[a]Primed atoms are related by either the mirror plane or the two-fold axis, whichever is applicable.

way as the rhenium analogue. In addition the anisotropic thermal parameters for the metals and the silicon atoms are similar in the two compounds. It therefore seems unlikely that the anomalous thermal parameters in both compounds are due to systematic errors in the data.

It was believed possible that the disorder, observed in the phenyl groups, where the data permit resolution of the disorder, could reflect a disorder of the whole molecule. A proper assessment of this possible disorder becomes important then, in order to obtain unambiguous bond lengths and angles.

The high anisotropy in the heavy atom vibrational ellipsoids observed in both the rhenium and manganese compounds provided the clue to the mode of disorder. Since the major axes of the thermal ellipsoids in both compounds were much larger than the other axes, it was believed that the disorder involved slight displacements of the molecule along the crystallographic *b* axis, as shown in Fig. 29. The vibrational ellipsoids are certainly large enough to contain two distinct rhenium and silicon populations, separated from their disorder averaged positions by approximately 0.15 Å.

Thus the completely disordered model was refined

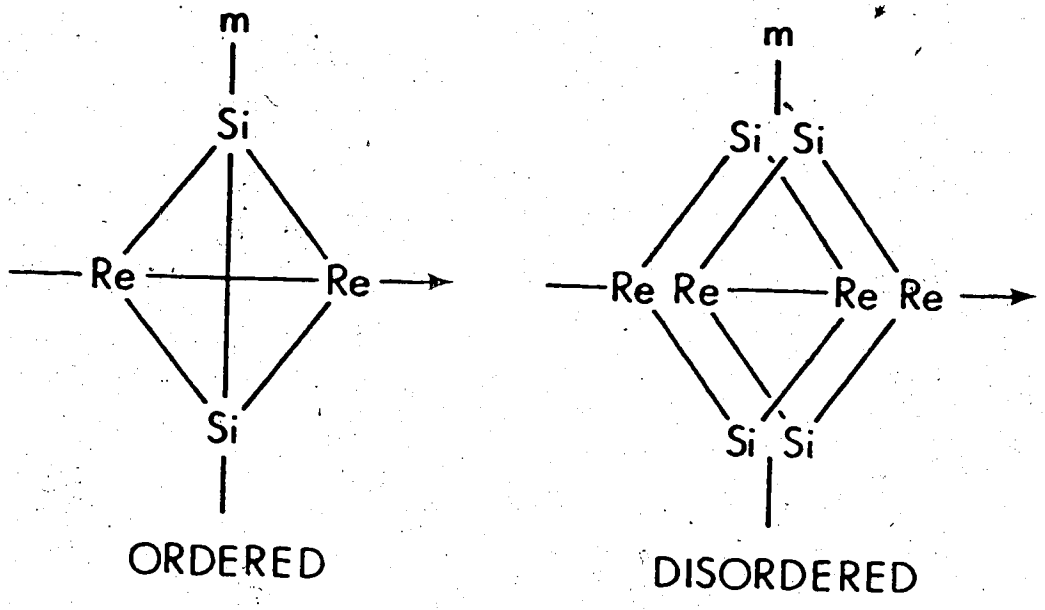

Fig. 29: Mode of Disorder in $Re_2(CO)_8[Si(C_6H_5)_2]_2$.

to test whether it gave any better fit to the experimental data than the model involving an ordered Re_2Si_2 cluster. In the least squares refinement the parameters for the rhenium and silicon atoms were refined without restriction, other than that imposed by symmetry. However all the parameters for the carbon and oxygen atoms of the carbonyl groups were not refined due to correlations between the x and z coordinates of the two disordered molecules. Thus for one of the disordered forms all coordinates were refined while for the other molecule only the y coordinate was refined. After a cycle of refinement

the x and z coordinates of the second molecule were set equal to those of its disorder-related mate and a further cycle was repeated with the same restrictions on the parameters. This was repeated until further iteration produced no significant shifts.

The final model had all atoms located at approximately 0.3 Å from their disorder-related partners. Thus the data were of good enough quality to differentiate the two disordered molecules although only 0.3 Å apart. The validity of the completely disordered model was verified by a Hamilton's R Test[79] at the 0.005 significance level, showing that the disordered model was significantly better than the ordered model. In the final least squares cycle $R_1 = 0.035$ and $R_2 = 0.056$ for 68 refined parameters. The anisotropic thermal parameters are shown in Table 53. The final positional parameters for all atoms in the completely disordered model are shown in Table 54 along with the isotropic B's of all atoms.

Electron density difference maps were also calculated for each model and were again found to be better for the completely disordered model with less residual electron density in its map. The highest peaks on each map were 1.39e $Å^{-3}$ and 1.11e $Å^{-3}$ for the ordered and disordered models respectively, this

TABLE 53: ANISOTROPIC THERMAL PARAMETERS FOR DISORDERED MODEL

Atom[a]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.0274(6)	0.0215(17)	0.0353(6)	0	0.0157(4)	0
Re'	0.0304(6)	0.0211(18)	0.0361(6)	0	0.0175(4)	0
Si	0.0318(12)	0.021(7)	0.0370(12)	0.0000(12)	0.0158(11)	0.0000(13)

[a] Primed atoms are the disorder-related atoms.

TABLE 54: POSITIONAL PARAMETERS AND ISOTROPIC B'S FOR DISORDERED MODEL

Atom	x[a]	y	z	B
Re	0.0	0.1578(4)	0.0	2.18*
Re'	0.0	0.1266(3)	0.0	2.24*
Si	0.1387(2)	0.0178(11)	0.1678(3)	2.37*
C1	0.0743(11)	0.1594(19)	-0.1030(13)	3.3(4)
C1'	0.0743	0.1303(20)	-0.1030	3.5(5)
C2	0.1037(10)	0.2773(20)	0.1056(11)	2.9(5)
C2'	0.1037	0.2486(20)	0.1056	3.8(5)
O1	0.1169(10)	0.1697(16)	-0.1672(11)	5.0(4)
O1'	0.1169	0.1349(16)	-0.1672	5.1(4)
O2	0.1674(13)	0.3450(17)	0.1639(13)	4.0(4)
O2'	0.1674	0.3308(25)	0.1639	8.7(6)
C11	0.1423(8)	0.0146(13)	0.3295(6)	3.1(2)
C12	0.1268(10)	0.1254(10)	0.3817(10)	4.1(3)
C13	0.1301(10)	0.1224(10)	0.4990(10)	4.9(4)
C14	0.1488(8)	0.0086(13)	0.5641(6)	5.2(2)
C15	0.1643(10)	-0.1022(10)	0.5119(10)	5.3(3)
C16	0.1610(10)	-0.0992(10)	0.3946(10)	4.7(3)
C21	0.2861(26)	0.0167(12)	0.2009(33)	3.5(2)
C22	0.3175(22)	-0.0094(15)	0.1092(19)	3.9(2)
C23	0.4259(29)	-0.0036(14)	0.1382(21)	4.6(2)
C24	0.5029(16)	0.0283(12)	0.2589(33)	4.6(3)

Table 54 (con't)

Atom	x	y	z	B
C25	0.4715(22)	0.0544(15)	0.3505(19)	6.5(4)
C26	0.3631(29)	0.0486(14)	0.3215(21)	4.4(3)

*Equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 53.

[a]Where standard deviations are not given, the parameters were not refined.

density being located in the vicinity of the rhenium atoms in each map.

Thus although it seems that the data are best fitted using the disordered model, the initial ordered model (involving only disordered phenyl groups) is believed to provide a good description of the average geometry, and therefore bond lengths and angles obtained from this model are suitable. This is due to the mode of disorder which involves only a small translation of the whole molecule collinear with the Re-Re bond. The thermal parameters in this model cannot, however, be given any chemical significance since they (especially the U_{22}'s) reflect the disorder present. That the ordered model provides a good description of the average geometry of the molecule is also seen from the bond lengths and angles, which are all reasonable and in good agreement with the related molecules, $Re_2(CO)_8H_2Si(C_6H_5)_2$,[65] $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$.

APPENDIX 2: PROGRAMMES USED IN CRYSTAL STRUCTURE SOLUTION, REFINEMENT AND ANALYSIS

AUTHOR	PROGRAMME	DESCRIPTION
D. P. Shoemaker	MIXG2	Calculates Picker diffractometer settings from unit cell dimensions and cell type.
M. J. Bennett	PMMO	Transforms raw data to intensities, applying Lp corrections.
M. Elder and K. A. Simpson	D-REFINE	Refines cell parameters for all space groups.
A. Zalkin	FORDAP	Fourier summation for Patterson or Fourier maps.
W. C. Hamilton	GONO9 [a]	Absorption corrections for Picker data.
P. Coppens	DATAP [b]	Absorption and Extinction corrections.
C. T. Prewitt	SFLS5	Structure factor calculation and least squares refinement of parameters. Modified by B. M. Foxman and M. J. Bennett for rigid body routine, and by W. L. Hutcheon and M. J. Bennett for the hindered rotor.
J. S. Woods	MGEOM [a]	Calculates bond lengths, angles and best planes.
M. E. Pippy and F. R. Ahmed	NRC-22 [b]	Calculates least squares planes.
W. Busing and H. A. Levy	ORFFE	Calculates bond lengths, angles, and associated standard deviations; modified by B. Penfold for I.B.M. 360 and W. L. Brooks and M. Elder for hindered rotors and rigid bodies.

AUTHOR	PROGRAMME	DESCRIPTION
C. Johnson	ORTEP	Writes Plot Command for Calcomp plotter, for plotting three dimensional molecular representations. Calculates bond lengths and principal axes of anisotropic thermal motion.
M. J. Bennett and B. M. Foxman	MMMR	Calculates starting parameters for rigid bodies and hindered rotors.
M. Cowie	PUBE	Sorts data according to any desired sequence of h, k, or ℓ.
R. C. Elder	PUBTAB	Prints Structure Factor Amplitude Tables; modified by M. Cowie to work in conjunction with PUBE.
G. J. B. Williams	FRAME [c]	Converts continuous paper tape output from automatic diffractometer, in ASCII code to "framed" output on cards in EBCDIC coding, suitable for PMMO input.

[a]This programme was used for the two rhenium hydrides.

[b]This programme was used for the three tris dithiolene complexes.

[c]This programme was used only for $[Ph_4As][Nb(bdt)_3]$. In the other two structures collected by automatic diffractometer, magnetic tape output was used. This was translated from ASCII by a subroutine added to PMMO by myself.