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THE UNIVERSITY OF ALBERTA

SPECTROSCOPIC STUDIES OF NITROSO COMPOUNDS AND OF TRIARYL CARBONIUM IONS

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE
STUDIES IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

by

Eric Kwong-Sun Ng
Calgary, Alberta
August, 1964

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

SPECTROSCOPIC STUDIES OF NITROSO
COMPOUNDS AND OF TRIARYL CARBONIUM
IONS

submitted by Eric K.S. Ng in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

This research consists of two independent low resolution spectroscopic studies. The first deals with an investigation into the characteristics of the long wave length transition in various nitroso compounds. The results imply that previous assignments of this transition as involving promotion of a nitrogen unshared electron to a π molecular orbital are correct. Attempts to obtain fluorescence from various nitroso compounds were unsuccessful under a great variety of experimental conditions. Possible reasons for this are discussed.

The second study concerns the near ultraviolet and visible spectra of the various triarylmethyl carbonium ions. The polarization of the absorptions relative to the fluorescence band were determined. An assignment of the transitions was made, using as a basis simple molecular orbital calculations and expectations based on the structure representation method. These are compared to the assignments made in earlier investigations. The calculated intensities were found to agree favorably with the observed values especially as considered from the point of view of the structure representation and the classical valence picture used to describe these molecules. Proton magnetic spectra for these compounds were obtained but were too complex to give useful information regarding the ground state wave functions.

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Above all, I should like to take this opportunity to express my gratitude to Dr. F.C. Adam for his encouragement, guidance and unfailing support.

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INTRODUCTION

Spectroscopy is the study of absorption and emission of electromagnetic radiation by matter. The electromagnetic spectrum covers a considerable diversity of wave lengths ranging from gamma rays ($\sim 10^{-8}$ cm.) to radio waves (~ 25 cm.) and depending on the wave lengths of the radiation used to stimulate such matter, different spectroscopic phenomena will occur. In the optical and ultraviolet region (2000 - 8000Å), absorption and emission processes involve transitions between states which differ mostly in their electronic distributions.

Among the many physical and chemical methods of studying molecular structures and properties, spectroscopy ranks high in importance. Apart from its obvious application as an analytical tool, it can be used to provide valuable information of theoretical interest. For instance, energy levels and electronic charge distribution may be inferred from the analysis of the absorption spectrum. Furthermore, spectroscopy remains as the only direct method for the study of excited species. Since excitation involves movement of electrons, absorption spectra can also give data concerning the change of charge distribution in the excited molecule. In favorable situations, the analysis of vibrational fine structure of an absorption band enables the geometry of an excited molecule to be determined. Whenever emission is possible, the measurement of its decay reveals a wealth of information concerning the life time of the excited molecule, and the various energy transfer processes the molecule may undergo. Solvent interaction can also be studied most effectively by spectroscopic methods. In simpler systems, notably diatomic molecules, very accurate estimates of dissociation energies and of the ionization potentials can be obtained from an analysis of the absorption spectrum. With larger molecules, the vibrational analysis becomes exceedingly difficult due to the number of vibrational modes and the fact that many overlapping excited electronic states may be found before dissociation occurs. Even so, much information may be obtained regarding the excited states by what might be called "low resolution spectroscopy".

The present work consists of two relatively disconnected low resolution spectroscopic studies, concerning two different classes of compounds. On one hand, the spectroscopic behavior of neutral nitroso compounds has been investigated and on the other hand, the spectroscopic behavior of a series of aromatic carbonium ions has been studied. Although many of the underlying assumptions and techniques are similar, there are sufficient differences in the nature of the molecular energy levels to warrant separate discussion and treatment of these subjects. Accordingly, this and the following sections will be treated separately where it is found practical, and an attempt will be made to show how molecular information may be obtained from the relatively featureless spectra of these compounds. The reader may find it advantageous to consider each of the two subjects serially throughout this presentation.

PART A: Nitrosobenzene

In a recent review article on the subject of nitroso compounds, Gowenlock and Luttke (1) offered the following statement as a concluding remark:

> "The major details of the structures of monomeric and dimeric compounds having been solved, it appears to the Reviewers that apart from further confirmatory evidence for the structures the major problems to be solved are the related thermochemical and kinetic investigations, our knowledge of which is so scanty."

It is the purpose of this section to summarize these major details about nitroso compounds in general and nitrosobenzene in particular, and to point out the areas which involve neither thermodynamics nor kinetics, but where further investigation might be profitable.

The electronic absorption spectra of a variety of aliphatic and inorganic nitroso compounds consist of three characteristic bands; one in the range 6300 - 7900Å with a molar coefficient, (ϵ_{max}), between 1 and 60, one in the range 2700 - 2900Å with a ϵ_{max} of about 80, and a third lying below 2200Å and having an ϵ_{max} of about 5000. These transitions are common to all nitroso monomers. However, the two higher energy transitions are often obliterated by the strong aryl absorptions in the aromatic series. The position of the long wave length absorption maximum depends to some extent on the nature of the aromatic or aliphatic group attached to the nitrogen.

The nature of the first visible transition has received far more attention than have the higher energy transitions. On the basis of its relatively low intensity, Lewis and Kasha (2) suggested that the long wave length absorption was due to a singlet-triplet transition. Current belief is that this transition arises from the promotion of a lone pair electron of the nitrogen atom to an anti-bonding π orbital and is classified as an $n \rightarrow \pi^*$ transition (3). Justification for this assignment is provided by the observation that on dimerization or on oxidation, the visible absorption disappears. The unshared electrons are now participating in bond formation and are therefore unavailable for the transition. The absorption band is also displaced to the blue when the solvent medium is changed from non-polar to polar. This is an experimental criterion that the transition involved is an $n \rightarrow \pi^*$ process (4). Finally, analysis of the complex, diffuse vibrational structure of this visible absorption band of nitrosyl fluoride (5) shows that the N-O stretching frequency in the excited state is about 200 - 300cm^{-1} less than in the ground state. According to Badger's Rule, this decrease in frequency is associated with an increase in the N-O bond length. Such is to be expected when the anti-bonding π orbital is singly occupied.

The polarization of this transition was investigated by Nakamoto and Suzuki by means of the dichroism of the absorption of meta-nitro nitrosobenzene in the crystalline state (6), and was found to be perpendicular to the molecular plane. A similar assertion was made by J. Mason (5) on the basis of a gas phase vibrational analysis. However, neither paper indicates conclusively the nature of the transition in liquid solutions.

It has also been noted that nitroso compounds are diamagnetic, and this has been confirmed by a variety of measurements (7). Only one X-ray crystallographic examination of a monomeric nitroso compound has been reported (8); p-iodo-nitrosobenzene is a planar molecule with a C-N-O angle of 125°, C-N distance of 1.28Å and a N-O distance of 1.24Å. This implies considerable double character in the C-N and N-O bonds. Dimers of p-bromonitrosobenzene and 2, 4, 6 - tribromonitrosobenzene have also been studied by crystallographic methods (9).

However, very little work has been reported concerning the emission properties of these compounds, especially in the aromatic series. One of the main purposes of this research was, therefore, to carry out a complete analysis of the nitrosobenzene absorption and emission spectra.

Cursory investigation indicates that the nitroso group is not drastically affected by conjugation to aromatic systems. The effect is similar to the observed shift in the weak carbonyl absorption of benzaldehyde related to that of formaldehyde, but is much smaller. This seems to indicate that the nitroso group itself is only weakly coupled to the remainder of the aromatic system and the presence of this group acts only as a small perturbation to the existing π electronic transitions of the aromatic molecules.

Since the polarizations of aromatic transitions are generally of considerable interest, it was hoped that judicious substitution of a nitroso group into an aromatic system would be of use in determining the polarization of the major aromatic absorptions. This would be achieved by comparing the relative orientation of the dipole transition for these aromatic absorptions with that of the weakly coupled nitroso group. To do this effectively, the polarization of the nitroso group transitions and the geometrical orientation of the nitroso group to the plane of the aromatic ring must be known with certainty. This latter factor is not necessarily determined from solid state experiments since the crystal forces may be of sufficient magnitude to change the configuration of the attached nitroso group from that which is found in the liquid phase.

This orientation in liquid solution has never been determined. The fact that the coupling between the nitroso group and the rest of the molecule is weak, and the fact that the nitroso group is ortho-para directing rather than meta directing implies that the plane of the nitroso group is tilted at a fairly large angle to the aromatic plane. Of course, this latter observation depends to some extent upon the precise nature of the reaction conditions, and that, in fact, the observation may be due to reaction of the dimer rather than the monomer, or due to formation of a complex before actual reaction. In any case, verification of the angle of twist may be obtained by an analysis of the fluorescent polarization. Considerations of this nature warranted a complete spectroscopic study of nitrosobenzene, especially since an emission spectrum had already been reported for a nitroso compound by Lewis and Kasha (82).

PART B: Carbonium Ions

In 1902, Walden (10) noted that when either triphenylmethyl chloride, or any of its complex salts, was dissolved in liquid sulphur dioxide, the conductivity of the resulting solution was comparable to that obtained when potassium iodide was dissolved in the same solvent. By postulating the following ionization mechanism he became the first person to conceive the idea of an ion where the electron deficiency was associated with a carbon atom

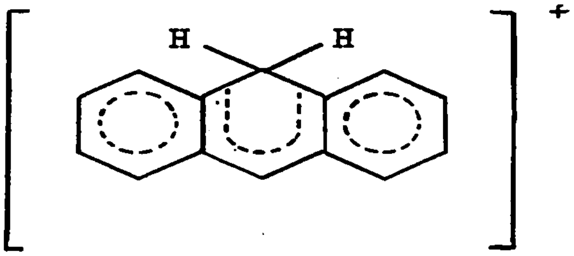
$$(C_6H_5)_3\ C \cdot Cl \rightleftharpoons (C_6H_5)_3 \cdot C^+ + Cl^-$$

$$(C_6H_5)_3 \cdot C \cdot SnCl_5 \rightleftharpoons (C_6H_5)_3 \cdot C^+ + SnCl_5^-$$

Since then, the identity of these carbonium ions as a class has been firmly established and in the following brief survey an account of the present status of carbonium ion chemistry is presented.

The original concept of the carbonium ion as envisaged by Walden has been extended considerably. Kinetic studies which suggest that S_N1 type reactions pass through such an intermediate and mass spectrometric investigations of alkyl halides in the gas phase (11) support this view. Further attempts have been made to obtain more direct evidence for the existence of these species and in this respect, Symons (12) has suggested that the U.V. absorption at 293mμ which occurs when t-butanol is dissolved in 98 % sulphuric acid is caused by the t-butyl carbonium ion. Deno (13), however, has repudiated this assignment and ascribed the absorption to a cyclopentenyl cation. Allylic carbonium ion absorption at 273mμ has also been suggested (14).

Of more interest to spectroscopists are the carbonium ions derived from aromatic hydrocarbons. Frequently, these may be generated by dissolving the parent compound in a strongly acidic medium, when a color develops. An investigation by Dallinga (15) of the optical spectra produced from a series of aromatic hydrocarbons dissolved in oxygen free, anhydrous HF and HF - BF_3 mixtures has suggested that this color is due to a protonated species such as, for example, in the case of anthracene



Although this conclusion is supported by an analysis of the nuclear magnetic resonance spectra of the solutions (16), non-protonated carbonium ions are produced when anthracene, tetracene and perylene are dissolved in concentrated sulphuric acid. The spectroscopic behavior of these ions has been fully investigated by Weijland (17). The diphenyl polyene series has also been studied by Van Der Meij (18) who found that in sulphuric acid, measurements of the absorption spectra revealed that the color was due to the divalent positive ions but no monopositive ions were found. It is also interesting to note that the electron spin resonance spectrum of tetracene in sulphuric acid has been measured (19), and points to an oxidized, but not protonated, carbonium radical cation.

In the triphenylmethyl series, triphenylmethyl carbonium ion itself has received the most attention. Since our research concerns principally carbonium ions of this type, work done on this will be reviewed more closely. Triphenylmethyl carbonium ions may be prepared in two different ways. In concentrated sulphuric acid, triphenylmethyl carbinol ionizes according to the equation

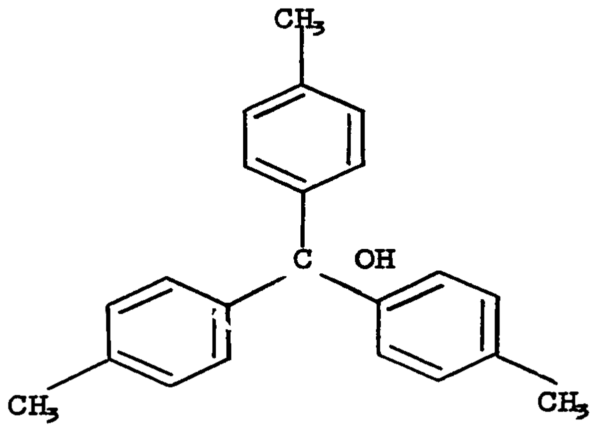
$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + H_3O^+ + 2HSO_4^-$$

This mode of ionization has been demonstrated by the fact that the solution is conducting; that cryoscopic measurements give a Van't Hoff i factor of four (20); and that the absorption spectrum of the solution is very similar to that of triphenylmethyl chloride in sulphur dioxide (21). Apparently, the ionization is complete. The second way to prepare the ion is to dissolve triphenylmethyl chloride, perchlorate or fluoroborate in an ionizing solvent. However, conductivity measurements of triphenylmethyl chloride in liquid sulphur dioxide (D = 16) indicated that this compound is only partly ionized and that the conductance data can be analysed in terms of two discrete processes; ionization to ion pairs, and a dissociation to free ions (22):

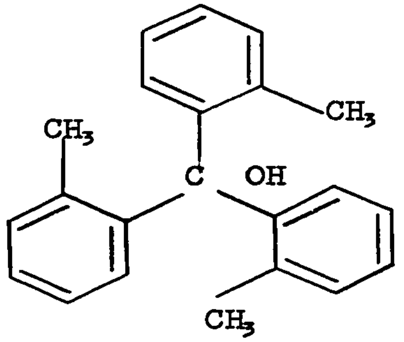
$$(C_6H_5)_3C\text{-}Cl \rightleftharpoons (C_6H_5)_3C^+Cl^- \rightleftharpoons (C_6H_5)_3C^+ + Cl^-$$

In nitromethane (D = 37) triphenylmethyl chloride ionizes to a smaller extent than in liquid sulphur dioxide, but the ionized portion appears to be entirely in the form of free ions (23). It is therefore very important in discussing "ionizing solvents" to differentiate between their capacity to assist ionization and their capacity to sustain dissociation. It is not surprising, therefore, that triphenylmethyl chloride which gives rise to significant concentrations of free ions in liquid sulphur dioxide does not appear to do so in acetic acid (D = 62), even in the presence of Friedel-Crafts catalysts (24). However, Gatzke and Stewart (25) speculated that the lowering in the apparent degree of ionization of triphenylmethyl salts in organic solvents may be due to the rapid hydrolysis of the carbonium ion by the small amounts of water present in these solvents.

The exceptional stability of this ion has also been the subject of considerable interest. Undoubtedly resonance stabilization of the ion is to a large extent responsible. However, Deno (26) has provided experimental results in support of his view that resonance, if important at all, involves only one or at the most two of the aromatic rings. His line of reasoning is based on two observations. The first was that

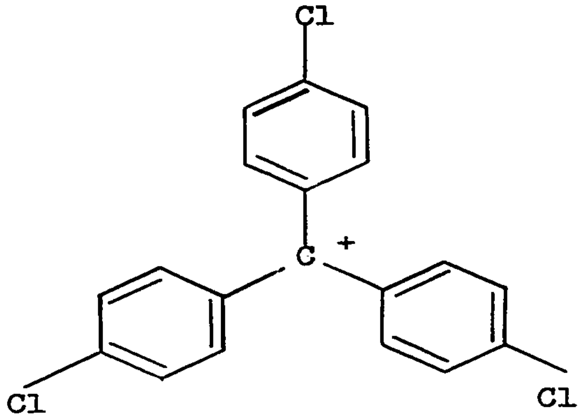


(I)

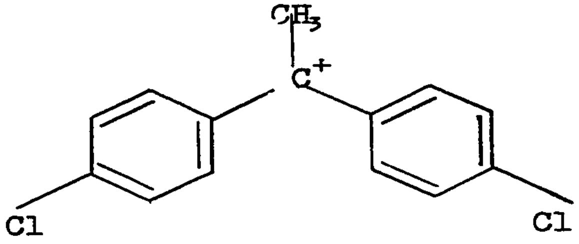


(II)

(I) and (II) have approximately the same ionization constant in concentrated sulphuric acid. This similarity in the tendency to ionize suggested that the o-methyl groups in (II) were not inhibiting the resonance stabilization of the carbonium ion. The second observation was that



(III)



(IV)

(III) and (IV) have the same absorption peak at 450 mµ. This he interpreted in two ways:

(a) the third phenyl ring contributes very little to the resonance stabilization,

(b) each of the three rings in (III) makes an equal contribution but that this contribution is small because of the angle of twist of the rings.

On the other hand, it has been known that a regular relationship exists between the ionization constant of a series of triarylmethyl chlorides measured in liquid sulphur dioxide at 0°C and the difference of delocalization energy between the ion and the molecule as calculated using molecular orbitals. Streitweiser (27) has plotted K_i v.s. Δ(DE) and obtained a smooth curve. There also appears to be a correlation between the pK_{ROH} and the change of resonance energy in going from the carbinol to the carbonium ion as shown by Gold (28).

Most of the information discussed was obtained by non-spectroscopic techniques such as conductance, kinetics or equilibrium measurements. In deriving conclusions pertaining to intrinsic molecular properties, it is important to bear in mine the grossness of such methods. For instance, in the correlation between pK or K_i values, with resonance energy, it is actually the free energy change, ΔF, of the reaction which is being compared. ΔF of a reaction, however, depends on many factors other than resonance energy, such as steric energy, and solvation energy. Unless these factors can be neglected or kept constant, conclusions based on this kind of comparison may be erroneous.

Closely related to the question of resonance is that of the geometric arrangement around the central carbon in the carbonium ion. Stereochemical evidence seems to indicate that in S_N1 solvolytic reaction, in which a carbonium ion is likely to be involved, the central carbon has a planar sp^2 hybridization. Until 1950, it was generally believed that the three benzene rings around the central carbon atom could exist in two isomeric forms (29), one symmetric "propeller-like" and one asymmetric. In terms of symmetry groups, the flat-plane, symmetrical propeller, and asymmetric propeller configuration belong to D_{3h}, D_3 (or C_{3v}) and D_2 respectively. Spectroscopic analysis seems to favor the D_3 (or C_{3v}) configuration (30). The analysis by Sharp and Sheppard (31) of the infrared spectrum of crystalline triphenylmethyl salts has supported the D_3 configuration of this ion. Furthermore, the work of Looney, Simpson and Adam (32) indicates that it is unnecessary to invoke two isomeric forms to explain the spectra of the closely-related triarylmethyl cations.

Compared to triphenylmethyl, relatively little work has been done on Mono-, Di- and Tri-xenyl methyl carbonium ions. The bulk of the work done has been in connection with the methods of synthesis (33).

Although the work done on the subject of aryl carbonium ions is considerable, it is by no means exhaustive. For instance, it would be of interest to be able to estimate the charge distribution and to determine the state of association of these ions. Secondly, in the work of Weissman (30), a tentative symmetry assignment of the energy levels of these ions has been made. However, in the opinion of the author, the assignment is ambiguous and it needs further clarification. Thirdly, the empirical method of structure representation has been applied successfully by Adam (32) to systems of triphenylmethyl and diphenylmethyl dyes, notably in the cases of Crystal Violet, 4, 4'- Bisdimethyl amino Fuchsone, and Methoxy Malachite Green. The close similarity between these dyes and triaryl carbonium ions suggests a fruitful extension of the method to the present system. The extension is more attractive when the simplicity of the hydrocarbon system is compared to the complexity of the dyes where the effects of the heteroatoms on bond energies, bond dipole moments and electronegativities can only be estimated. Considerations such as these constitute the main purpose of the present investigation.

According to quantum mechanics, the motion of the electrons in a molecular system is described by the Schrödinger equation which may be written symbolically as:

$$H\Psi = E\Psi,$$

where: H = Hamiltonian operator of the system,
Ψ = stationary state wave function of the system,
E = energy of the system in the given state.

The possible solutions of the above equation give the energy levels as well as the wave functions from which any other dynamic property of the system can then be calculated according to the formula:

$$\langle op \rangle = \int \Psi (op) \Psi \, d\tau ,$$

where: $\langle op \rangle$ = expectation value of the desired variable,
Ψ = wave function for the state of interest,
(op) = the operator of the desired variable,
$d\tau$ = volume element.

A chemical problem is thus reduced to the solution of a mathematical equation. However, the mathematical complexity involved is formidable and only for the simplest cases are there exact solutions. For systems of interest to chemists, various drastic approximations have to be introduced into this theoretical framework in order to obtain useful conclusions.

The general methods for tackling this complicated problem involve two kinds of approximation. One of these is called the 'method of variation'. From the Schrödinger equation, one notices that the important quantities involved are the Hamiltonian H and the wave function ψ. The method of variation is most useful when H of the system can be written down with confidence. Then the wave function is approximated by synthesis until the energy of the system becomes a minimum. Under this general approach, one would expect minor variations depending on the manner of approximating the wave function. The better known of these approximations are the molecular orbital method, in which the wave function is constructed by a linear combination of atomic orbitals of the system, and the valence bond method, in which the wave function is approximated by the different structures or bond eigenfunctions,

Another equally versatile approach is the 'perturbation method'. This is most appropriate in systems where the wave functions are known with reasonable accuracy but the Hamiltonian is difficult to express. One can then treat the awkward part of the Hamiltonian as a perturbation on the Hamiltonian of a well-established and closely-related system, provided that this perturbation is small enough for the method to be applicable.

(A) Molecular Orbital Method:

In the molecular orbital description of molecules, it is assumed that the atoms comprising the molecule do not preserve their individual atomic orbital character but rather that the individual orbitals are combined into a set of wave functions called molecular orbitals that encompass the whole molecule. The electrons are assigned to these molecular orbitals in accordance with the Aufbau principle and the Pauli exclusion principle. In the case of orbitals of equal energy, Hund's rules apply just as in the case of atomic orbitals.

With conjugated hydrocarbons, it is further assumed that the total number of electrons can be divided into two types, i.e. the σ and the π electrons. The former group, together with the 1s electrons of the hydrogen atoms, is involved in the formation of the σ bonds of the molecule and move in orbitals which are strongly concentrated along the axes of the bonds between the atoms. The orbitals of the π electrons are, however, concentrated in directions perpendicular to the plane of the molecules. Moreover, due to the fact that the overlap of the π and σ orbitals is negligble, the exchange between these electrons is usually neglected or, at most, considered as an additive constant to the potential energy of the π electrons.

Assuming that the π electrons move in the field of the core of the molecule, the complete Hamiltonian operator for the π electrons may be given by

$$H = \sum_i h(i) + \frac{1}{2} \sum_i \sum_j \frac{e^2}{r_{ij}} \qquad i \neq j \qquad (1)$$

where $h(i)$ represents the sum of the kinetic and potential energy of electron i moving in the field of the core, and $\frac{e^2}{r_{ij}}$ the potential energy due to the repulsion between electrons i and j.

In general, the eigenfunctions of this Hamiltonian cannot be obtained, so that one is in practice limited to the use of suitable approximations. There are several approximations of different degrees of sophistication within the context of this method and which have application to this work.

(a) Hückel Molecular Orbital Approximation (H.M.O)

Hückel replaced the complete Hamiltonian (1) by a sum of one electron operators $\overline{H}_{(i)}$:

$$H = \sum_i \bar{H}_{(i)}, \tag{2}$$

each term of which stands for the kinetic energy of an electron i and the average potential energy of the π electron. Explicit electron-electron repulsions are neglected. According to Schrödinger's equation, the total wave function Ψ must satisfy the condition,

$$H \Psi = E \Psi .$$

The best one-electron molecular orbitals describing the configuration Ψ are those which minimize the total energy of the configuration in a variational procedure. This results in the condition that each must be an eigenfunction of the one-electron Hamiltonian $\bar{H}_{(i)}$

$$\bar{H}_{(i)} \Psi = \epsilon \Psi . \tag{3}$$

Since the true eigenfunctions of this operator are not easy to obtain, Hückel approximated the one-electron m.o.'s by linear combinations of the $2p_z$ orbitals of the 2n carbon atoms as

$$\Psi_i = \sum_p^{2n} c_{ip} \varphi_p , \tag{4}$$

where φ_p is the normalized $2p_z$ orbital of the carbon atom p and the summation extended over all carbon atoms. The best m.o.'s of this type are those which minimize the energy ϵ . They can be found by varying the coefficients for each of the m.o.'s resulting in the following 2n homogeneous linear equations:

$$\sum_p^{2n} c_{ip} \left(H_{ps} - \epsilon_i S_{ps} \right) = 0 , \tag{5}$$

where: $H_{ps} = \int \varphi_p(i) \; \bar{H}_{(i)} \; \varphi_s(i) \, d\tau ,$

$$S_{ps} = \int \varphi_p(i)\ \varphi_s(i)\ d\tau .$$

These equations will have a non-trivial solution only if the secular determinant

$$\left| H_{ps} - \epsilon S_{ps} \right| = 0, \qquad (6)$$

is satisfied. The one-electron energy ϵ_i is then one of the 2n roots of this secular determinant.

In order to evaluate ϵ_i and C_{ip}, Hückel made the following assumptions:

(1) the overlap integrals for all $2p_z$ orbitals are neglected

i.e. $S_{ps} = 0$.

When starting from normalized atomic orbitals, the integral S_{pp} becomes unity.

(2) all Coulomb integrals $\overline{H}_{pp}$ are equal to α,

(3) all "resonance" integrals $\overline{H}_{ps}$ are equal for neighboring atomic orbitals and may be neglected if p and s are non-adjacent atoms,

$$\text{i.e. } \overline{H}_{ps} = \beta, \qquad p = s \pm 1,$$

$$\overline{H}_{ps} = 0, \qquad p \neq s \pm 1.$$

With the aid of these assumptions the secular determinant can be solved, giving a set of 2n roots ϵ_i, expressed in terms of two parameters α and β:

$$\epsilon_i = \alpha + \chi_i \beta . \qquad (7)$$

Solving the homogeneous linear equation (5) for each root ϵ_i gives a set of coefficients C_{ip} which according to equation (4) form the one-electron molecular orbitals ψ_i, of energy ϵ_i.

Even with these simplifying assumptions, the secular equation is usually of such a high order that the mathematics are rather involved. To help overcome this, the symmetry properties of the molecule are utilized. Instead of molecular orbitals defined as in equation (4) a new set of symmetry-adapted m.o.'s are constructed. The basis of this application is that the probability of electron behavior must be the same at all equivalent points of space. The new set of m.o.'s are such that there is no interaction between m.o.'s of different symmetry representations as determined by the symmetry group of the molecule. Consequently, the original secular determinant is reduced to a number of determinantal blocks of lower order with concommitant reduction of algebraic difficulties. Each individual block can usually be solved quite easily.

The use of symmetry has far greater significance than the mere simplification of the secular determinant. It plays a vital role in the interpretation of electronic absorption spectra of conjugated molecules as will be seen shortly.

For a number of conjugated hydrocarbons, the m.o.'s have some special properties. If the carbon atoms of a conjugated hydrocarbon are divided into two classes (usually called the "starred" and the "unstarred") in such a way that neighboring carbon atoms invariably belong to a different class, then this hydrocarbon is called 'alternant'. Alternant conjugated hydrocarbons can further be subdivided into 'even alternant', if the number of "starred" atoms is the same as that of the "unstarred" atoms, or 'odd alternant' if the number of "starred" atoms exceeds that of the "unstarred" atoms by an odd number. This cannot be done in the molecule of the non-alternant conjugated hydrocarbons, for in their structure one or more carbon rings occur with an odd number of atoms.

For the even alternant hydrocarbons, the roots of the secular determinant are "paired", i.e. if for example ϵ_j is paired to ϵ_k, the relation

$$\chi_j = -\chi_k ,$$

holds. Also between the coefficients of the corresponding molecular orbitals, Ψ_j and Ψ_k, the relation

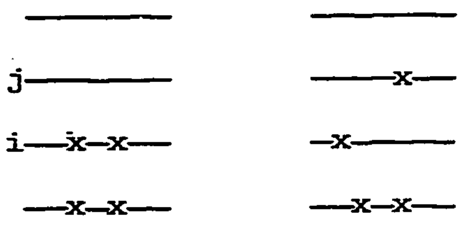
$$C_{jp} = \pm C_{kp} ,$$

holds with the upper sign if p is a "starred" atom, and the lower sign if p is an "unstarred" atom. For the odd alternant hydrocarbons, one of the roots of the secular determinant is zero, i.e. $\chi_j = 0$, and the rest of the roots are paired symmetrically to this value. The molecular orbital corresponding to the zero root is called a non-bonding orbital, whereas those corresponding to positive χ are bonding, and to negative χ anti-bonding. The charge density at an atom p in a conjugated molecule may be defined as

$$q_p = \sum_{i}^{\mathrm{Occ.}} C_{ip}{}^2 , \tag{8}$$

where the summation is over the occupied orbitals.

In this approximation, the electrons are placed into the available m.o.'s in order of increasing energy as follows:



(1) (2)

In neutral alternant hydrocarbons, the ground state of the molecule can be represented as in (1) and the first excited state as in (2). The one-electron excitation energy for the transition from (1) to (2) is then :

$$(\alpha + \chi_j\beta) - (\alpha - \chi_i\beta) = (\chi_j - \chi_i)\,\beta.$$

These results are usually compared to the observed spectrum, and a value of $\beta = 25{,}000\text{cm}^{-1}$ is generally found for aromatic hydrocarbons (34).

There are a number of refinements to the H.M.O. method, for instance the inclusion of overlap integrals and corrective terms to account for the variation of α and β within the same molecule. One such technique has been investigated with respect to the carbonium ions and is described briefly in the following section.

In molecules where a net positive or negative charge exists, one no longer expects the Coulomb integral α to have the same value as in a neutral atom, especially when the net charge is not evenly distributed over all atoms. The existence of net positive charge means that the screening seen by any one electron is reduced and the Coulombic attraction to the nucleus is therefore increased. α for such a carbon atom should have a more negative value. Conversely, a carbon atom with a negative charge should have a less negative value of α. Wheland and Mann (35) proposed that the value of α should be linearly related to the charge. Their proposal may be formulated as

$$\alpha_r = \alpha_0 + (1 - q_r)\,\omega\,\beta_0\,, \qquad (9)$$

where ω is a dimensionless parameter whose value may be chosen to give the best agreement with the experiment. With one empirical parameter, this ω -technique introduces some electron repulsion within the framework of the simple H.M.O. method. The use of this method in the literature is still rather limited, but it has been shown to lead to improved calculated dipole moments for hydrocarbons and greatly improved energy values for organic cations (36). The values proposed for the empirical parameter ω have ranged from 0,33 to 1.8, and an intermediate value of 1.4 seems now to be soundly established (37).

In principle, one first obtains the charge distribution according to the H.M.O. method; this charge distribution is used to calculate new α's according to equation (9). New orbital energies and charge distributions are then calculated. This iteration process is continued until the charge distribution no longer changes. The calculation is then self-consistent. In practice, one cycle of iteration often suffices for many purposes, although in the present application the values obtained give a divergent sequence, so that consistency could not be obtained.

In spite of reasonable success and simplicity, the H.M.O. method leaves much to be desired. One very important deficiency in this method is the neglect of all explicit inter-electron repulsions. A further deficiency is apparent when the total wave function for the system is examined. This function, Ψ, is a product wave function made up of individual one-electron m.o.'s, i.e.,

$$\Psi = \psi_1(1)\,\psi_1(2)\,\psi_2(3) .$$

However, due to the indistinguishability of electrons, other product functions such as

$$\Psi = \psi_1(3)\;\psi_1(2)\,\psi_2(1)\,\psi(4) ,$$

where the electrons have been permuted among the available levels, must also be considered. The complete wave function should therefore be taken as a sum of individual product wave functions in which complete permutation of electrons and orbitals has been effected. Finally, being constructed as a product of one-electron orbitals, the wave function does not, and cannot, take into account explicitly or adequately the mutual replusion between electrons with the result that the electrons of opposite spin in the same orbital get too close to each other too often. These and other shortcomings will have to be remedied by further refinements and such is the topic of the next section.

(b) Self-Consistent Field

This more refined procedure requires that we give each electron a wave function which in addition to the space co-ordinates also contains the spin co-ordinates of that electron, and which will be called a molecular spin orbital, ψ_i^u, where u stands for the co-ordinates of the uth electron and i labels the different molecular spin orbitals. To take into account properly the identical nature of the electrons as well as the Pauli exclusion principle, the total wave function is formed as a determinant usually called the Slater determinant.

$$\Phi = (N!)^{-1/2} \begin{vmatrix} \psi_2^1 & \psi_2^1 & \cdots & \psi_N^1 \\ \psi_1^2 & \psi_2^2 & & \\ \vdots & & & \\ \psi_1^N & & \cdots & \psi_N^N \end{vmatrix} \qquad (10)$$

The total Hamiltonian can be written as

$$H = \sum_{v}^{2m} F_{(v)} ,$$

where 2m is the number of π electrons in the system and the one-electron Hartree-Fock operator, $F_{(v)}$, may be defined by:

$$F_{(v)} = h(v) + \sum_{i}^{m} (2J_i - K_i) . \tag{11}$$

The summation must be taken over all the doubly-occupied orbitals in the ground state and the operators J_i and K_i may be given by:

$$J_i(v)\ \psi_j(u) = \left(\int \frac{\psi_i^2 (v)}{r_{uv}} \right) \psi_j (u)\, d\tau , \tag{12}$$

$$K_i(v)\ \psi_j(u) = \left(\int \frac{\psi_i (v) \psi_j(v)}{r_{uv}} \right) \psi_i(u)\, d\tau . \tag{13}$$

The best possible ground state wave function Ψ is obtained when the corresponding energy, determined by:

$$H \cdot \Psi = E \cdot \Psi , \tag{14}$$

is minimized by varying the normalized one electron m.o.'s. It can be shown that the m.o.'s which minimize the energy of the ground state must be eigenfunctions of the Hartree-Fock operator:

$$F \psi_i = \epsilon_i \psi_i . \tag{15}$$

The general procedure for solving Fock's equations is one of trial and error. One assumes a set of ψ_i's, calculates the operator F, solves equation (15) for the n lowest eigenvalues, and compares the resulting ψ_i's with the assumed ones. Guided by this comparison, a new set of ψ_i's is chosen and the procedure is repeated. This cyclic process continues until the assumed and the calculated ψ_i's agree. This method for solving Fock's equations is called the Hartree-Fock self-consistent field (S.C.F.) method.

The application of this method to the problem of molecules is greatly simplified by the suggestion of Roothaan (38) that the trial m.o.'s may be represented by a linear combination of atomic orbitals. If one substitutes:

$$\Psi_i = \sum_p^{2n} c_{ip} \varphi_p \ ,$$

where φ_p is the normalized $2p_z$ orbital of the carbon atom p into equation (15), the following results:

$$\sum_p^{2n} F \cdot c_{ip} \varphi_p = \epsilon_i \sum_p^{2n} c_{ip} \varphi_p \ . \qquad (16)$$

Multiplying both sides of this equation by φ_s and integrating over the spatial co-ordinates, one obtains:

$$\sum_p^{2n} c_{ip} F_{ps} = \epsilon_i \sum_p^{2n} c_{ip} \cdot S_{ps} \ . \qquad (17)$$

This can be rewritten into 2n linear homogeneous equations:

$$\sum_p^{2n} c_{ip} \ (F_{ps} - \epsilon_i S_{ps}) = 0 \ ,$$

which will have only a non-trivial solution if the corresponding determinant is zero.

$$\left| F_{ps} - \epsilon_i \cdot S_{ps} \right| = 0 \ . \qquad (18)$$

The general procedure for this method is then similar to that of solving the Fock equations. A set of coefficients for the m.o.'s which can be taken from a H.M.O. calculation are substituted and solved as in equation (18). The resulting C's are compared to the assumed ones and this process reiterated until the C's no longer change and are self-consistent. This method with further simplifications has been applied by Pople (39) to some chemical systems of interest to the present work.

(B) Valence Bond (V.B.)

Historically the valence bond method was developed at an earlier date than the H.M.O. method and is characterized by considering the combining atoms as a whole. The formation of a molecule is thought of as arising from the approach at great distance of atoms in their valence state. These are allowed to interact one with the other and in this regard differs from the m.o. method where only the nuclei or nuclei plus inner shell electrons are first brought into position at molecular interatomic distances. The valence electrons are then allotted to polycentric molecular orbitals and their interactions calculated.

For a system of n atoms, each with one valence electron, a possible eigenfunction for the system may be constructed as a product of one-electron wave functions :

$$a(1)\ b(2)\ c(3)\ldots\ldots\ldots n(n)\ ,$$

where a(1) represents that electron 1 is in atomic orbital a. Any function which may be obtained from this by permutation of the numbers 1, 2....n is an equally good wave function. To be complete, each of the wave functions must be multiplied by a spin function of the type $\alpha(1)\ \alpha(2)\ldots\alpha(n)$. According to the exclusion principle, only those functions are allowed which are anti-symmetric with regard to electron interchange and this condition can be automatically satisfied by writing the wave function as a Slater determinant. A shorthand notation of the determinant in which only the diagonal term is written out explicitly is:

$$\psi = \begin{pmatrix} a & b & c \ldots\ldots\ldots n \\ \alpha & \alpha & \beta \ldots\ldots\ldots \alpha \end{pmatrix} ,$$

where the a, b's are the individual atoms and the α or β are the spins of the electron assigned to the atom written above it. For a system of n electrons, there will be 2^n such determinants. This number can be materially reduced under certain circumstances.

Of paramount importance in the valence bond method is the concept of electron-pair bonds. A bond is said to form between atoms a and b, if the electrons in a and b have opposite spins. The system will be most stable if there is a bond between every pair of atoms. For atoms of low atomic number, such a distribution of spins corresponds to $S_z = 0$, since the z components of spins of each electron pair cancel each other. It is also reasonable to assume that the most stable configuration of the system would be that corresponding to the maximum number of short bonds. Therefore, for the ground state of the system, only those determinants where S_z equals zero are of importance. However, not all of these functions are necessarily independent, and some may be expressed as linear combinations of others. The number of linearly independent functions is given by Rumer's rule:

$$N = \frac{n!}{(\frac{n}{2})!\,(\frac{n}{2}+1)!} ,$$

where n is the number of atoms. Similar rules exist whereby the simplest "cannonical structures" or linearly independent bond eigenfunctions may be chosen. Under certain circumstances it is possible to eliminate some of those wave functions which correspond to bonds over long distances (long bonds) such as the "Dewar" structures for benzene.

These bond eigenfunctions constitute the bases of a variation treatment and eventually a secular equation of the following form is obtained:

$$\left| H_{ij} - E S_{ij} \right| = 0 ,$$

where $H_{ij} = \int \psi_i H \psi_j \, d\tau$, $S_{ij} = \int \psi_i \psi_j$ and ψ_i, ψ_j are the bond eigenfunctions. Matrix elements are expressed in terms of Coulombic integrals, Q, and exchange integrals, A, where:

$$Q = \int (a\ b\ c\ d)\ H\ (a\ b\ c\ d)\ d\Gamma ,$$

$$A = \int (a\ b)\ H\ (b\ a)\ d\Gamma ,$$

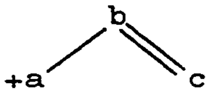
a, b, are the atomic orbitals, and the order for the electrons is 1, 2, 3...etc. To facilitate the calculation of matrix elements, a number of empirical rules have been proposed and among these, Pauling's method is the most widely used (40).

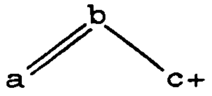
Although this scheme works very well with certain small molecules, it becomes very involved as the number of centres increases. It should also be realized that in the form outlined, only neutral atoms at large internuclear distances are involved, a situation which corresponds in the limit to homolytic cleavage of the bonds. At shorter internuclear distances, corresponding to the actual molecular size, the possibility of charge separation exists in that one carbon atom may, on the average, have more than its share of the electrons, while another has less. These polar structures have high energies at large internuclear separations but may not be neglected in an actual molecule with the appropriate equilibrium distance. Accordingly, many polar bond eigenfunctions should be added to a valence bond calculation if exactness is desired. Needless to say this adds considerable difficulty to the already complex case of large molecules.

It can be shown that the valence bond method and the molecular orbital method are equivalent in the ultimate refinement. However, these methods often become very cumbersome and it is instructive to compare their respective merits based only on their simple approximations. J.W. Linnett (41), in connection with his proposal for a new approach to the molecular calculation problem, gave the following comparisons for the ground state energy of the allyl positive ion:

Method	Energy (e.v.)
Valence Bond	-28.678
M.O. (H.M.O.)	-28.830
"Best" method	-30.396 .

The "best" method in this case is based on the valence bond method taking into account all the possible structures of the ion including long bonds and polar structures, while that of the "valence bond" method is based only on two non-polar structures,





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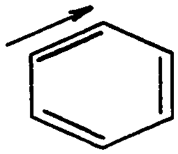
This comparison indicates that the two methods are equivalent in this simple system but both fall short when compared to the "best" method. Mathematically the m.o. method is simpler than the valence bond method. However, the latter has the advantage of being more closely related to the classical theory of valence in chemistry and it would therefore be highly desirable to have an empirical method based on valence structures. An attempt in this direction is treated in the following section.

(C) Structure Representation:

In a series of papers (42, 43, 44) W.T. Simpson proposed an empirical method of classifying the π electronic state of molecules based on structures. In this scheme, the π electronic states are divided into two classes; one arising from resonance among "normal" structures (N states) and the other from resonance of "excited" structures (E states).

Normal structures as used in this method are those structures written according to the classical theory of valence. For instance, in the case of benzene, the two Kekulé structures are the normal structures. The three Dewar structures are excluded on grounds of stability. Excited structures are those which arise from excitation of a particular double bond. In benzene, these structures were represented as: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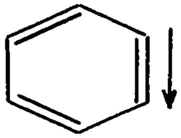
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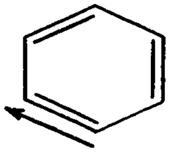
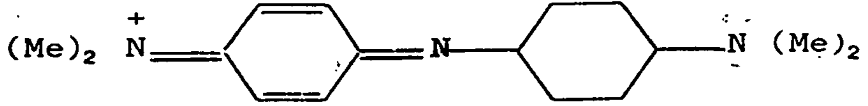

(3)

The position of the arrow indicates the particular bond which is being excited, and the direction of the arrow gives the direction of the instantaneous transition moment. Each of the two Kekulé structures therefore generates three excited structures.

Compared to normal structures, excited structures are higher in energy and they therefore usually represent the upper states of the molecule. The method begins on the hypothesis that there are as many low-lying states as there are normal structures, and also, as many excited states as there are excited structures. For this to be valid, it is required that all the wave functions corresponding to the normal and excited structures be linearly independent. It is fundamentally difficult to prove the independence because explicit expressions corresponding to these structures are usually lacking. In cases where there is no ambiguity as to what normal structures should be considered, it is possible to show this independence, as for example in benzene and butadiene.

On the other hand, it is easy to justify this hypothesis from experimental observations. For instance, using only the two Kekulé structures and the point group (D_{6h}) of benzene, only two states with symmetry A_{1g} and B_{2u} may be generated. These will be the normal states of the molecule, and experimental observation indicates that the first transition of benzene is in all probability of $A_{1g} \longrightarrow B_{2u}$. The best examples for excited states are those of polyene in which there is only one normal state and as many excited states as there are double bonds. Absorption spectra of polyenes and carotenes had been treated satisfactorily (45, 46) by this method.

This method provides not only a symmetry classification of electron states for π electron systems but also predicts the polarization of the optical transitions. When there are just two equivalent normal structures, the prediction of the polarization of a transition between states involving these structures is particularly simple. In general, the direction of polarization of the transition moment vector is the difference in the moments of the structures. Thus, for example, with a dye having the following structures:



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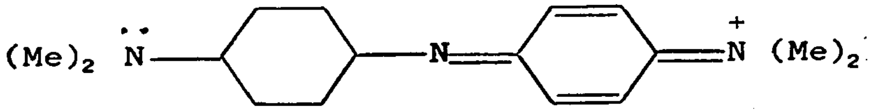

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the electric vector of the light interacts most strongly with the molecule along the nitrogen-nitrogen line. Qualitative examples of this nature are ample in the literature. However, to convert this idea into an empirical method capable of yielding quantitative results requires a certain formalism which is given as follows.

In this method, it is considered as given; (i) n structures and their behavior under the operations of the point group of the molecule; (ii) n energy levels and their symmetry species; and, (iii) that the transformation properties of the structures are consistent with the species of the state of the molecule. The plan is to start with the observed electronic energies for a given system, regarding them as diagonal elements of the energy matrix in a Heisenberg representation. Then instead of making the prohibitively difficult transformation to the Schrödinger representation, a transformation is made to an intermediate representation characterized by the property that the base vectors are associated with structures. This new representation is the "structure representation". It has certain of the qualities of the Schrödinger scheme in that there is a "shape" or configuration aspect, but there is also greater opportunity for the exercise of quantum mechanical and chemical intuition. The given structures and the transformation properties one uses in defining the structure representation, are not considered to be quantum mechanical entities. They are considered to be defined instead by the classical theory of valence. These shall be referred to as 'structures ⟨1⟩'. On the other hand, matrix elements in the structure representation are, when derived from observed energies, exact quantum mechanical quantities. They may then certainly be considered as derived from interactions among wave functions in suitable combinations which exactly represent the various energy eigenstates. The squares of these component wave functions are called 'structures ⟨2⟩'.

One fundamental assumption is that 'structures ⟨1⟩' are equivalent to 'structures ⟨2⟩' with respect to transformation properties, energies and other quantities. This equivalence must be understood to be a relation which is not quantum mechanical. In other words, when we use structures, we ignore the detailed shape of the true wave functions of the state, retaining only the transformation properties of the structures. For instance, the ground state of benzene, when properly represented should include the two Kekulé structures, the Dewar structures, and some of the ionic structures. But in the present method all these are lumped together into two Kekulé-like structures, with the hope that the linear combination of them will generate a function which transforms as that of the true wave function. Obviously, this is a rather drastic approximation, but the success of the method in many applications affords a certain degree of justification. Mathematically, the formalism is represented as:

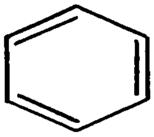
$$\underset{\sim}{E}' = \underset{\sim}{S}^{-1} \, \underset{\sim}{E} \, \underset{\sim}{S} \, , \qquad (22)$$

where: $\underset{\sim}{E}'$ = non-diagonal energy matrix in the structure representation,

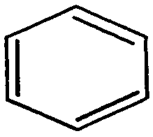
$\underset{\sim}{S}^{-1}$ = inverse of the transformation matrix,

$\underset{\sim}{E}$ = diagonal energy matrix in the Heisenberg representation.

To illustrate the foregoing procedure, we may consider benzene with only two equivalent structures:



(1)



(2)

After performing the operations of the point group D_{6h}, two combinations persist after normalization; $\frac{1}{\sqrt{2}}\left\{(1) + (2)\right\}$ of symmetry A_{1g} and $\frac{1}{\sqrt{2}}\left\{(1) - (2)\right\}$ of symmetry B_{2u}. These vectors form the columns of $\underset{\sim}{S}^{-1}$ and the complete matrix is then:

$$\underset{\sim}{S}^{-1} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} .$$

The observed energy of the $A_{1g} \longrightarrow B_{2u}$ transition is 3.81 in units of 10^4cm.^{-1}. Thus the Heisenberg energy matrix has the following form:

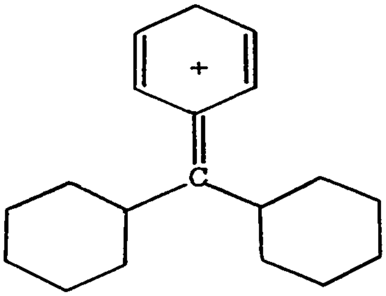
$$\underset{\sim}{E} = \begin{pmatrix} 0 & 0 \\ 0 & 3.81 \end{pmatrix} ,$$

if the ground state is taken as the zero energy point. From equation (22) the energy matrix E' in the structure representation is:

$$\underset{\sim}{E'} = \underset{\sim}{S}^{-1} \underset{\sim}{E} \underset{\sim}{S} = \begin{pmatrix} 1.91 & -1.91 \\ -1.91 & 1.91 \end{pmatrix} = \begin{pmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{pmatrix} .$$

The matrix elements E_{11} and E_{22} give the energy of a single Kekulé structure, and E_{12} and E_{21}, the interaction energies of the two structures. It also represents the vertical resonance energy.

In some complicated cases, the transformation matrix $\underset{\sim}{S}^{-1}$ may not be found so conveniently. When the structures of a molecule are not all equivalent, then there may be more than one non-zero linear combination belonging to the same symmetry species. For instance, in triphenylmethyl carbonium ion, there are four structures with low energy



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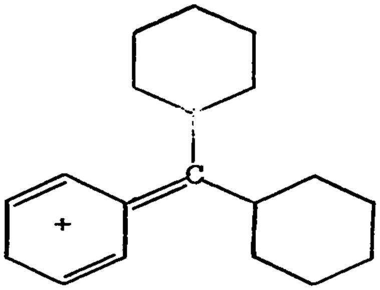

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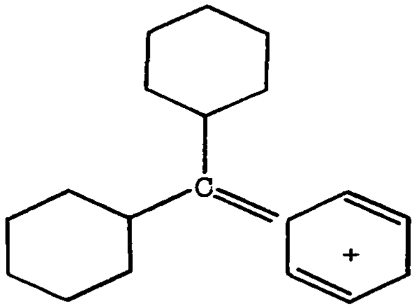

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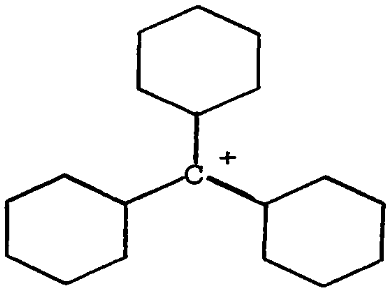


(4)

Structures (1), (2) and (3) are equivalent to each other, but not to structure (4). Taking C_3 as the molecular point group there will be two non-zero linear combinations belonging to the A species, namely:

$$(1) \quad + \quad (2) \quad + \quad (3) ,$$

and $\quad (4)$.

A linear combination of these two would therefore be necessary to represent the A species and consequently the $\underset{\sim}{S}^{-1}$ matrix will be a function of one variable, namely the mixing coefficient "c".

This method is particularly fruitful when applied to a homologous series of molecules as in the present research. For these, stationary state energy level shifts due to slight structural changes can be predicted and the problem associated with determining the variable "c" can also be solved. This possibility occurs when the following assumption can be made:

$$\underset{\sim}{E'_{(B)}} = \underset{\sim}{E'_{(A)}} + \underset{\sim}{\delta E'},$$

where: $\underset{\sim}{E'_{(A)}}$ = energy matrix of the parent molecule,

$\underset{\sim}{E'_{(B)}}$ = energy matrix of the perturbed molecule,

$\underset{\sim}{\delta E'}$ = perturbation energy matrix brought about by the structural variation.

Since this perturbation energy matrix has the form:

$$\delta E' = \begin{pmatrix} \delta E_{11} & \cdots\cdots\cdots & \delta E_{1n} \\ \delta E_{21} & & \\ \delta E_{31} & & \\ \vdots & & \\ \delta E_{n1} & \cdots\cdots\cdots & \delta E_{nn} \end{pmatrix},$$

and the matrix elements correspond to classical structures and their interactions, they may be chosen with the help of chemical intuition. By carrying out the reverse transformation:

$$E_{(B)} = \underset{\sim}{S}\, E'_{(B)}\, \underset{\sim}{S}^{-1},$$

energies will be obtained in the Heisenberg form, and compared to the experimental observations for molecule B. At best fit, the problem is then considered solved.

The ordinarily difficult calculation of transition intensities can be treated in a similar way. If x' and y' are the electric moment matrices in the x and y direction for the molecule in the structure representation, then the transformation equations:

$$\underset{\sim}{x}' = \underset{\sim}{S}^{-1}\, \underset{\sim}{x}\, \underset{\sim}{S},$$
$$\underset{\sim}{y}' = \underset{\sim}{S}^{-1}\, \underset{\sim}{y}\, \underset{\sim}{S},$$

still hold. In this case, the electric moment matrix is diagonal in the structure representation and in favorable cases it may be estimated from bond length and bond angles for the molecules under consideration. $\underset{\sim}{S}^{-1}$ will be the same transformation matrix as found in the transition energy problem. The transition moments may be read from the non-diagonal elements of the $\underset{\sim}{x}$ and $\underset{\sim}{y}$ matrices.

The application of this method hinges upon the requirement that the absorption spectrum of at least one molecule must be fully analysed with regard to energy, intensity, and polarization. The transformation matrix $\underset{\sim}{S}^{-1}$ is of paramount importance in this formalism and its determination will be shown in detail in a later section .

(D) Nuclear Magnetic Resonance:

For a very long time, energy has been the only criterion of accuracy of a theoretical wave function. This was so because the most powerful and widely-used technique for getting approximate solutions to the wave equation has been that of minimizing the energy function. Even after discounting the great difficulties associated with this procedure, the energy itself is found to be too insensitive to indicate the best fit of a wave function. Recently, the rapid development of spectroscopy in the radio and microwave region has opened up other possibilities for testing wave functions. With the realization that in addition to the kinetic, potential and mutual repulsion energies of the electrons, the Hamiltonian should rigorously include terms to account for spin-spin coupling, spin-orbital interaction, the coupling of electron spins and nuclear spins, quadruple moment interactions, and for the interactions that result from the coupling to externally applied electric and magnetic fields. These terms have been neglected in the previous discussion because of their minute magnitudes. Although the energies involved are inconsequential in ultra-violet spectroscopy, it now appears that experimental measurement of the effect of these terms provides an excellent test for any proposed electronic wave function. This is possible because these terms are not large enough to cause any serious modifications of the wave function (or of the electronic energy) but, on the other hand, their effect may be used as microscopic measuring probes with the ability of being placed within the electronic charge-cloud without affecting it in any gross way. In other words, the sole criterion of energy may give general ideas about the wave functions, but these smaller interactions provide the detailed shape of the functions. The quantity most appropriate for the present research is the proton chemical shifts as measured by nuclear magnetic resonance experiments.

It is well-known that an isolated nucleus with spin I in a uniform external magnetic field H_o has an interaction energy equal to

$$E = \hbar r_i H_o I_z , \qquad (23)$$

where: r_i = nuclear magnetogyric ratio,

I_z = z component of nuclear spin I.

In a molecule, the energy is modified according to the actual magnetic field experienced by the individual nucleus so that

$$E = \hbar r_i H_i I_z(i) . \qquad (24)$$

The resonant frequency is therefore:

$$V_i = \frac{r_i H_o (1 - \sigma_i)}{2\pi} ,$$

where σ_i is the screening constant of nucleus i.

Accordingly, for nuclei in different environments, the absorption frequency will differ by virtue of the different screening constants. This can be expressed as:

$$\nu_A - \nu_B = (\sigma_A - \sigma_B) H_o = \delta_{AB} H_o , \qquad (25)$$

where A and B designate different locations in the molecules. δ_{AB} is called the chemical shift parameter and is measured experimentally with respect to some suitable standard.

Nuclear screening arises from the secondary magnetic field produced by the induced electronic circulation around the individual nucleus when a uniform external magnetic field is applied. The magnitude of this secondary magnetic field may be calculated, and from this the screening constant. For the simplest system of a free atom in a ^1S state, it is given by Lamb's formula:

$$\sigma = \frac{4\pi e^2}{3mc^2} \int_0^\infty r \, \rho_{(r)} \, dr , \qquad (26)$$

where $\rho_{(r)}$ is the electron density at a distance r from the nucleus. However, if the nucleus is in a molecule, this simple formula can no longer apply. The general expression for an isolated molecule was given by Ramsey:

$$\sigma_{zz} = \frac{e^2}{2mc^2} \int \frac{x^2 + y^2}{r^3} \rho \, dr + \frac{e^2 \hbar^2}{2m^2 c^2} \sum_{n \neq 0} (E_n - E_0)^{-1} \qquad (27)$$

$$(0 | \Sigma_j \frac{\delta}{\delta \phi_j} | n) \times (n | \Sigma_k r_k^{-3} \frac{\delta}{\delta \phi_k} | 0) + (0 | \Sigma_k r_k^{-3} \frac{\delta}{\delta \phi_k} | n)$$

$$(n | \Sigma_j \frac{\delta}{\delta \phi_j} | 0) ,$$

where: $E_n - E_0$ = electronic excitation energy from state $0 \longrightarrow n$,

$0, n$ = ground and excited electronic state wave functions, respectively,

ϕ_j = azimuthal angle for rotation about the z axis.

The first term in the Ramsey formula is similar to the Lamb formula for atoms and becomes identical with it when averaged over all directions. The integral is taken over the entire molecule, so that physically it corresponds to what the shielding would be if the whole electronic structure of the molecule is rotated about the nucleus. The second term corrects for the hindrance to this free rotation by the nuclear field. In other words, the chemical shift is the sum of a diamagnetic and a paramagnetic term.

In its present form, the Ramsey formula is not convenient for practical use. It gives the total screening of the molecule as a whole and in large molecules, these two terms essentially cancel each other. In order to derive specific information from the measurement of chemical shifts, it is therefore highly desirable that the total screening be broken down into local contributions for a particular nucleus. Saika (47) suggested that the molecular screening could be approximately divided into separate atomic contributions. They are:

(1) the diamagnetic correction for the atom in question,
(2) the paramagnetic correction for the atom in question,
(3) the contribution from other atoms.

The mathematical basis of this breakdown into atomic parts has been shown by Pople (49) to be valid.

Of more immediate interest to the present research is the recognition that proton chemical shifts in aromatic molecules seem to reflect the π electron density on the carbon atom to which the proton is bonded. For example, Corio (49) measured the proton magnetic resonance spectra of a number of mono-substituted benzene molecules and found that the measured chemical shifts indicate differences in the electron distribution at the ortho, meta and para positions of the benzene ring. The compounds investigated range from the electron-withdrawing nitro group to the electron-donating amino group. The chemical shifts clearly reflect the relative deshielding and shielding effects of these two types of functional groups. More convincing evidence of the charge effect in proton chemical shifts comes from the resonance spectra of non-alternant hydrocarbons. In such cases, the ring current model which gave a satisfactory interpretation of the proton chemical shifts in the spectra of alternant hydrocarbons was found to be inadequate. For instance, in azulene (50), the total spread of the multiplet predicted by the ring current model is only 0.5 p.p.m. (parts per million), whereas that observed is 1.3 p.p.m. This failure of the model is attributed to the highly asymmetric nature of the electron charge distribution in these molecules.

Experimental evidence in this direction has led to the proposal of a simple linear correleation between the proton chemical shifts, δ, and the local "excess" charge, $\Delta\rho$, located on the carbon atom, in aromatic systems; thus,

$$\delta = k\,\Delta\rho \,, \tag{28}$$

where the constant k was found empirically to have a value near 10 p.p.m./electron. The validity of equation (28) has been tested in cases where electron densities can be calculated (51) and reasonable agreement with experiment is obtained.

These considerations have application in the present research in the following way; if the charge distribution in the ground state may be determined from the proton resonance spectrum, then this may be compared to the wave functions obtained from considerations of the optical spectrum. In fact in certain favorable cases it might be possible to calculate the N.M.R. spectrum from the optical spectrum and vice versa. This new approach has accordingly been investigated in the present research.

The essential features which characterize an absorption spectrum in the optical region are the energy of absorption, the intensity of the absorption and the vibrational or rotational structure of the band. Another feature which is not obvious from an inspection of the spectrum is the polarization of the various transitions, which is to say the direction in which the excitation has changed the dipole moment of the molecule when referred to a molecular frame. Since the emission process is essentially the reverse of absorption, these features are equally important in the study of luminescent processes. Although emission of gaseous molecules at very low pressures is the exact reversal of the absorption process (resonance radiation), in condensed phases the emission process may be modified somewhat by intermolecular collisions and other processes which carry off some or all of the excess energy of the excited molecules. The effect of intermolecular interactions is to broaden both rotational and vibrational structure so that electronic spectra in solution are characterized by very broad bands which have at best only little vibrational fine structure remaining.

In these cases, it is evident that discrete vibrational states still exist although for a particular molecule they may be modified by the exact nature of the solvent environment in which the particular molecule finds itself excited. For a given molecule in the ground state, the vibrational levels will be populated according to a Boltzman distribution, and at typical temperatures most molecules will have zero point vibrational energy. On absorption of radiation they will enter some excited state which may have more than zero point vibrational energy, but with a probability in part dictated by the geometrical similarity between the vibrations in the two states. This process is very rapid, occuring in about 10^{-15} seconds. Collision and vibrational deactivations occur nearly as rapidly, and any excess vibrational energy is quickly carried away by the solvent. This occurs in a time interval of 10^{-11}- 10^{-13} seconds, and thermal equilibrium with the medium is soon established. Thus any emmission act, a process which takes at least 10^{-9} seconds, must follow this vibrational "cascade" so that emission nearly always occurs from the lowest vibrational state of the excited molecule. As a consequence of this, the emission has vibrational fine structure characteristics of the ground state while the absorption has the characteristics of the excited state vibrations. This situation may be better understood with the help of Figure (1). When these vibrations are associated with large aromatic molecules, where the geometry between the electronic states does not markedly change, then the vibrational fine structure will be similar for the absorption and emission bands except that they will be mirror images and the emission will be displaced to the red end of the spectrum. The process may be represented as in Figure (1), where process (a) is absorption, followed by vibrational deactivation (b) and emission (c). When other excited states are available (B and C in Figure (1)), conversion from the higher state to the lower excited state may occur when vibrational displacements and velocities are similar between the two states. This vibrational cascade then takes the molecule to its lowest possible excited state much more quickly than the emission process can occur with the result that emission from higher excited states is rarely observed (52).

In many cases the lowest excited state is not one which combines

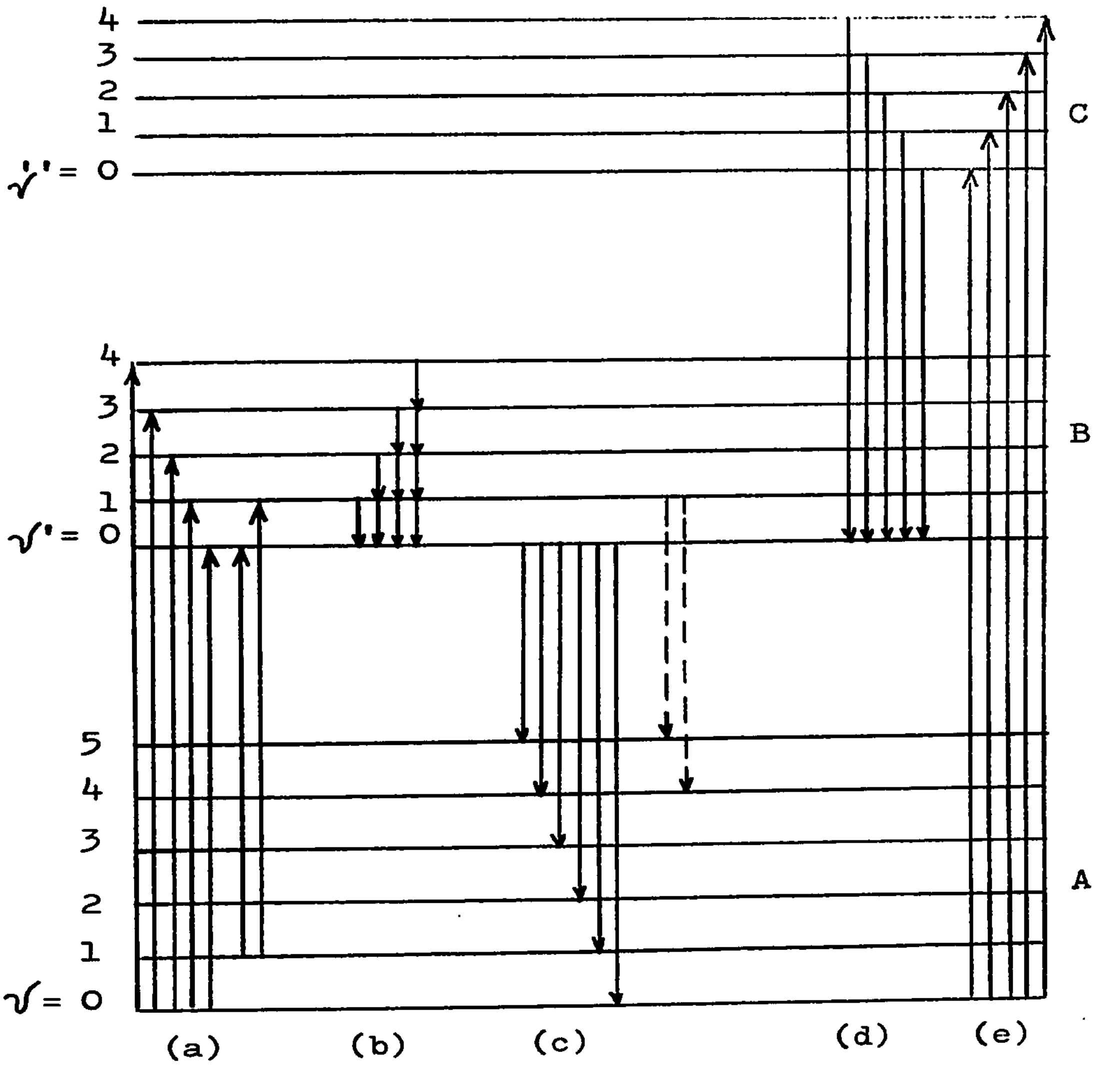


Figure (1)

Absorption and Emission Processes

(a) Absorption
(b) Vibrational Deactivation
(c) Fluorescence
(d) Internal Conversion
(e) Absorption to Higher Excited State

readily with the ground state, and the probability of emission is very low. This results in a meta-stable state which will be discussed later, but is experimentally characterized by the observation that emission occurs a long time $(>>10^{-9}$ sec.) after the initial absorption. This is called "phosphorescence" or "after glow" to differentiate it from the rapid process or "fluorescence". Phosphorescence is not the reverse process of absorption and usually does not have the "mirror image" quality and is shifted to much lower energies than the absorption. Nor will the phosphorescent band have a similar polarization to the fluorescent band.

To understand the question of polarization, recourse must be made to the quantum theory of radiation, wherein a molecule absorbs radiation only when there is a change of electric dipole moments between the final and initial states of the molecule. The intensity of an absorption band is proportional to the transition moment which is given by:

$$R = \int \Psi_i \sum(m_i) \Psi_f \; d\Gamma , \qquad (29)$$

where: R = transition moment,

Ψ_i, Ψ_f = wave function of initial and final state,

$\sum(m_i)$ = operator of the sum of electric dipole moments and the integration is carried out over all co-ordinates.

In order that a transition 'be allowed', R must not vanish. The conditions under which R has a finite value, or vanishes, can be most conveniently investigated by the group theoretical method. It demands that the symmetry product of the integrand contains the totally symmetric representation. In most organic molecules, Ψ_i, the initial state is already totally symmetric and this reduces to the requirement that

$\sum(m_i)\,\Psi_f$ must be totally symmetric. This is possible only if $\sum(m_i)$ and Ψ_f belong to the same symmetry representation.

The operator $\sum(m_i)$ is a vector, and therefore has three components $\sum m_x$, $\sum m_y$ and $\sum m_z$ with respect to the molecular frame. The space component which meets the above symmetry requirements determines the direction (or polarization) of the transition. The importance of the polarization of a transition cannot be over-estimated since it gives the symmetry classification of the final state function Ψ_f and very often is the decisive criterion in the theoretical assignment of electronic absorption spectra and energy levels.

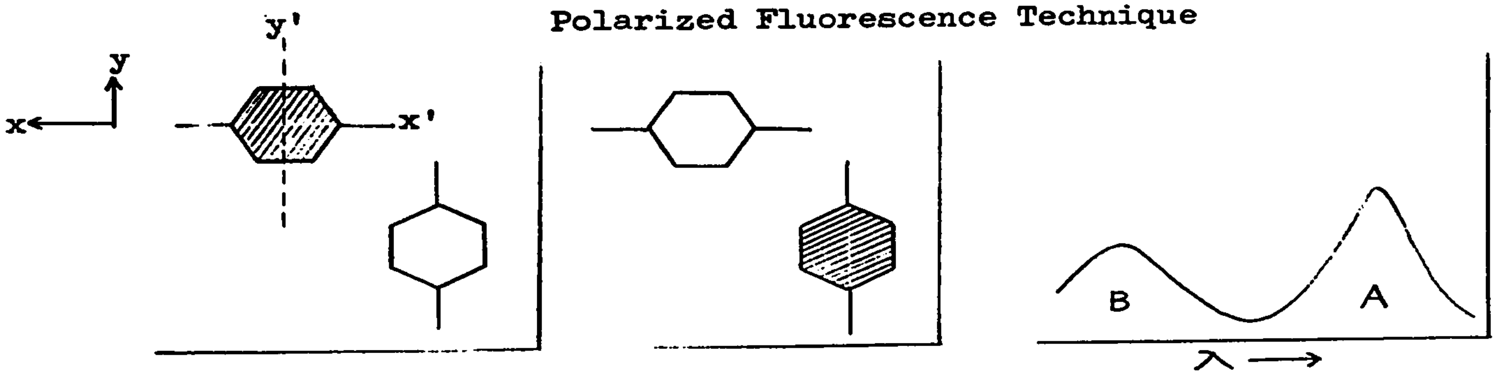
Experimentally, there are two general approaches to determining the polarization of a transition. The first and most obvious is by actually orienting the molecules by some means. Single crystals are ideal in this respect, but suffer from the limitation that the high density of absorbing species makes absorption spectroscopy difficult. There is often uncertainty in the crystal structure as well. Techniques involving substitution solids have overcome these problems, at least where a suitable host crystal can be found, and where the host and guest spectra do not overlap in the spectral region of interest. Aromatic hydrocarbons very often possess such characteristic properties and the best example of this technique is in determining the polarization of the naphthalene transitions using a solid solution of naphthalene in durene (53). Other methods under this category include the study by dichroism of either stained cellophane films (54), or orientation effects produced in stretched fibers or streaming long chain dye molecules (55). None of these methods, however, has yet been developed into a broadly applicable tool for determining polarizations.

The alternative approach does not require actual orientation of the molecules, but utilizes instead the anisotropic property of linearly polarized light. Such radiations will select and excite only certain molecules within a randomly oriented sample, and will give rise to a polarized fluorescence. This is the method used in the present research, and a more detailed description of this technique follows.

The principle of this method can best be illustrated by referring to Figure (2) which represents a somewhat idealized case of a disubstituted benzene

Figure (2).

Polarized Fluorescence Technique



(a) (b) (c)

Imagine that individual molecules are held rigidly in place in an inert transparent matrix and that each of the molecules has a long axis, x', and a short axis, y', in the molecular frame. The co-ordinates of the laboratory frame are x and y. Suppose further, that this molecule has two absorption bands, a long wave length (A) transition polarized in the direction of x' and a short wave length (B) transition polarized y' as in Figure (2)(c). In a sample, the molecules will be oriented randomly with respect to x and y. For the sake of simplicity, two molecules, one oriented with its x' axis along x, and the other its x' axis along y, are chosen. When light polarized along x and of wave length A is passed through the sample, the only molecule excited would be the shaded one in Figure (2)(a) which has x' parallel to x. In a rigid glassy medium, this molecule will be "clamped" in this particular orientation, and after a time interval of about 10^{-8} sec. will fluoresce. The axis of fluorescence is the same as that of absorption, i.e. along x', so that if the polarization of this fluorescence is measured, it will be found to be parallel to the incident light. Let this absorption be called the "parallel band". When, however, light polarized along x as before but of wave length B is passed through the sample only the unshaded molecule will be excited, but to a second excited level. Such a molecule will lose energy by vibrational cascade until it reaches the first level whence it fluoresces. However, the polarization of the fluorescence will be in the y direction and will therefore be perpendicular to that of the incident light. Let this be called the "perpendicular band". Similarly, the polarization of other bands can be determined by measuring the polarization of the fluorescence of the sample relative to the incident light, which is to say the relative polarization of the different bands with respect to the first absorption. For example, relative to the A band, the B band is perpendicular in the case under discussion. To determine the absolute polarizations, the polarization of at least one band has to be known unequivocally. This is often possible through either independent experimental determinations or from theoretical considerations.

In actual practice, the polarization of the fluorescence has finite values in both the parallel and perpendicular directions. This is due to the fact that not only molecules with their axis oriented parallel to the incident light vector will be selected, but also those with slightly different orientation wherein the transition probability is proportional to the cosine of the angle between the transition moment vector and the vector plane of the light. For this reason, a quantity called the 'polarization ratio' is defined:

$$p = \frac{I_{\parallel}}{I_{\perp}}$$

p has the maximum value of 3 for parallel and the minimum value of .5 for a perpendicular band, and a value of 1 for a depolarized band.

Naturally, the use of polarized fluorescence technique depends upon the emission being experimentally observable, and is most easily applied to the system when the emission and low energy absorption processes are the reverse of each other. However, in many cases, fluorescence and phosphorescence are observed simultaneously in the same molecule (56). As a result, the phosphorescence must be discriminated against in a polarization determination if reliable results are to be obtained. Some cases are known where the fluorescence has the mirror image of the absorption but may exhibit the characteristic glow of phosphorescence. These cases may be explained by the Jablonski hypothesis wherein molecules in the phosphorescent state are thermally excited to the fluorescent state.

EXPERIMENTAL

Part A: Nitrosobenzene

(1) Materials:

(a) Nitrosobenzene

Commercial grade nitrosobenzene was used except in the spectroscopic determinations where high purity was necessary. In these cases it was purified either by recrystallization from alcohol or by vacuum sublimation. The latter was effected by connecting a cold-finger trap to the vacuum system using dry-ice-acetone mixture as a coolant. The nitrosobenzene thus formed was the colorless dimer with an uncorrected melting point of 67-69°C (lit. 68°C). Either material gave essentially the same results.

(b) Trimethyl nitrosomethane

The general method for the preparation of nitroso compounds was oxidation of the corresponding amines with Caro's acid. The acid was prepared by grinding potassium persulphate with concentrated sulphuric acid in a mortar well cooled with ice. The mixture, after standing for one hour, was poured onto crushed ice and neutralized with sodium carbonate (c.f. Gattermann (57)).

Tertiary butylamine was oxidized in the above manner to trimethyl nitrosomethane but the product was so unstable that it resisted all attempts to separate it in the crystalline state. Its spectrum could be taken only when freshly prepared and this seriously limited the quantitative aspects of the measurements.

(c) p-Nitroso dimethyl aniline

p-Nitroso dimethyl aniline was prepared by direct nitrosation of dimethyl aniline. This latter compound was dissolved in dilute hydrochloric acid and cooled to 0°C with ice. An aqueous solution of sodium nitrite was then added slowly and a yellow hydrochloride precipitated out. This was dissolved in a minimal amount of water and neutralized with base, after which the p-nitroso dimethyl aniline was extracted with ether, and recrystallized from either benzene, decalin, or petroleum. The deep green crystalline products were found to have uncorrected melting points lying between 84°C and 86°C (lit. 85°C).

(d) 2,6 - Dimethyl nitrosobenzene

This compound was prepared by oxidizing 2,6 - dimethyl aniline with Caro's acid, and was recrystallized from ethanol.

(e) 2,4,6 - Tribromo nitrosobenzene

2,4,6 - Tribromo aniline was prepared by direct bromination of aniline in dilute hydrochloric acid solution. Bromine was introduced into the solution by slight suction from a water pump, the reaction vessel being kept at ice temperature. Passage of bromine vapor was continued until the solution assumed a distinctly yellow color, after which the tribromo aniline was filtered and washed thoroughly with water to remove hydrobromic acid.

The tribromo aniline was then oxidized to 2,4,6 - tribromo nitrosobenzene by 30 % hydrogen peroxide in glacial acetic acid after the method of Holmer (58). The product was purified by successive recrystallizations from glacial acetic acid giving colorless needles which were finally vacuum sublimed to yield a product with an uncorrected melting point of 121-122°C (lit. 120°C).

(f) $K_2NO(SO_3)_2$

A sample of this material was kindly supplied by Miss B. Melanson.

(g) Solvent

Most of the solvents used in absorption work were spectral grade reagents. Methyl cyclohexane was dried over sodium and recycled through a silica gel column until spectroscopic constancy was obtained. Other solvents such as toluene, benzene, tetrahydrofuran and isopentane were each dried over sodium.

In emission studies, experiments had to be performed at or near liquid nitrogen temperatures so it was necessary to use solvents which glassed under such conditions. Besides this, they had to satisfy the criteria of non-fluorescence and non-interaction with the solute. One such glass-forming solvents is a mixture of three parts isopropanol to seven parts isopentane. However, such a protonic solvent was not entirely satisfactory for the nitrosobenzene work because of the possibility of protonation reactions in the excited state. A better mixture was found to consist of two parts methyl cyclohexane to one part isopentane.

(2) Experimental:

Beckman DK-1A and Beckman D.U. spectrophotometers were used for all absorption measurements, which were carried out at room temperature. In most cases, matched, one centimetre cells were used. Where weak absorption bands were observed, the complete spectrum was first determined using the cells of 1 cm. path length, after which, that part of the spectrum corresponding to low absorbancy was repeated using 10 cm. cells and solutions of the same concentration.

The acidity of the solutions of nitrosobenzene and p-nitroso dimethyl aniline were adjusted by the addition of either hydrochloric acid or sodium hydroxide. Solubility posed no problems and the solutions were prepared by weighing out the required amount of material and the pH of the solutions was checked with a Beckman pH meter.

To check that each of these solutions obeyed Beer's law, stock solutions were prepared and the absorption spectra displayed at successive dilutions. No discrepancies were noted.

The basic apparatus used in emission measurements is shown in Figure (3). However, because the factors governing the choice of each component part were numerous, these are discussed separately below.

(a) Light sources

Three light sources were used according to intensity and the spectral region under investigation. For excitations in the visible and near infrared, a 500 Watt General Electric CFX tungsten projection lamp was used. For excitation in the ultraviolet, either a GW Gates 100 Watt HBO - 109 mercury vapor lamp or a Hanovia 1000 Watt, 914 C - 1 high pressure mercury-xenon lamp were available. The former had applications where excitation at one of the mercury lines was desired, but for emission experiments, the latter was more desirable because of its much higher over-all luminosity.

(b) Filters

Interference from scattered radiation must be avoided in emission work, especially when fluorescent compounds having very poor quatum yields are being studied. This is because such spurious radiation may saturate the detector and for this reason the choice of optical

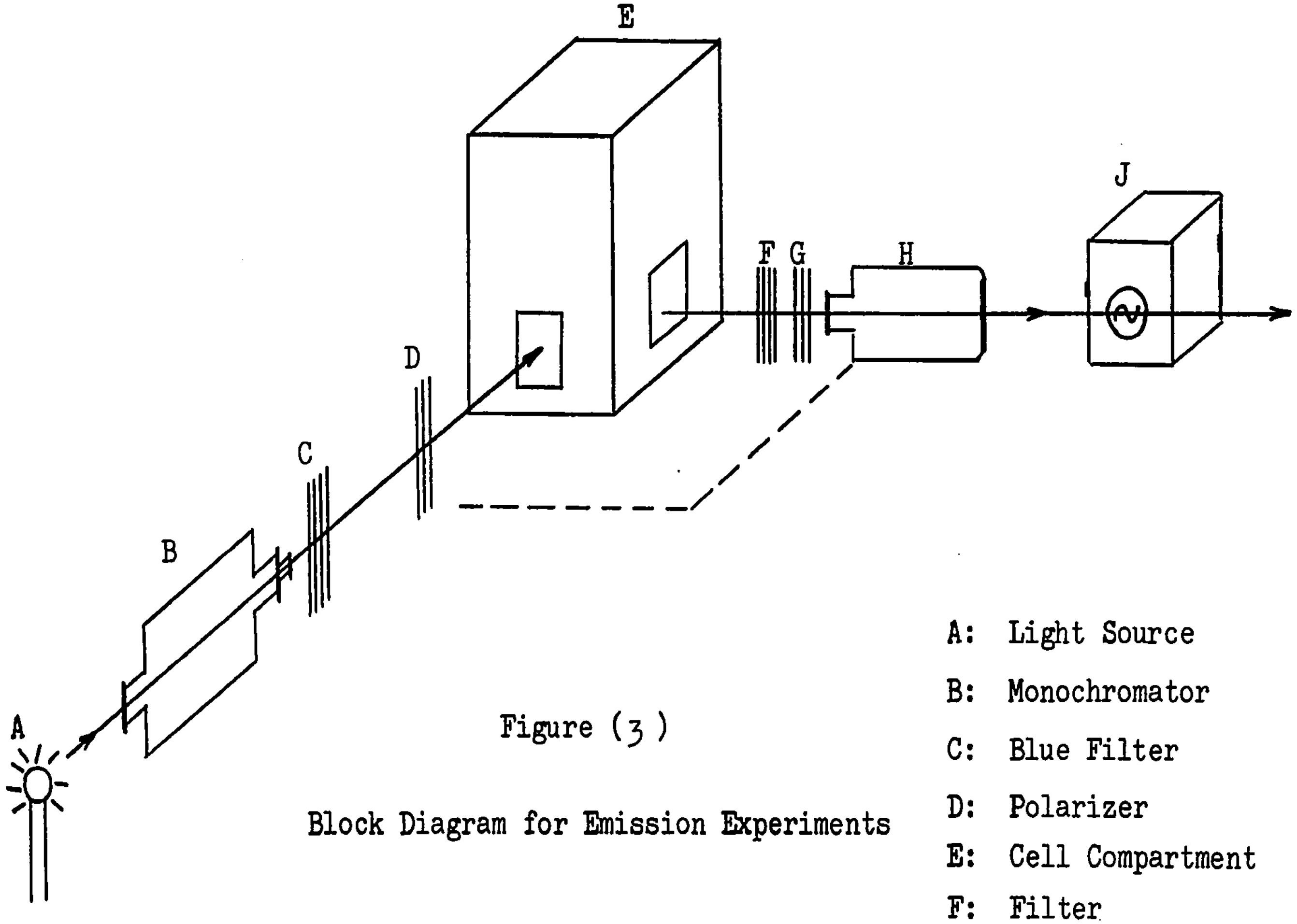


Figure (3)

Block Diagram for Emission Experiments

A: Light Source
B: Monochromator
C: Blue Filter
D: Polarizer
E: Cell Compartment
F: Filter
G: Analyzer
H: Photomultiplier
J: Oscilloscope

filters is very important. The spectral purity of the incident beam can be improved using a narrow band filter passing only the desired wave lengths for excitation. Further isolation is possible using a filter at the detector whose band pass is such as to allow only the fluorescent light to be transmitted. In favorable cases of good efficiency, this filter may be replaced by a monochromator, and the emission spectrum recorded. This luxury was not possible with any of the nitroso compound studied. Different filter systems were required for each compound studied depending largely on where absorption occurred. For instance, with nitrosobenzene, a combination of solutions L, T, and N as suggested by Bowen (59) were used for the incident beam, and a Corning 268 glass filter used in the detected beam. This filter let none of the incident light through, but would have passed any fluorescent light up to the glass absorption in the infrared.

(c) Sample compartment

This consisted of a light-tight wooden box with openings for both the incident and fluorescent beams. Within this was placed the quartz cell which was surrounded by a bath of liquid nitrogen in a Dewar which fitted into the sample compartment. The compartment was closed by a lid with a small opening to fit the sample tube snugly for the purpose of centering.

With samples such as nitrosobenzene, where it was necessary to prevent oxidation by air, the sample cell was prepared as follows: the sample was introduced into a cell, as shown in Figure (4), was frozen under liquid nitrogen, and the whole evacuated on a vacuum line. After isolating the cell from the line, it was warmed and the mixture

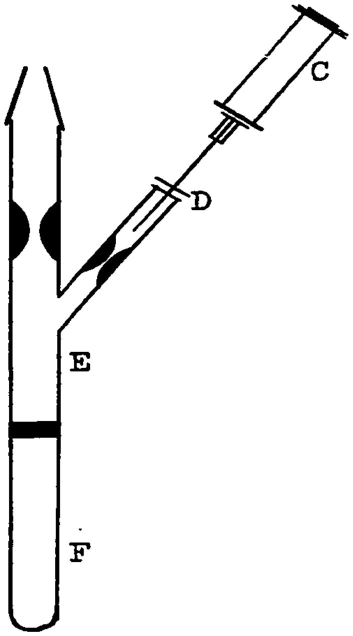


Figure (4)

Sample Preparation

C: Syringe
D: Rubber Cap
E: Pyrex Tubing
F: Quartz Tubing

of solvent introduced through a serum cap with a hypodermic syringe. The solution was completely degassed by successively cooling and pumping on the frozen sample. After sealing at the constrictions, the tube was then placed in the quartz Dewar under liquid nitrogen and after placing this in the sample compartment observations regarding polarization could be commenced. Although this method proved highly satisfactory, warm air had to be blown onto the Dewar to keep it from frosting. Since the light beam had to traverse a stream of rising nitrogen bubbles, the intensity fluctuations added to the general noise in the detection system.

(d) Detecting system

Initially, a Du Mont (K - 1292) infrared sensitive photomultiplier tube was used as the detector with an Eldorado photometer as the measuring device. Sensitivity of this arrangement was very low. A matched pair of Kodak Ektron lead sulphide cells, which are highly infrared sensitive, were then used in place of the photo-tube. The measuring circuit was a simple Wheatstone bridge with a direct voltage of about 30 V. across the bridge and the arrangement was cooled for maximum sensitivity as indicated in Figure (5). This circuit proved to be simple but very unstable. Due to the random A.C. components in the network and noises from other sources, the balance point was found to drift so much as to be unserviceable. Accordingly, a mechanically chopped incident light was used and the output signal was fed to an oscilloscope for display. As the wave length of the exciting light was varied, a change of amplitude of the square wave signal on the oscilloscope screen would then indicate emission. A further simplification was to use only one sulphide cell with a resistor in series as in Figure (5b). Other schemes, including a method which was used with

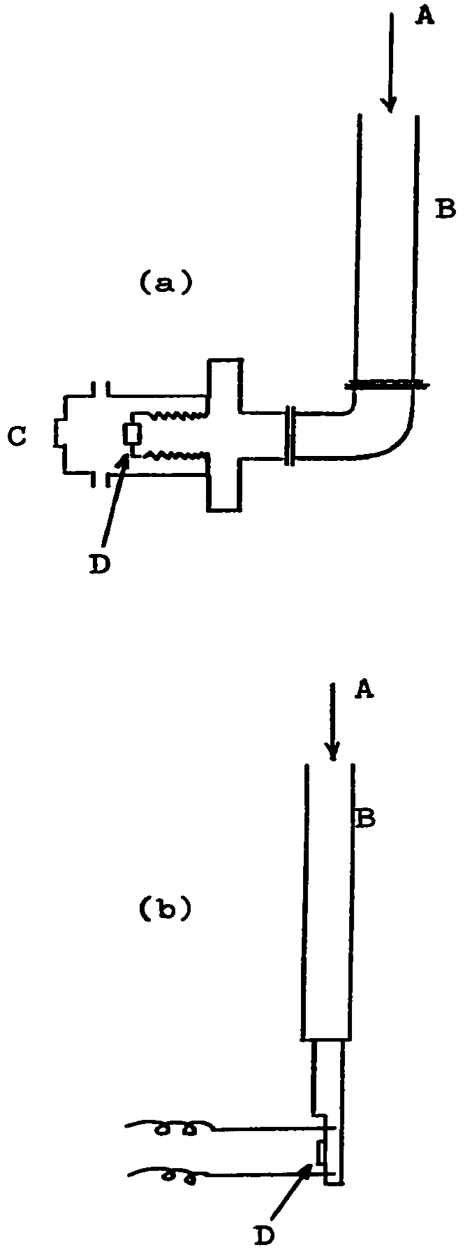


Figure (5)

Sulphide Cells

A: Coolant
B: Copper Tube
C: Quartz Window
D: Sulphide Cell

much success with the carbonium ions (see later section) were tried, but in no case could any detectable emission be obtained from nitroso compounds.

(3) Results:

The absorption spectra of nitrosobenzene and its derivatives are shown in Figures (6 - 17).

It is a well established fact that many doubly-bonded substances such as the azo compounds and those containing imino or nitroso groups, tend more or less to equilibrate between the monomeric and dimeric forms (83) either in solution or in the crystalline state. Nitroso compounds usually exist as dimers (colorless) in the crystalline state and as monomers (colored) in solution. In the case of nitrosobenzene, the degree of association in different solvents was determined by Hammick (84), and the results indicated that it is entirely unimolecular in 0.01M acetic acid solution and 16 % associated in 1.33M carbon disulphide solution. In view of this, the optical density of solutions of varying concentration were taken in order to determine the amount of dimerization in the range of concentration of interest. A departure from Beer's law indicates dimerization, and the determination is depicted in Figure (6).

By way of comparison, the spectra of both aliphatic and aromatic nitroso compounds were taken. The effects of conjugation and substituent groups on the spectra were evident and the pattern of the absorption bands was found to agree with the general conclusions mentioned in the introduction. These are shown in Figures (7) to (12). Due to the extreme instability of trimethyl nitrosomethane, this compound could not be isolated and the long wave length spectrum was taken using the reaction mixture. Various components in this solution absorb intensely in the 3000Å region so that the high frequency nitroso transitions were not obtained.

Figures (13), (14) and (15) show the spectra obtained at various pH levels in aqueous solutions. This determination was made in an effort to see whether the unshared pairs of electrons on the nitrogen or the oxygen were involved in protonation. Since the dimers of these compounds are colorless, the implication is that in this case it is the nitrogen pair that is involved in the dimer bonding. In Figure (14) it can be seen that protonation of the dimethyl amino group in p-nitroso dimethyl aniline does not shift the nitroso peak very much and that the unpaired electrons of the nitroso group may remain unprotonated down to a pH of about 10.0.

The data in these figures is summarized in Table (1). Compound (4) demonstrates the effect of steric crowding, and compounds (2) and (3) show the effect of ring substituents. Compound (3) also shows the effect of high atomic number substitution on the spectral intensity.

It became apparent early in the investigation that nitrosobenzene, at best, emits radiation very poorly. For this reason, 2,4,6 tribromo, and 2,6 dimethyl nitrosobenzene were prepared with the intent of finding whether the heavy atom effect or steric hindrance would improve the fluorescence probability. The near infrared and infrared region were also explored in the case of nitrosobenzene for indications which might increase our understanding of the nature of the 760 mµ band (Figures (16), (17)). For instance, it is possible that this band is, in fact, a harmonic of some vibrational mode belonging to the nitroso group, or

Table (1)

Absorption Characteristics of Nitroso Compounds

Compounds	$\lambda_{max.}$ (mμ)	ϵ
(1) Nitrosobenzene	760 304 282	40 3300 5500
(2) N, N dimethyl nitroso aniline	720 402	75 3500
(3) 2,4,6, tribromo nitrosobenzene	790 330 313	26
(4) 2,6 dimethyl nitrosobenzene	815 315 292	
(5) Trimethyl nitrosomethane	680	
(6) $K_2NO(SO_3)_2$	550 305 255	13.6

that there may be another optical band further to the red of the 760 mμ band. Information of this nature is vital not only in the assignment of the band, but also in finding the optical region of fluorescence for these compounds. The intensity of the infrared vibrational transitions on Figure (16) may be judged relative to the 760 mμ band, where under the experimental conditions, this latter transition has a value of 120 on the same scale of $-\text{Log } I/I_o$.

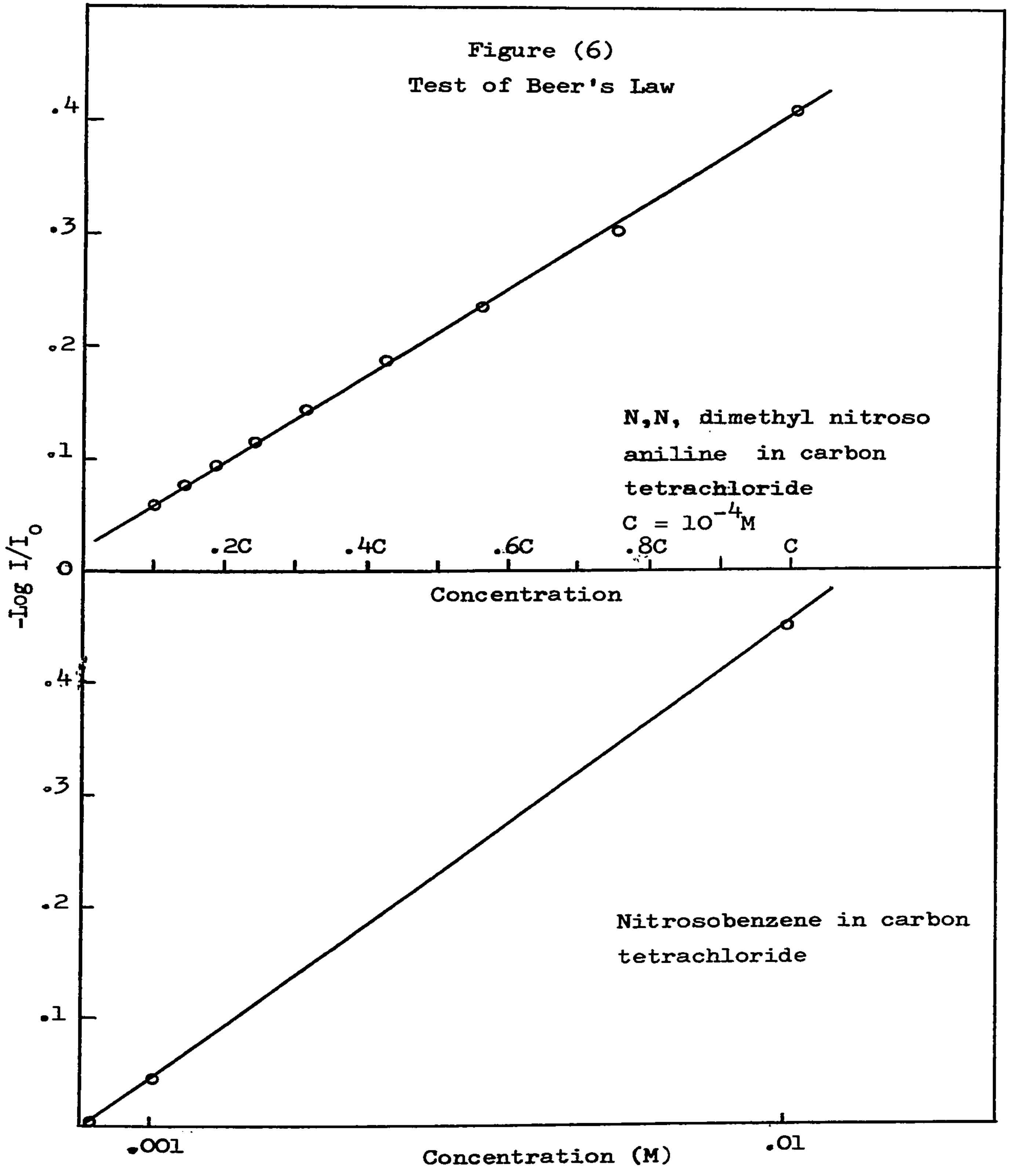


Figure (6)
Test of Beer's Law

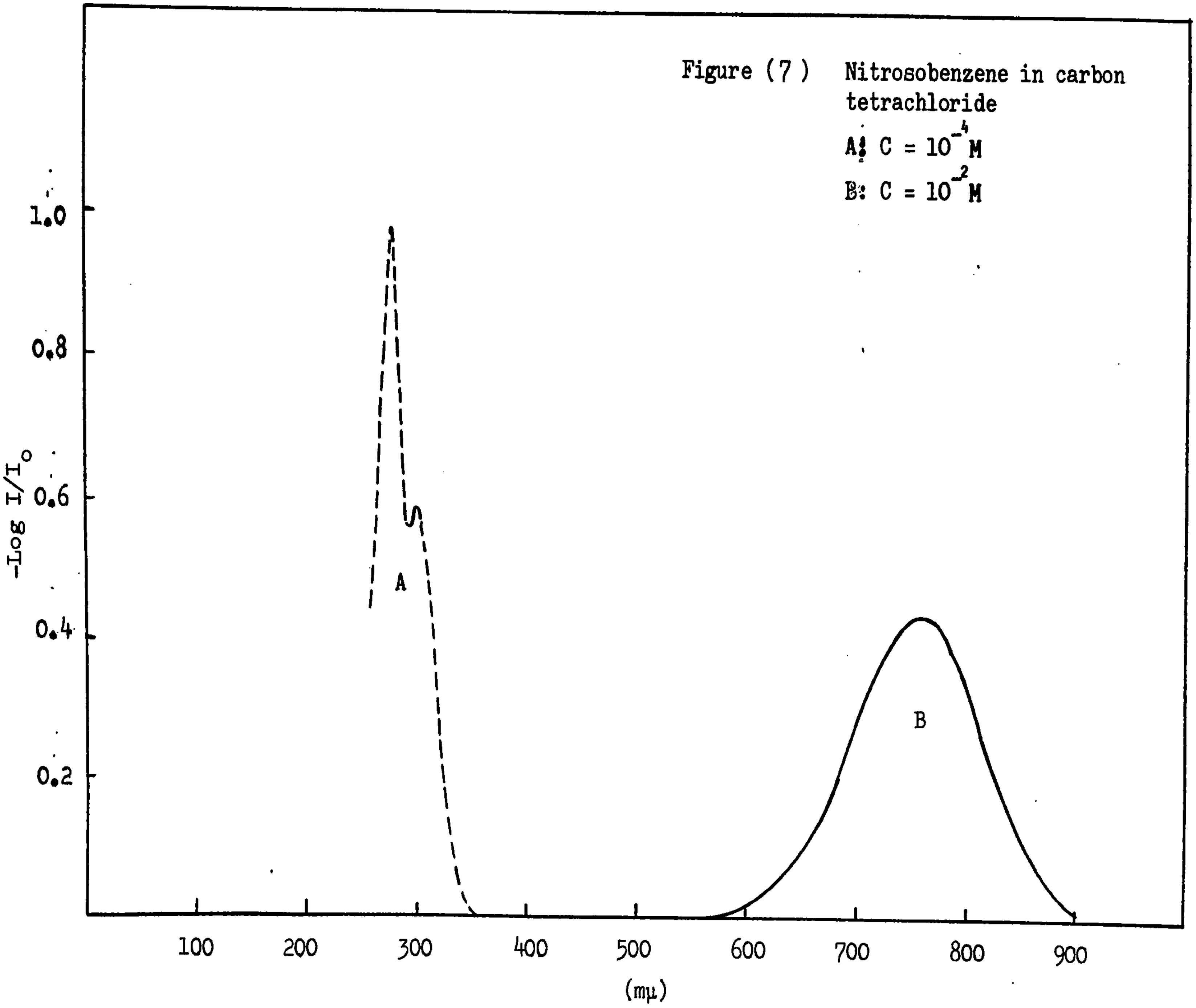


Figure (7) Nitrosobenzene in carbon tetrachloride

A: $C = 10^{-4}$ M

B: $C = 10^{-2}$ M

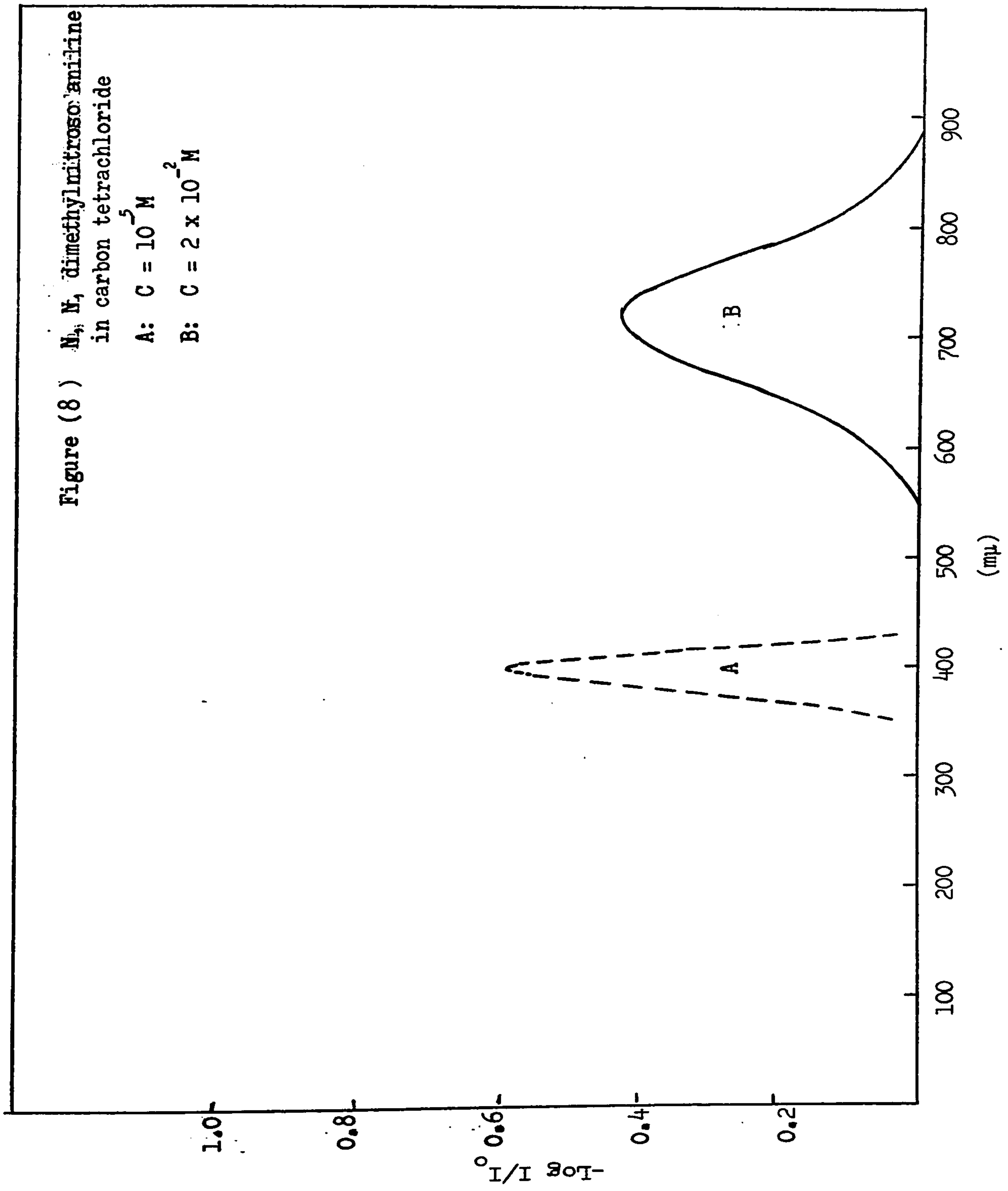


Figure (8) N, N, dimethylnitroso aniline in carbon tetrachloride

A: $C = 10^{-5}$ M

B: $C = 2 \times 10^{-2}$ M

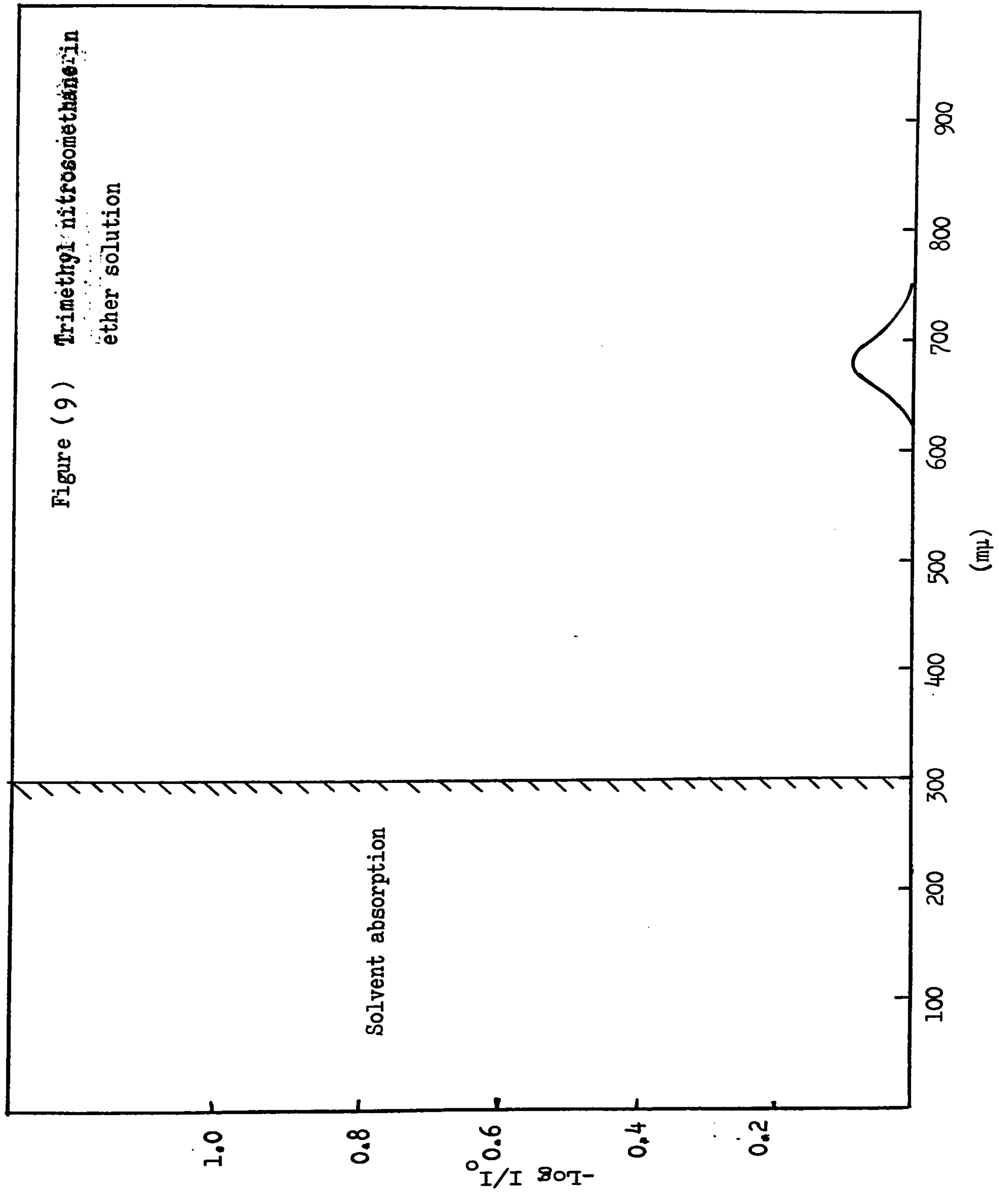


Figure (9) Trimethyl nitrosomethane in ether solution

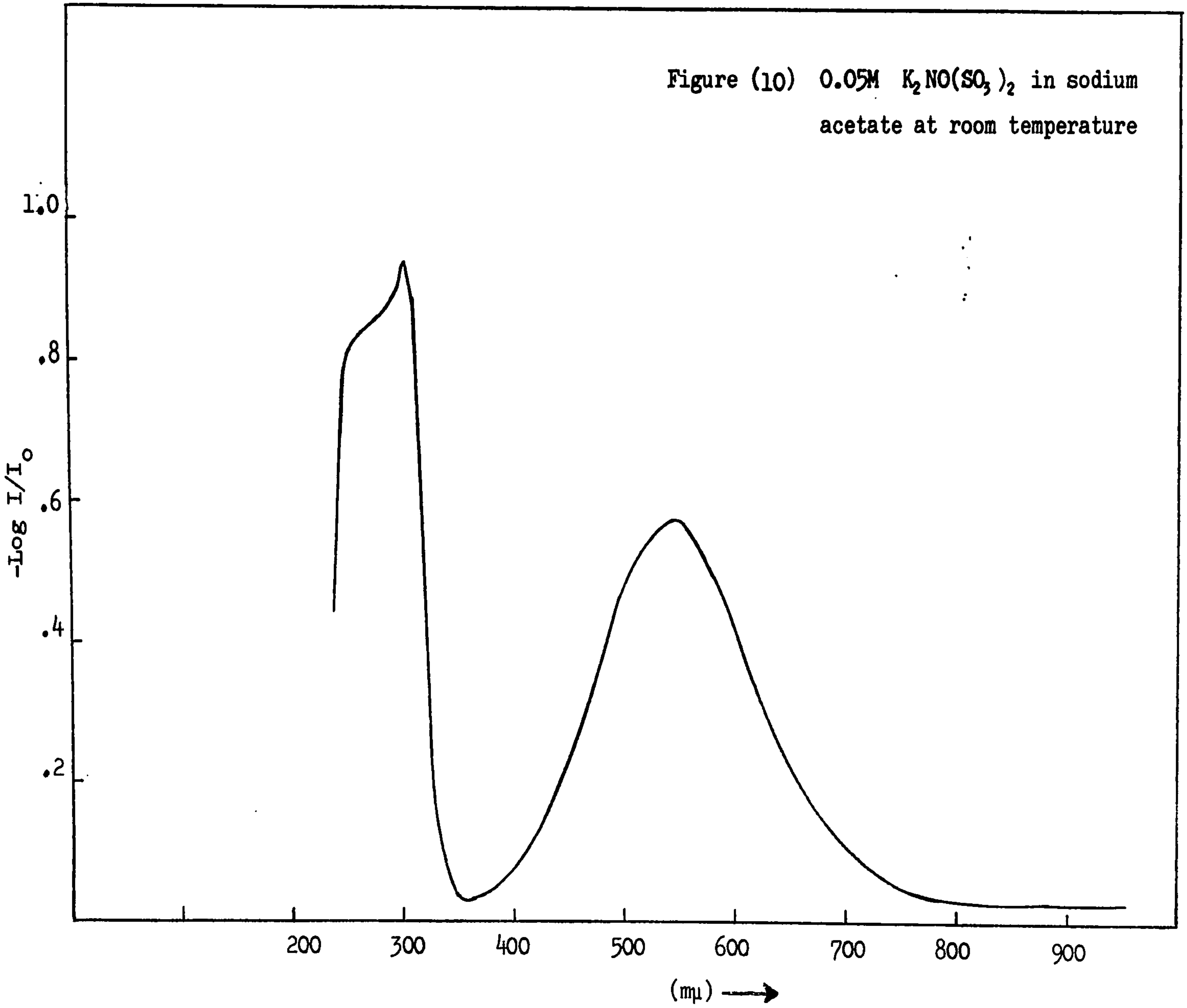


Figure (10) 0.05M $K_2NO(SO_3)_2$ in sodium acetate at room temperature

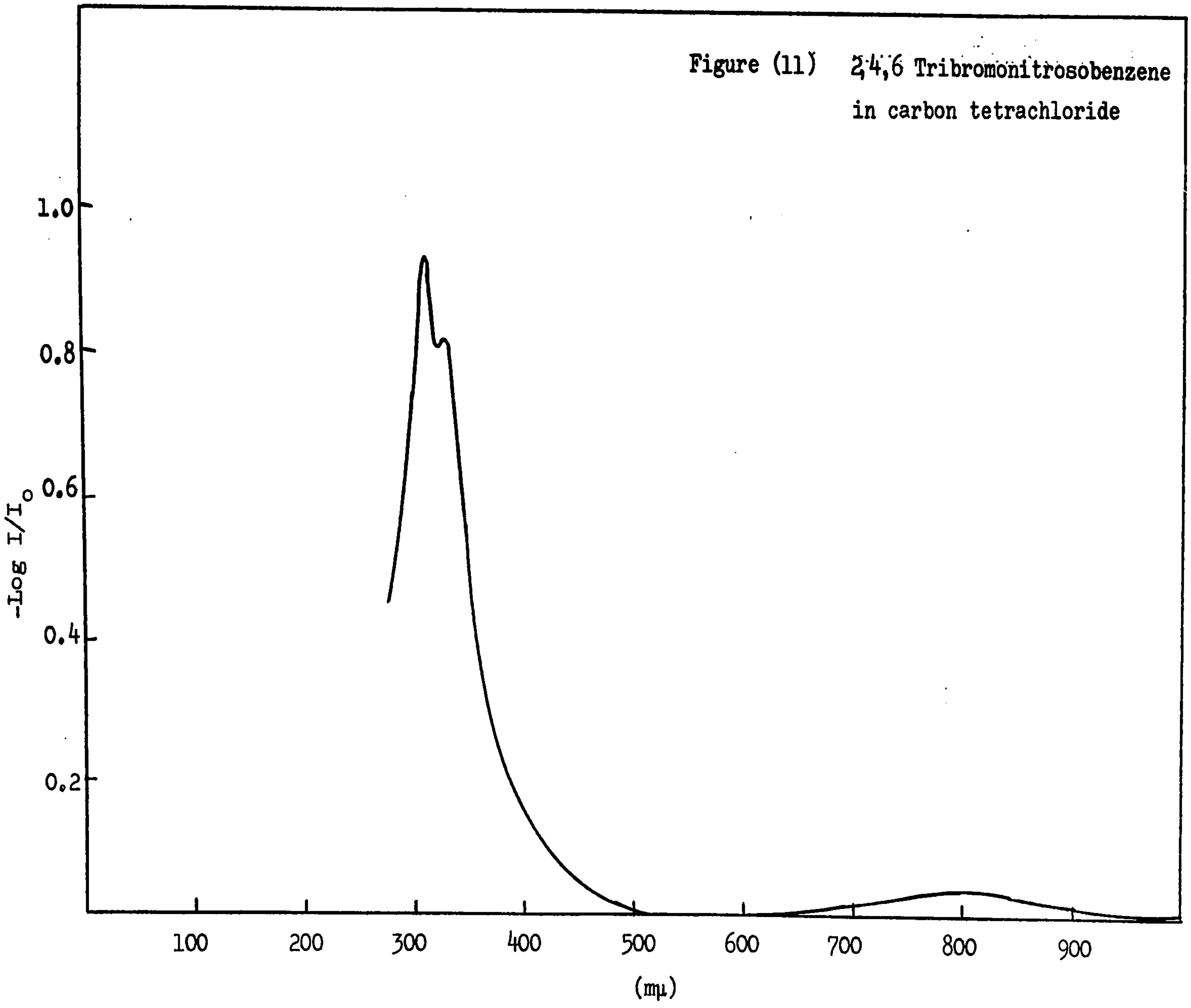


Figure (11) 2,4,6 Tribromonitrosobenzene in carbon tetrachloride

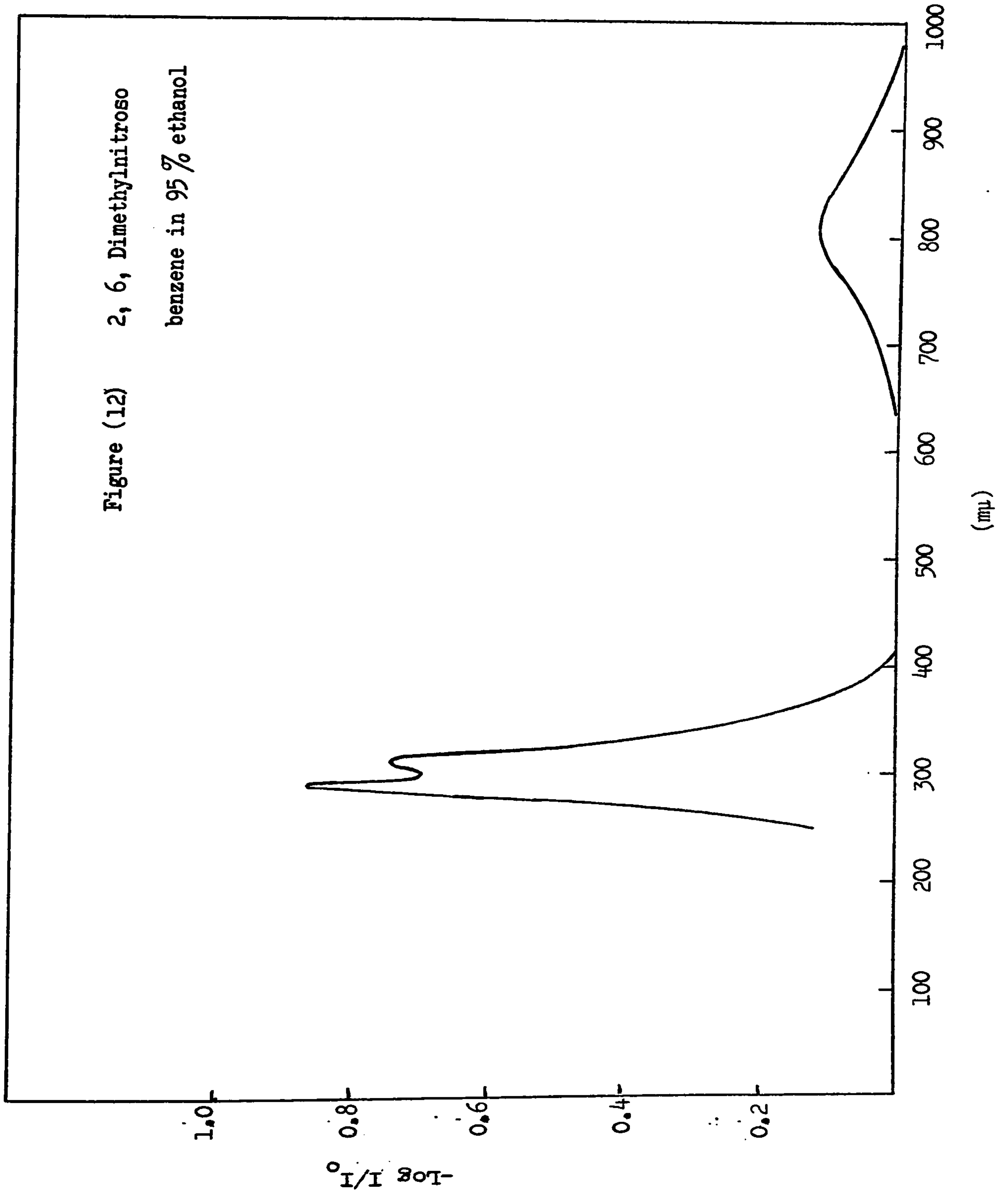


Figure (12) 2, 6, Dimethylnitroso benzene in 95% ethanol

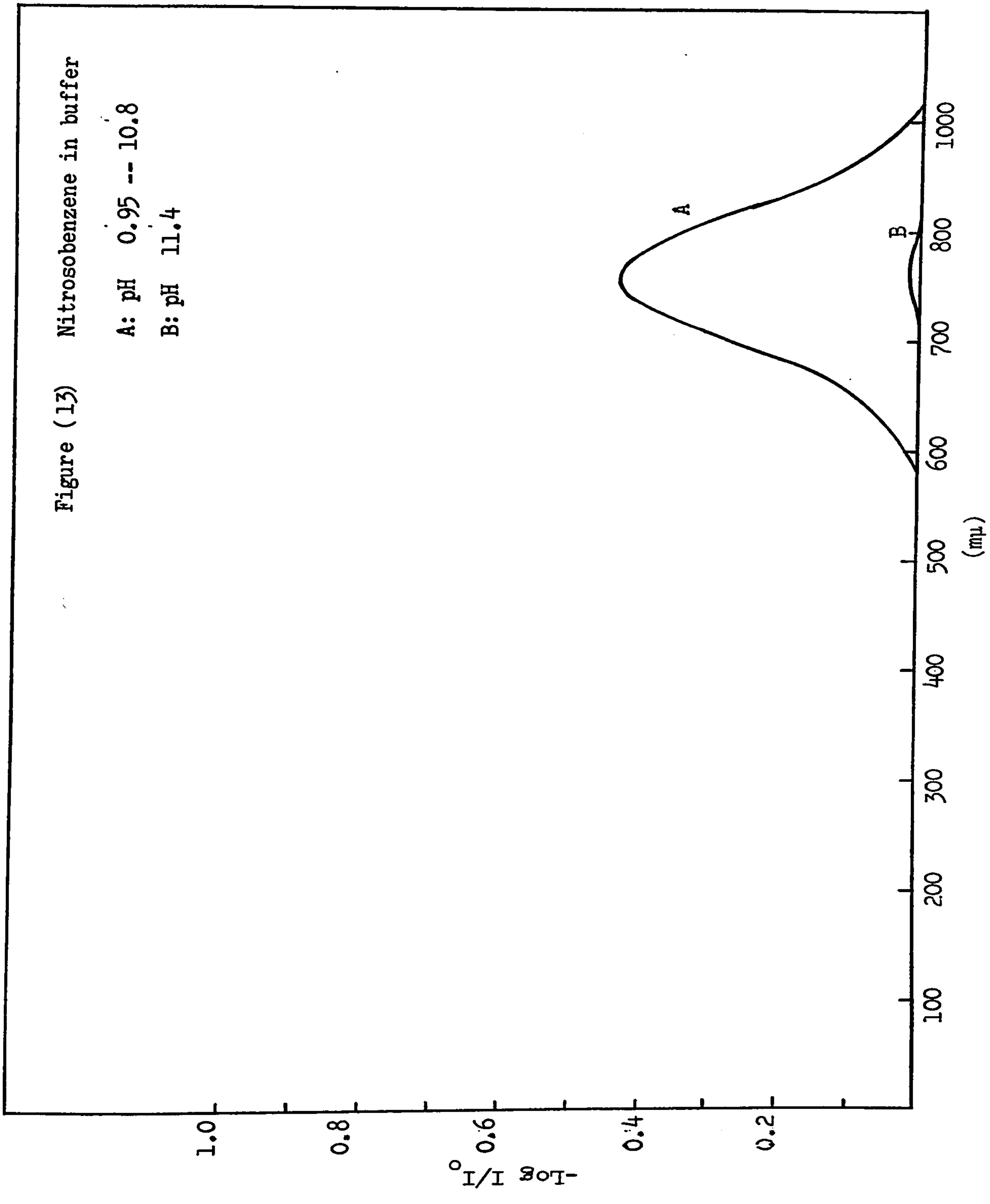


Figure (13) Nitrosobenzene in buffer

A: pH 0.95 -- 10.8

B: pH 11.4

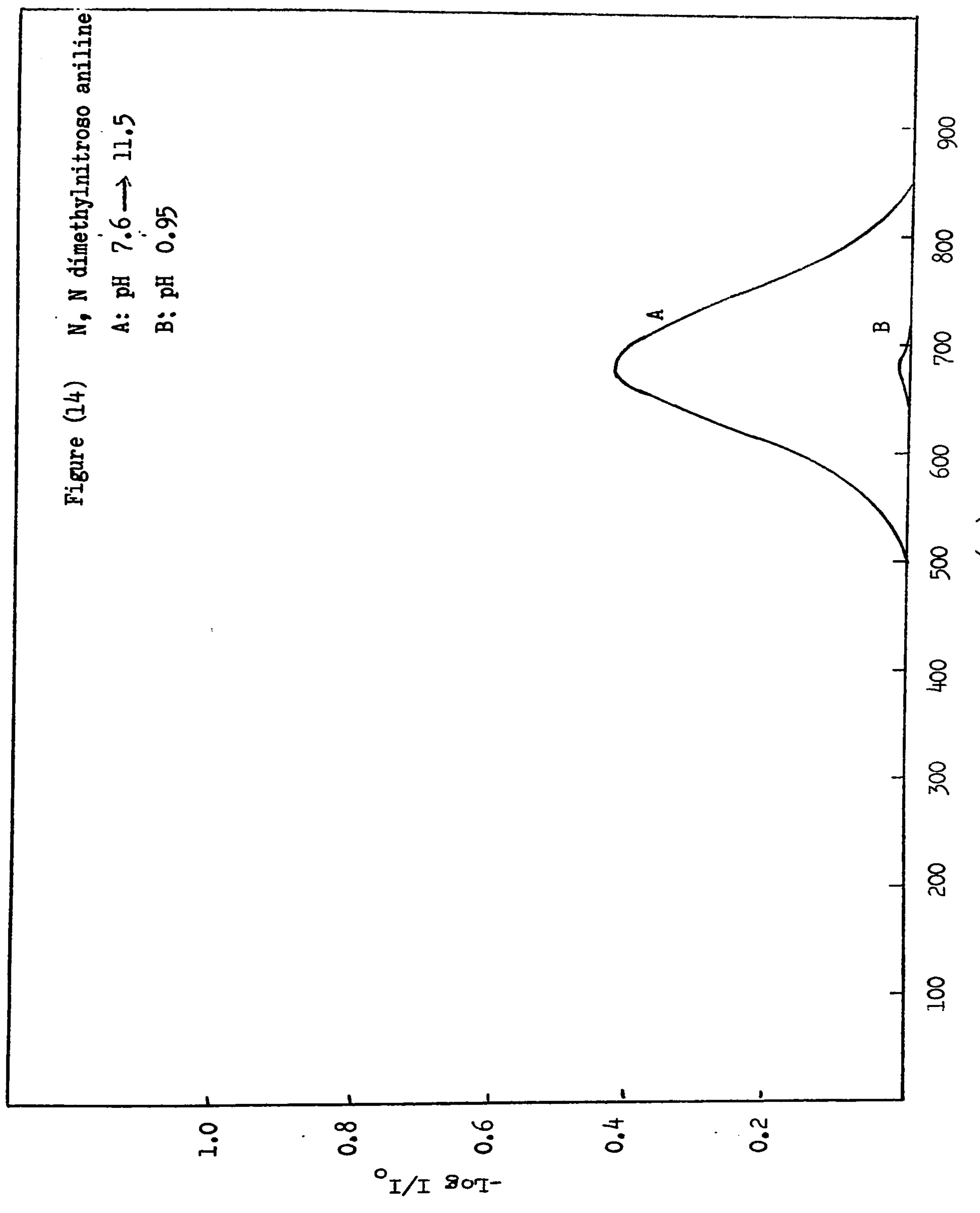


Figure (14) N, N dimethylnitroso aniline

A: pH 7.6 ⟶ 11.5

B: pH 0.95

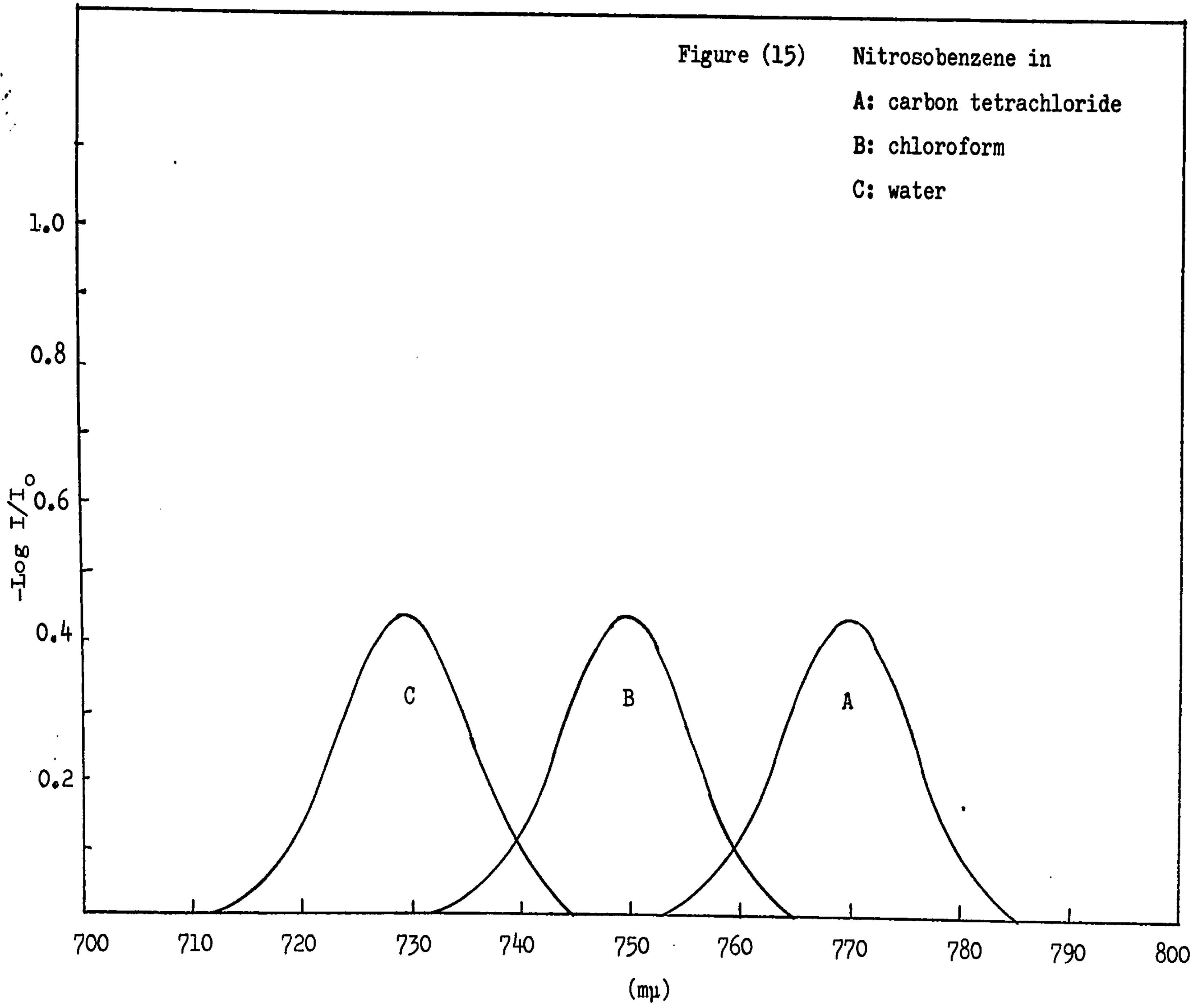


Figure (15) Nitrosobenzene in
A: carbon tetrachloride
B: chloroform
C: water

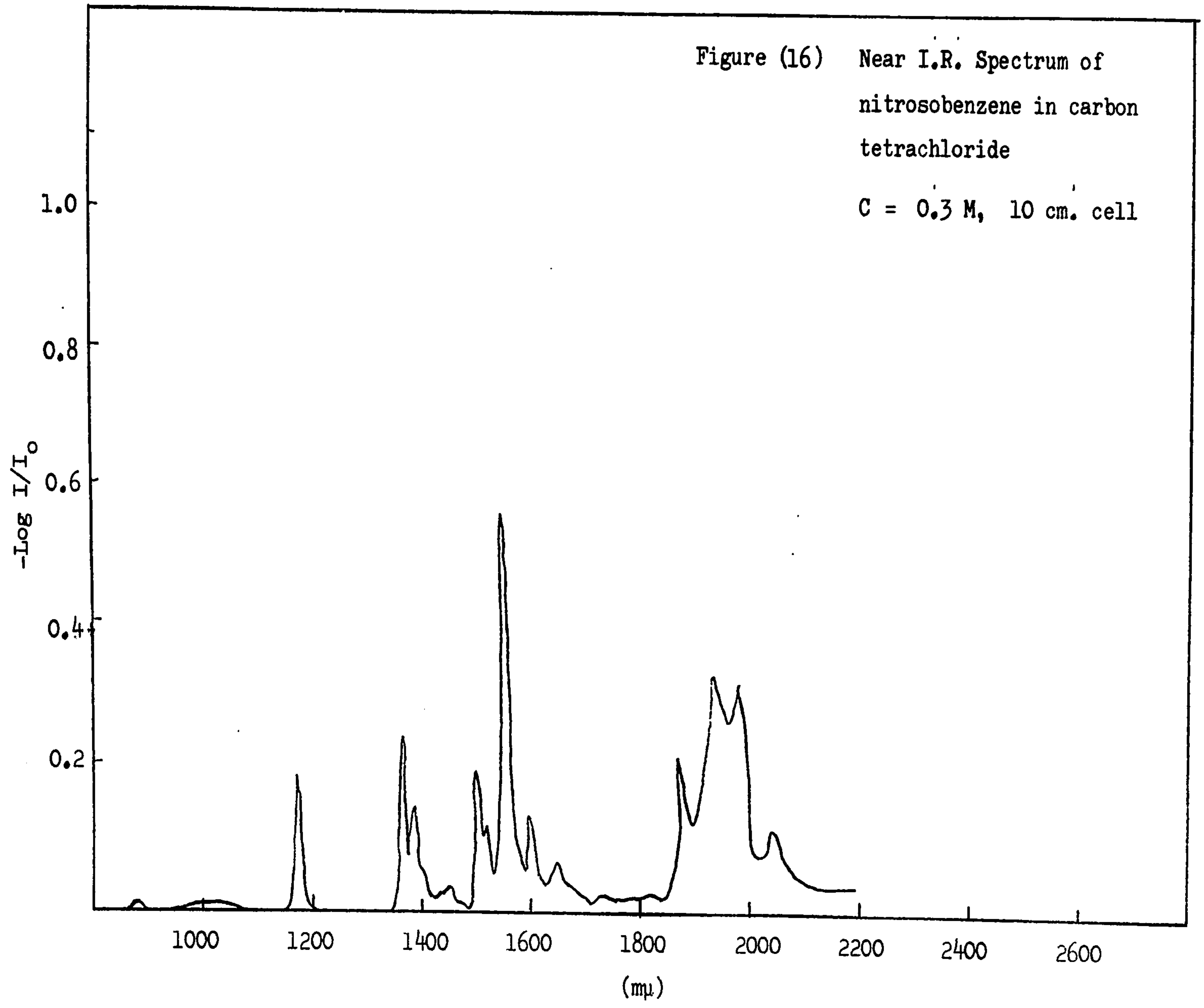


Figure (16) Near I.R. Spectrum of nitrosobenzene in carbon tetrachloride

C = 0.3 M, 10 cm. cell

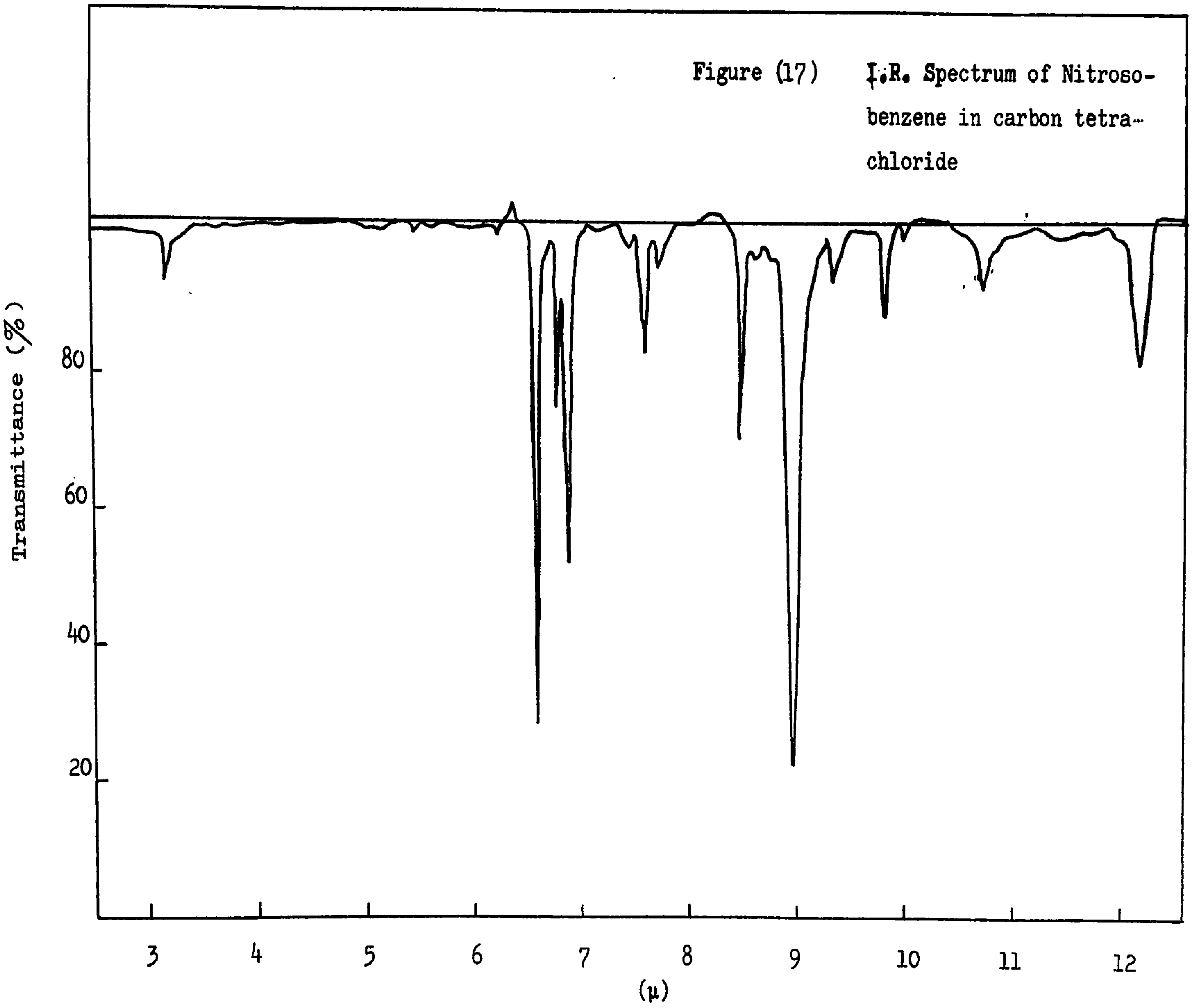


Figure (17) I.R. Spectrum of Nitrosobenzene in carbon tetrachloride

Part B: Triaryl Carbonium Ions

(1) Materials:

(a) Triphenyl methyl carbinol (T.P.M.)

Matheson Coleman and Bell commercial grade triphenyl methyl carbinol was fractionally crystallized from benzene until a constancy of absorption and a melting point of 158°C (uncorrected) was attainted (lit. 161°C).

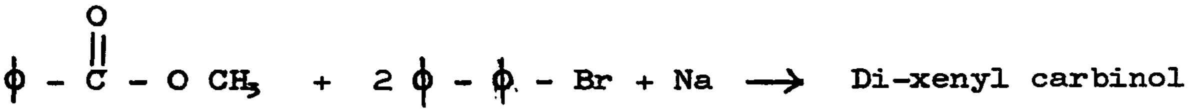
(b) Mono xenyl carbinol (Mono)

The starting material for this compound was p-phenyl benzophenone, which was prepared by the Perrier modification of the Friedel-Craft method (60). A mixture of benzoyl chloride was carefully heated together with fresh aluminum chloride. The solid of this addition complex was dissolved in carbon disulphide and biphenyl was added. The mixture was warmed to complete the reaction and then cooled thoroughly in an ice bath. The precipitate was washed with a small quantity of fresh solvent and dissolved in dilute hydrochloric acid solution. p-Phenyl benzophenone was extracted with ether and recrystallized from ethanol.

The resulting ketone was treated with phenyl magnesium bromide (Arapahoe Chemicals, Inc., 3M solution in ether). The desired product was isolated and recrystallized from hot acetic acid solution. Melting point of the final product was 103-105°C. There are several melting points for this material quoted in the literature. Bowden (62) gives the value of 106°C, which is close to that obtained in this present research. This is the most recent value in the literature.

(c) Di-xenyl carbinol (Di)

Two methods can be used for this preparation. One is by route of the Grignard reaction using commercially available diphenyl benzophenone and the other by a sodium condensation method described by A.A. Mortin (63). In essence, the latter method consists of refluxing a mixture of diphenylbromide, methyl benzoate and sodium metal for a period of several hours. The desired product is extracted after acidification with dilute hydrochloric acid. The reaction may be represented as



$$\phi - \overset{O}{\overset{\|}{C}} - O\,CH_3 \;+\; 2\,\phi - \phi - Br + Na \longrightarrow \text{Di-xenyl carbinol}$$

Both methods were successful and the product was crystallized from hot acetic acid solution. The melting point of the product was 152-153°C (uncorrected) (151°C reported (63)).

(d) Trixenyl carbinol (Tri)

The best procedure was found to be sodium condensation of diethyl carbonate with diphenyl bromide (63). The melting point of the purified product was 209-211°C (uncorrected) (207°C reported (63)).

(e) Salts of the carbinol

Each of the carbinols can be transformed to their salts after the method of Harmon (64). Small amounts of their fluoroborate salts were prepared by dissolving the carbinol in propionic anhydride and reacting the mixture with fluoroboric acid. The product slowly decomposes.

(f) Solvent

The concentrated sulphuric acid, syrupy phosphoric acid and glacial acetic acid used were reagent grade. Other solvents were reagent grade, dried over sodium wire.

(2) Absorption Spectra:

The instruments have already been discussed. Absorption spectra of the carbinols were taken in a variety of acidic solvents. For triphenyl methyl carbinol (T.P.M.) the best solvent was found to be 95 % sulphuric acid in which T.P.M. is completely ionized (21). The spectra of mono, di, and tri xenyl derivatives were taken in a 20 % sulphuric acid and 80 % acetic acid mixtures. In glacial acetic acid alone, the carbinols do not ionize at all. Comparison of the spectra in different solvents shows that there was a small solvent shift but the essential features of the spectra were the same.

However, in 95 % sulphuric acid, the spectra of mono, di, and tri xenyl methyl carbonium ions were found to vary with time as shown in Figures (20) and (21). The change was not reversible indicating that the phenomenon is not simple ion association. When an aged solution of the carbinols in sulphuric acid was poured into a saturated sodium chloride solution under ice cooling, it was possible to obtain a gelatinous precipitate. This precipitate possesses properties very distinct from the original carbinol, and similar to those of the sulphonic acids. They dissolved readily in water or concentrated ammonium hydroxide, in which the carbinols are insoluble. Also the observed melting points (235°C) were far too high for the original carbinols. The I.R. spectrum (Figure (23)) of the precipitate showed absorption in the region usually associated with the $-SO_3H$ functional group (65); asymmetric and symmetric stretching of the $-SO_2$ group occurs in the 1260—1150 cm.$^{-1}$ and 1080—1010 cm.$^{-1}$ ranges, respectively, and stretching of S–O in the region of

700—600 cm.$^{-1}$. Sodium fusion with lead acetate test indicated the existence of sulphur in the precipitate and it also gave a positive p-toluidine test for sulphonic acid derivates. More striking was the fact that this precipitate dissolved in 95 % sulphuric acid gave a spectrum of the aged solution of carbinol in sulphuric acid immediately. Solutions of the fluoroborate salts of the carbinols in anhydrous acetonitrile showed spectra which were indefinitely stable and similar to the initial spectra of carbinols in sulphuric acid. It is evident that the two spectra in sulphuric acid correspond to two distinct species, the initial one, the carbonium ion, and the other due to a sulphonated carbonium ion.

All intensities are expressed in terms of transition moments, in Å units, according to the formula:

$$\overrightarrow{q} = (9.17 \times 10^{-4} \int \epsilon \, d \log_{10} \lambda)^{1/2}$$

where $\int \epsilon \, d \log_{10} \lambda$ is the area under the absorption curve when ϵ is plotted against $\log_{10} \lambda$ (32). All absorption curves were determined in duplicate except in the case of T.P.M. in 95 % sulphuric acid. The highly hygroscopic nature of the solvent in the latter case necessitated repeated measurements until reproducible values of transition moments were obtained. The amount of sulphuric acid necessary to effect complete ionization of mono, di and tri xenyl carbinols in acetic-sulphuric acid mixtures was found to be approximately 20% by volume.

(3) Polarization Determination:

The arrangement for polarization determination was essentially the same as indicated in Figure (3). The individual carbinols were dissolved in syrupy phosphoric acid and cooled to form rigid glasses at -130°C in liquid nitrogen and ethanol slurries. The glasses were clear and uniform. No difficulty with air oxidation was experienced so that the samples could be prepared in open quartz tubes immediately before use.

The output of the Hanovia Mercury Xenon compact arc was passed through a Bausch and Lomb 250 mm. monochromator. The intensity of the beam was modulated at twice the line frequency since the arc was powered directly from the mains. In this way, any emission process of life time short enough to follow the modulated exciting light appears as a sinusoidal voltage at the detector with a voltage amplitude proportional to the intensity of the emission. Long lived phosphorescence would not be detected. The emergent beam from the monochromator was reflected from a stack of quartz microscope cover slips at a Brewster's angle in such a manner as to give a vertically-oriented electric plane of polarization.

Fluorescence from the sample was detected at 90° to the propagation direction of the incident beam using a Du Mont 1292 infrared sensitive photomultiplier tube with maximum response at 860 mμ. This fluorescence was detected through an adjustable Polaroid which could be oriented to transmit the vertical or horizontal components of the electric vector of the fluorescence.

This system was particularly susceptible to pickup of coherent electromagnetic radiation. Accordingly, the power supply for the photo-tube was constructed from batteries and shielded so that pickup was reduced to the level below the limit of detection of the capacitively coupled Tetronix 805 oscilloscope on its most sensitive range (½ mv per cm.)

Because of imperfections in the optical filtering system, it was necessary to measure the voltage readings of blank samples before determination of the emission at each setting of the analysing Polaroid. The polarization ratio was then taken for each 5mμ throughout the absorption spectrum. The absorption spectrum was again taken after emission measurements to be sure that no photodecomposition had occurred. The results are shown in Figures (32) to (35). The polarization ratios are depicted by the dashed curves. Ratios greater than 1.0 correspond to parallel transitions.

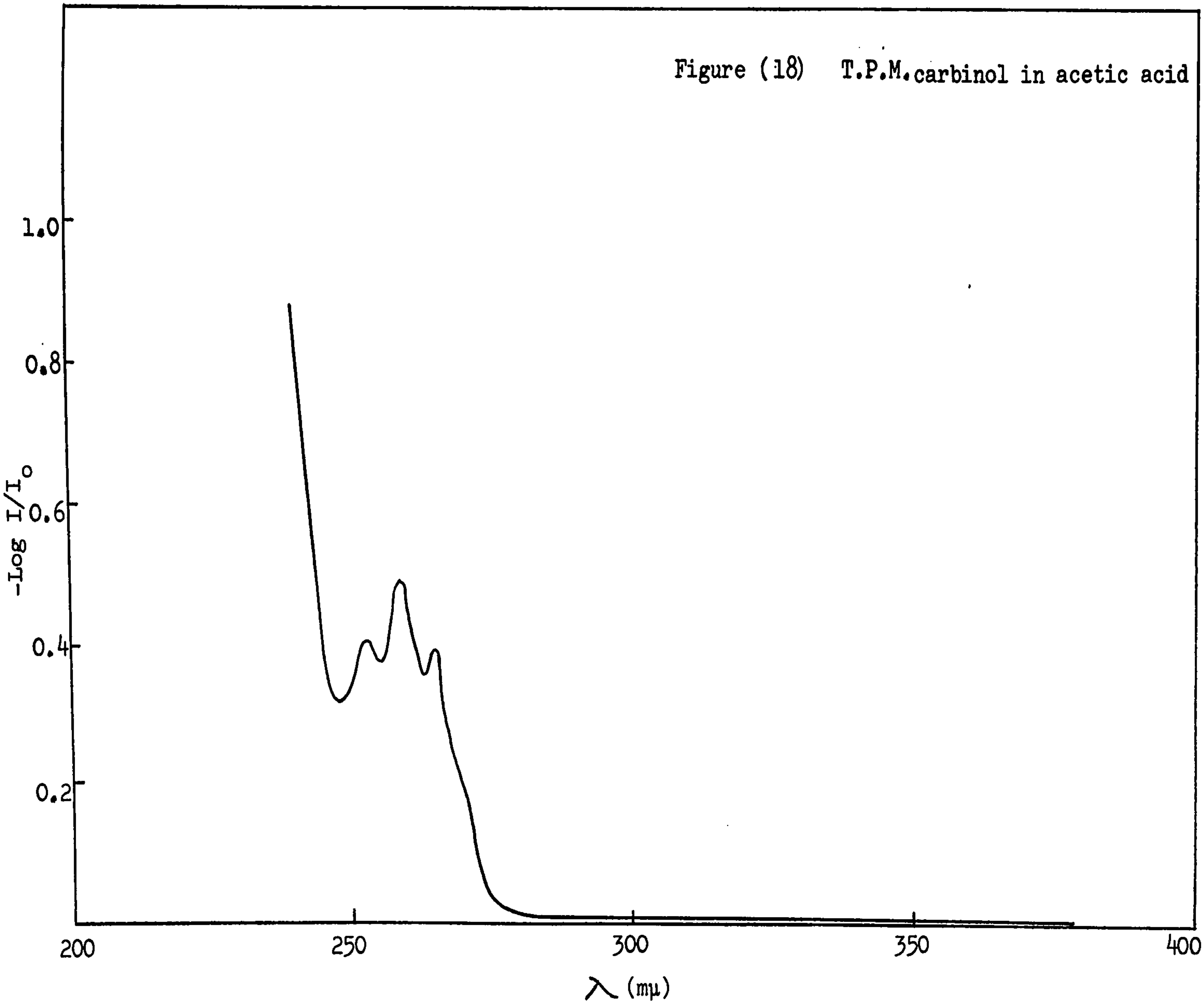


Figure (18) T.P.M.carbinol in acetic acid

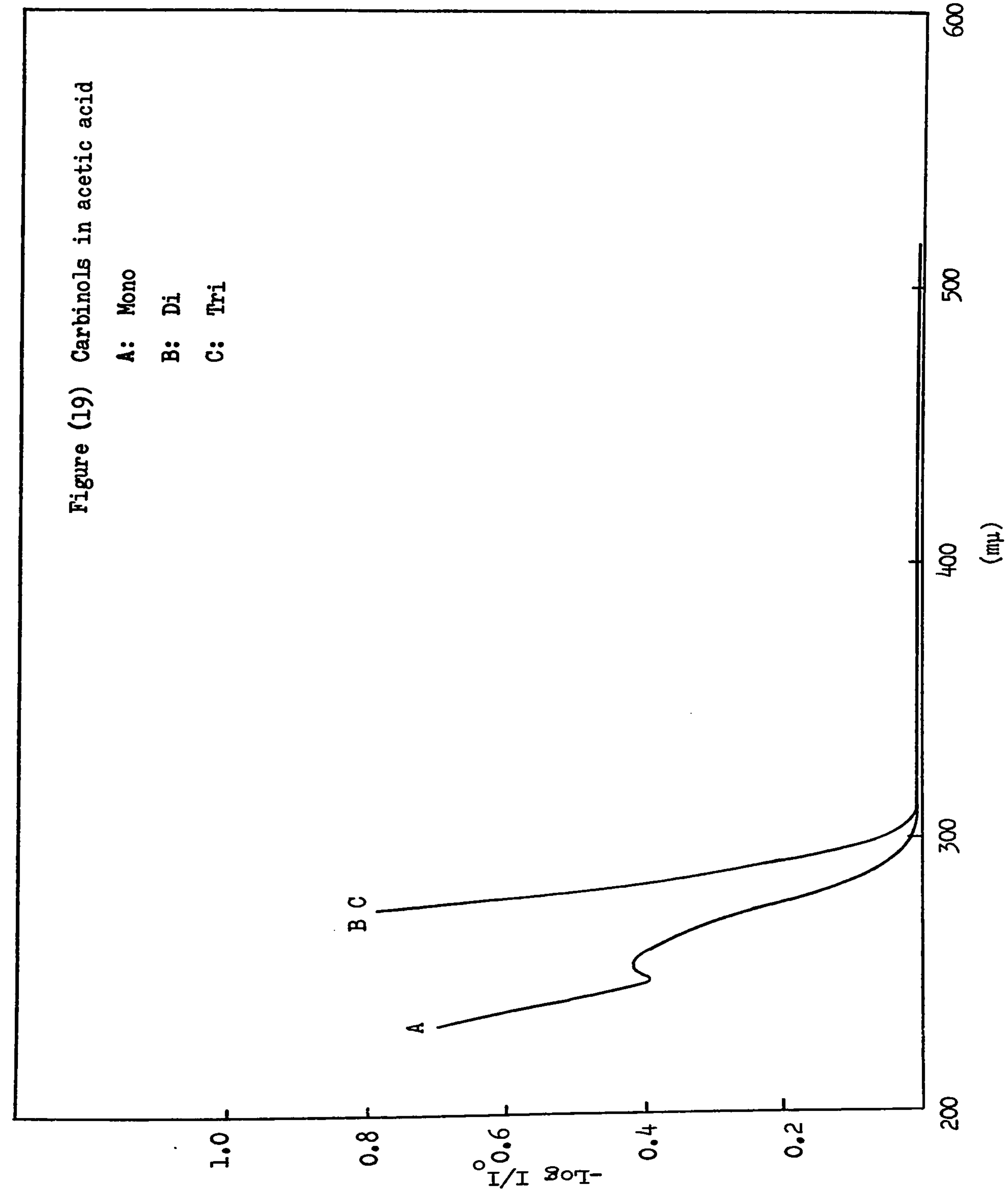


Figure (19) Carbinols in acetic acid

A: Mono

B: Di

C: Tri

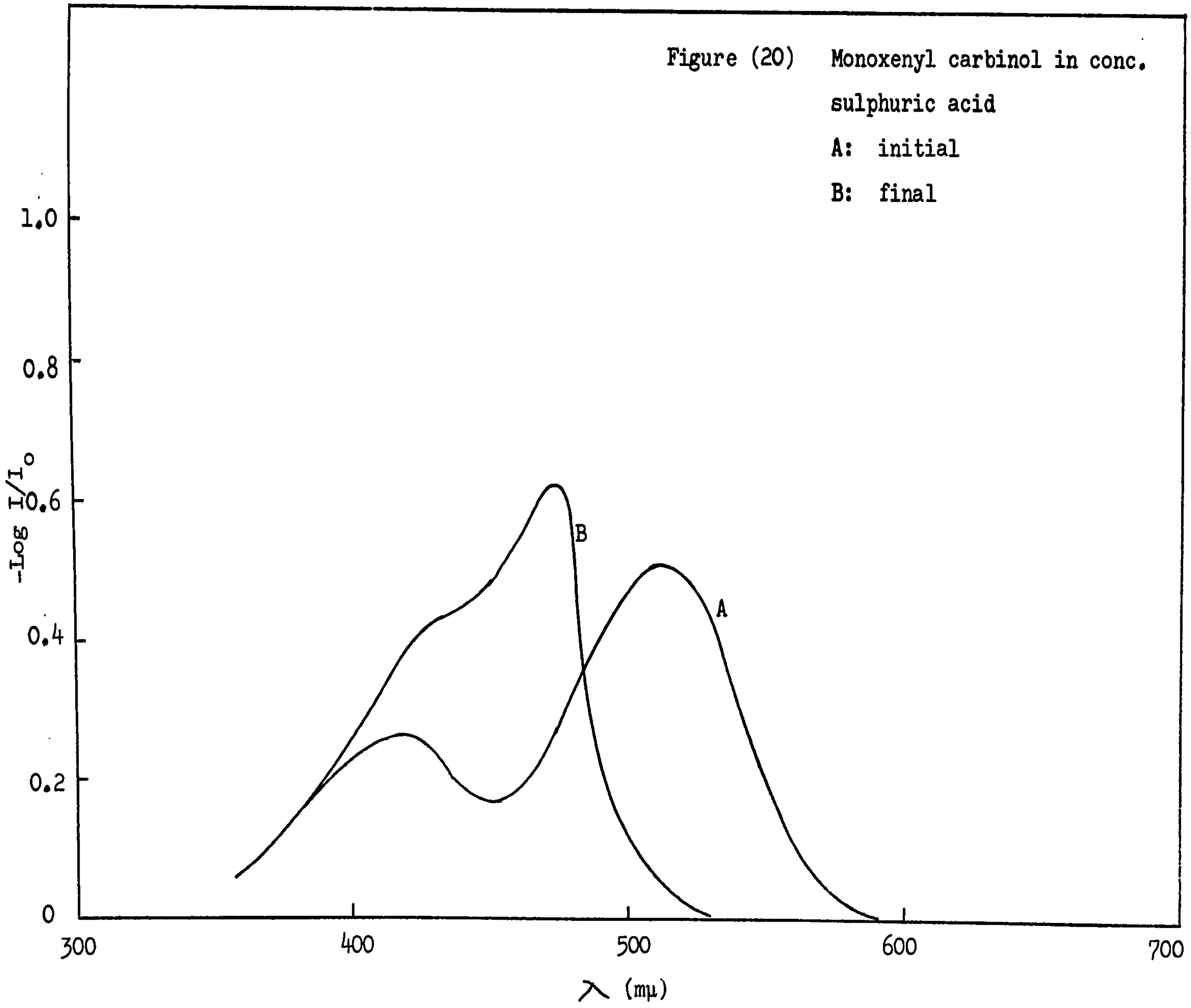


Figure (20) Monoxenyl carbinol in conc. sulphuric acid

A: initial

B: final

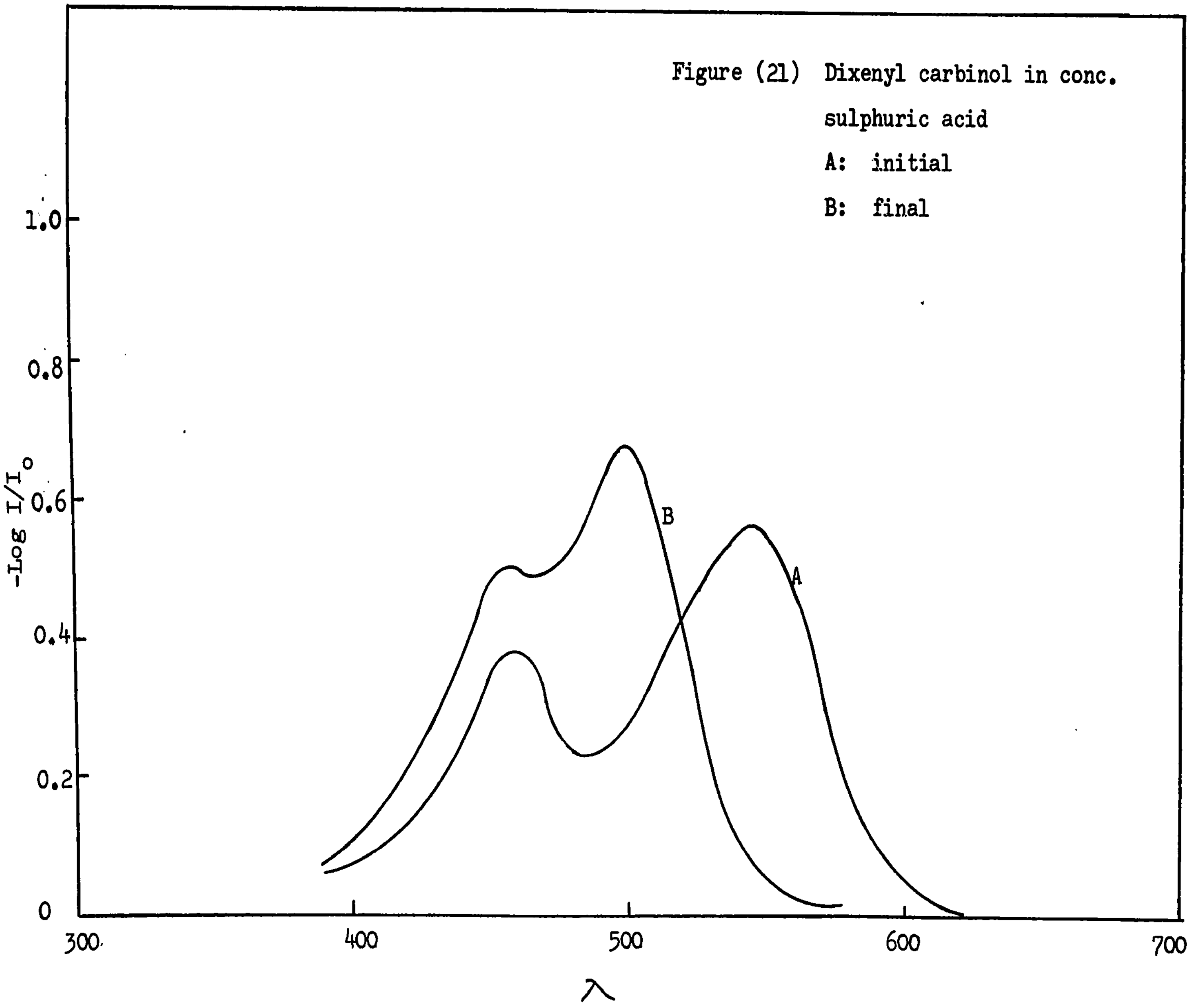


Figure (21) Dixenyl carbinol in conc. sulphuric acid

A: initial

B: final

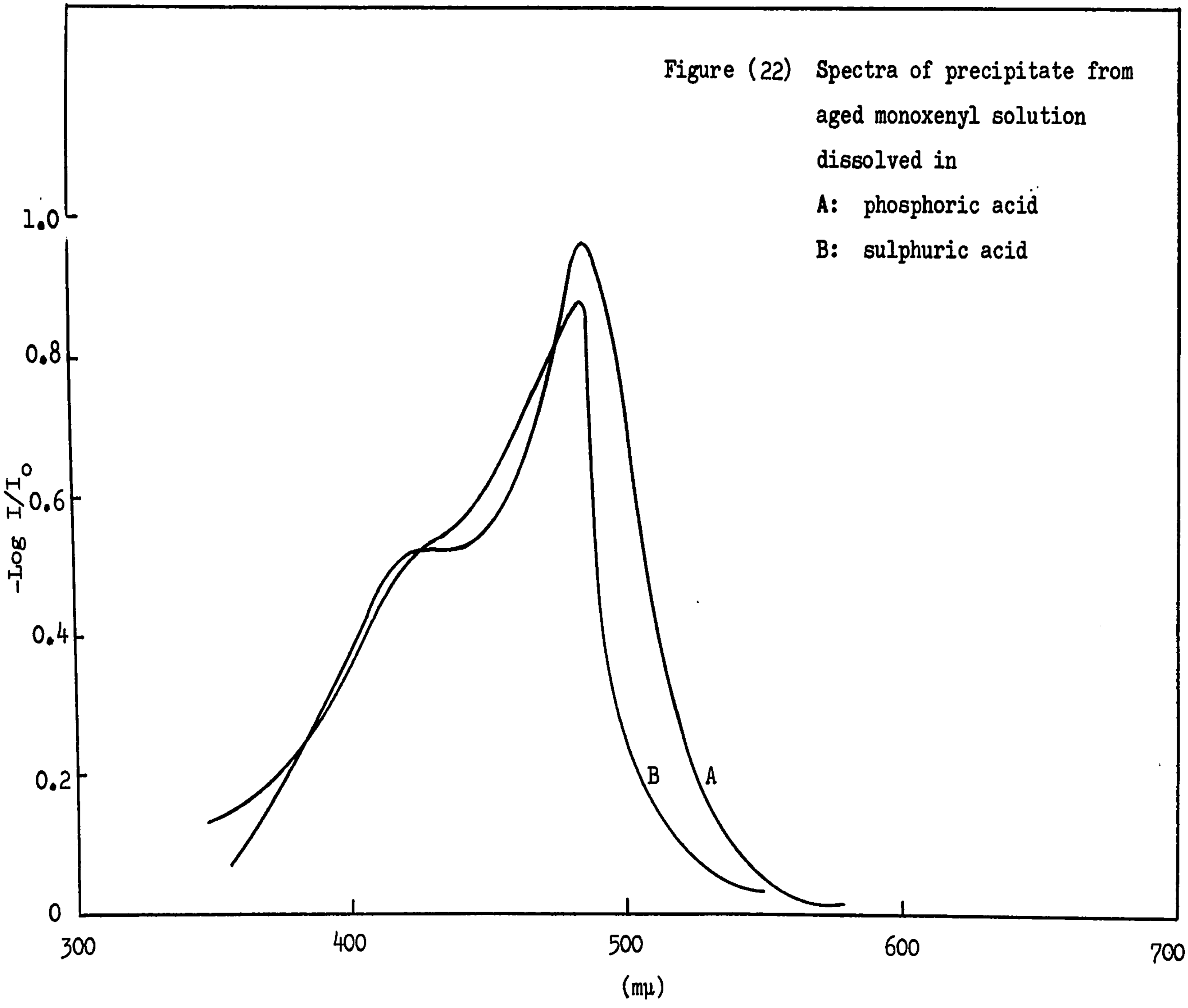


Figure (22) Spectra of precipitate from aged monoxenyl solution dissolved in

A: phosphoric acid

B: sulphuric acid

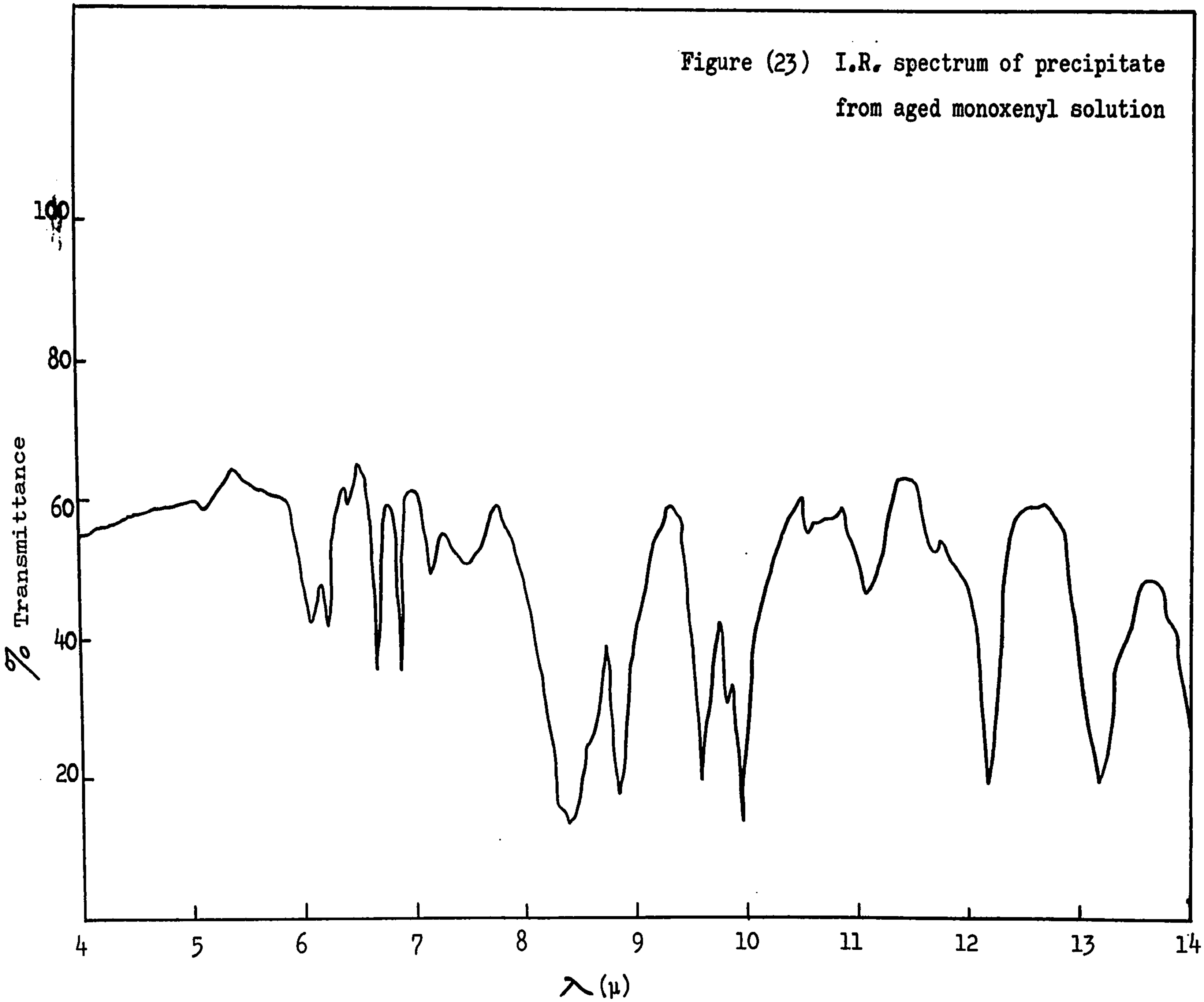


Figure (23) I.R. spectrum of precipitate from aged monoxenyl solution

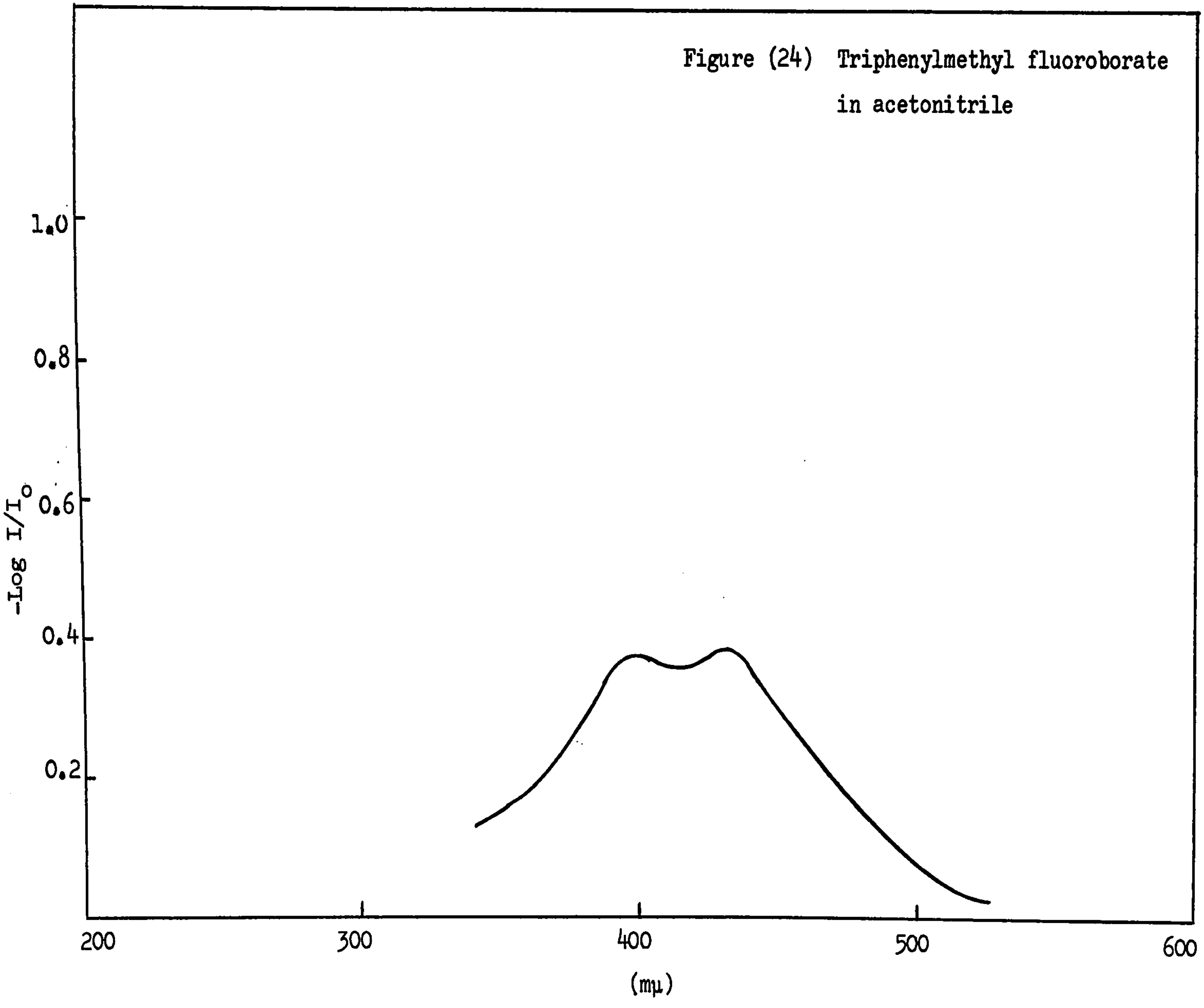


Figure (24) Triphenylmethyl fluoroborate in acetonitrile

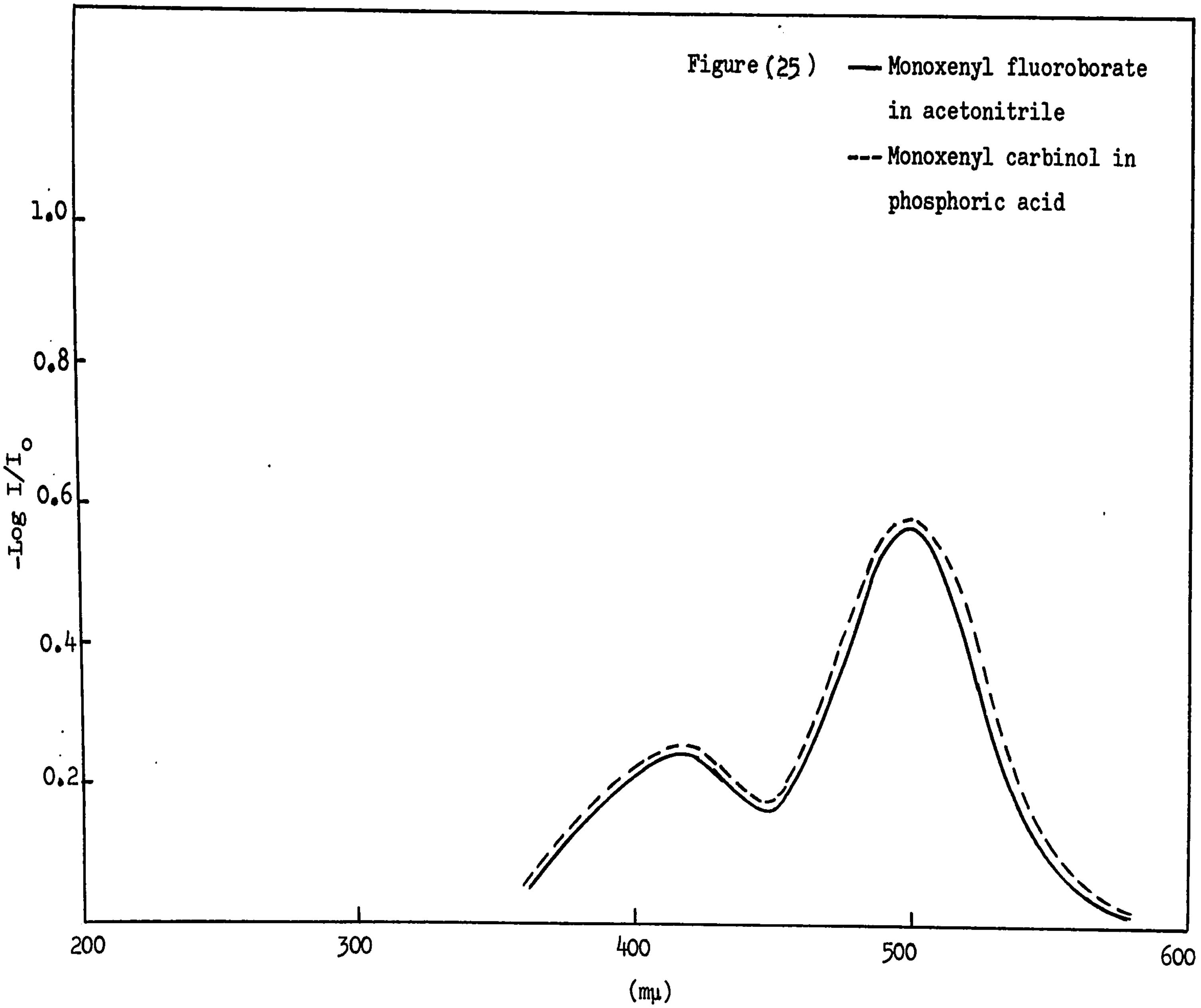


Figure (25)

—— Monoxenyl fluoroborate in acetonitrile
--- Monoxenyl carbinol in phosphoric acid
1.0
0.8
0.6
0.4
0.2
$-\text{Log } I/I_o$
200
300
400
500
600
(mμ)

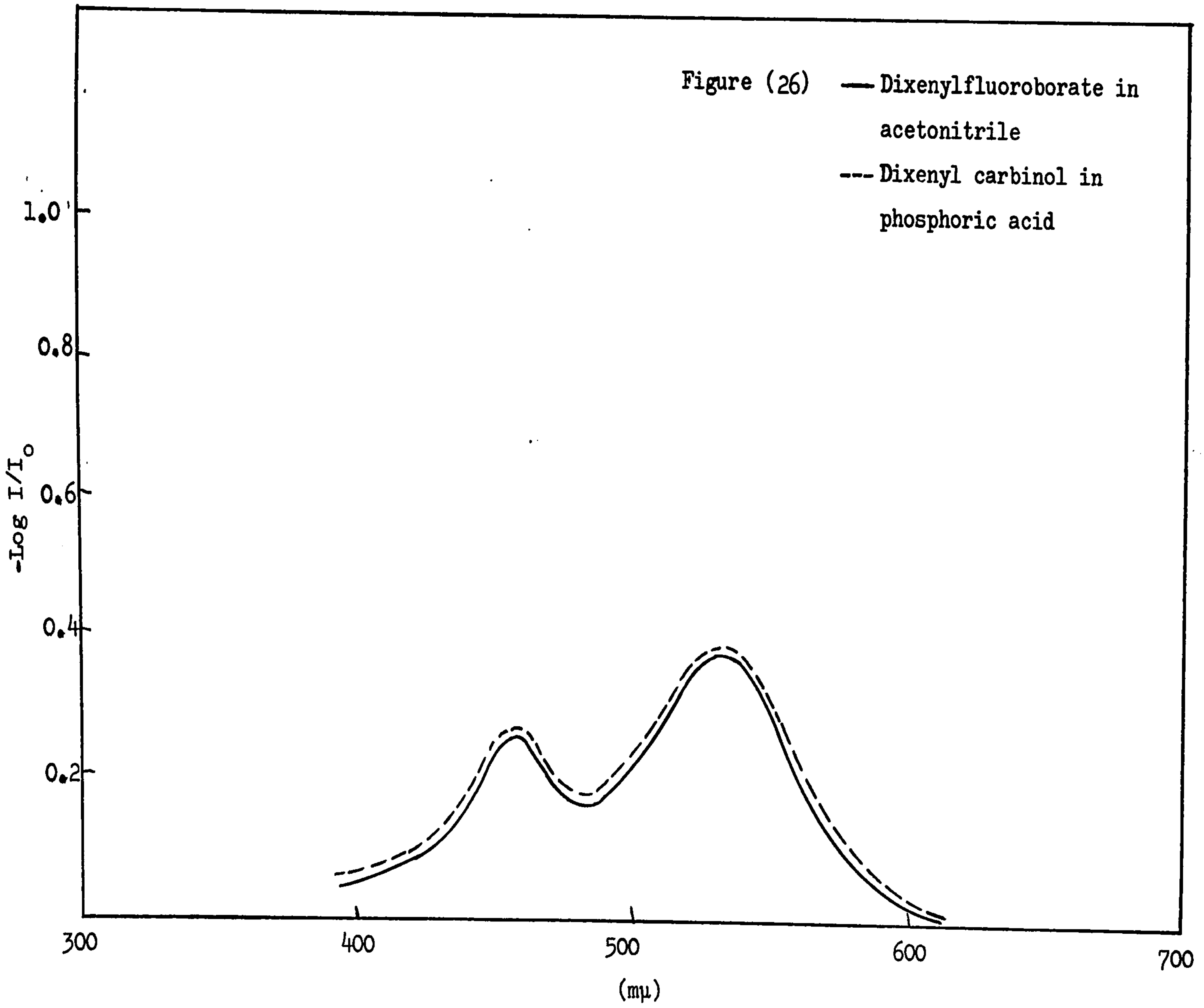


Figure (26)

—— Dixenylfluoroborate in acetonitrile
--- Dixenyl carbinol in phosphoric acid
-Log I/I$_o$
1.0
0.8
0.6
0.4
0.2
300
400
500
600
700
(mμ)

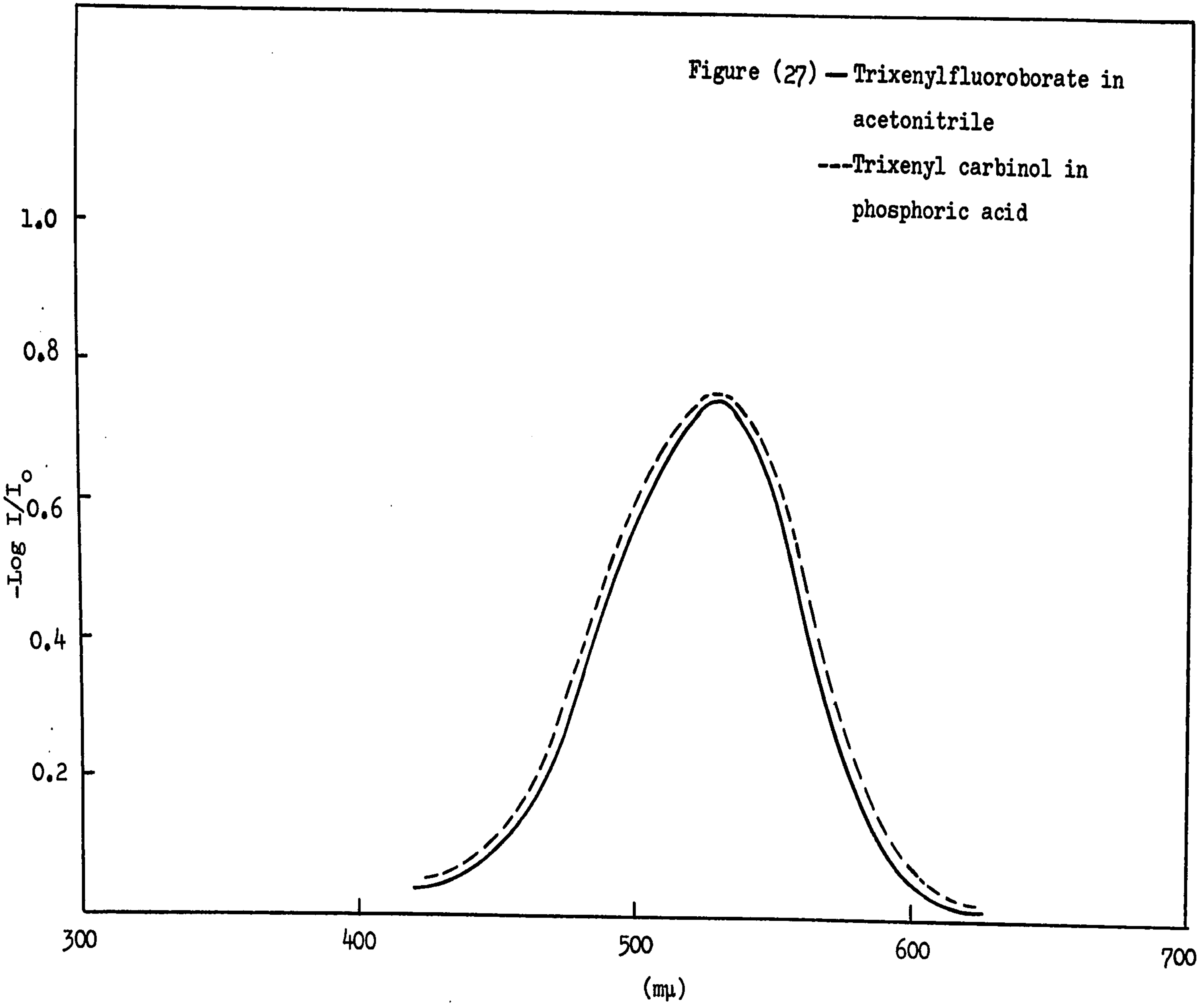


Figure (27) — Trixenylfluoroborate in acetonitrile

---Trixenyl carbinol in phosphoric acid

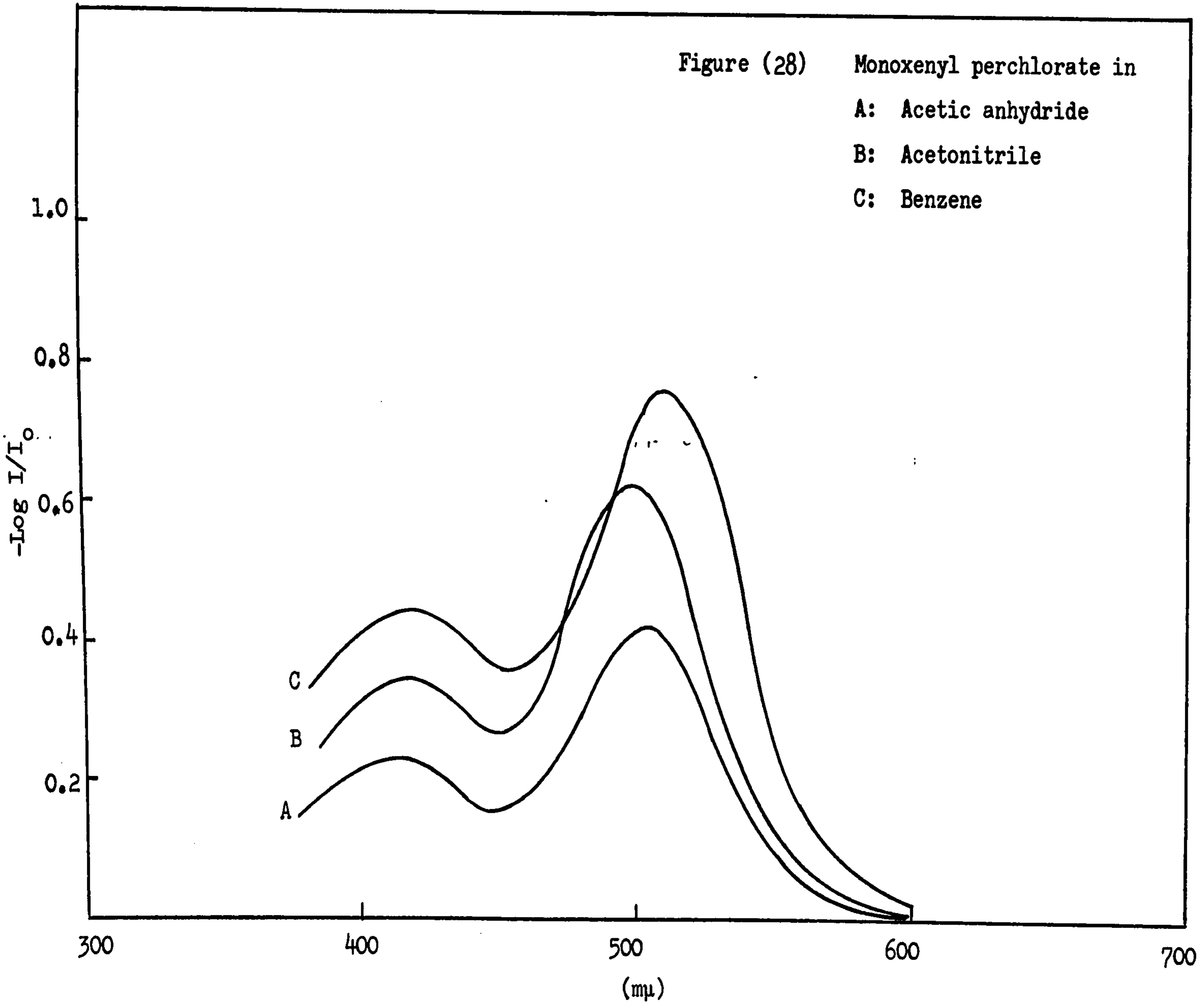


Figure (28) Monoxenyl perchlorate in

A: Acetic anhydride

B: Acetonitrile

C: Benzene

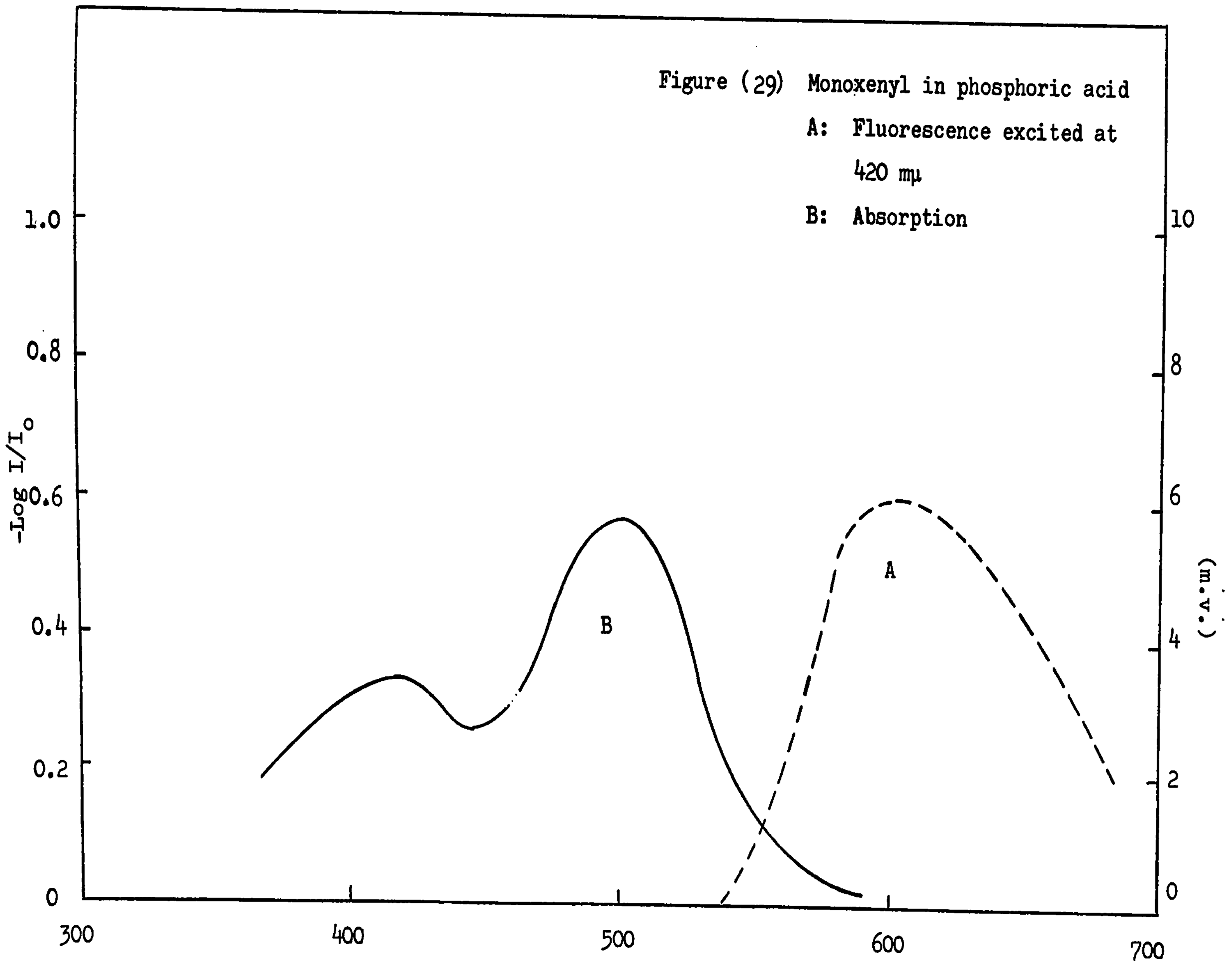


Figure (29) Monoxenyl in phosphoric acid

A: Fluorescence excited at 420 mμ

B: Absorption

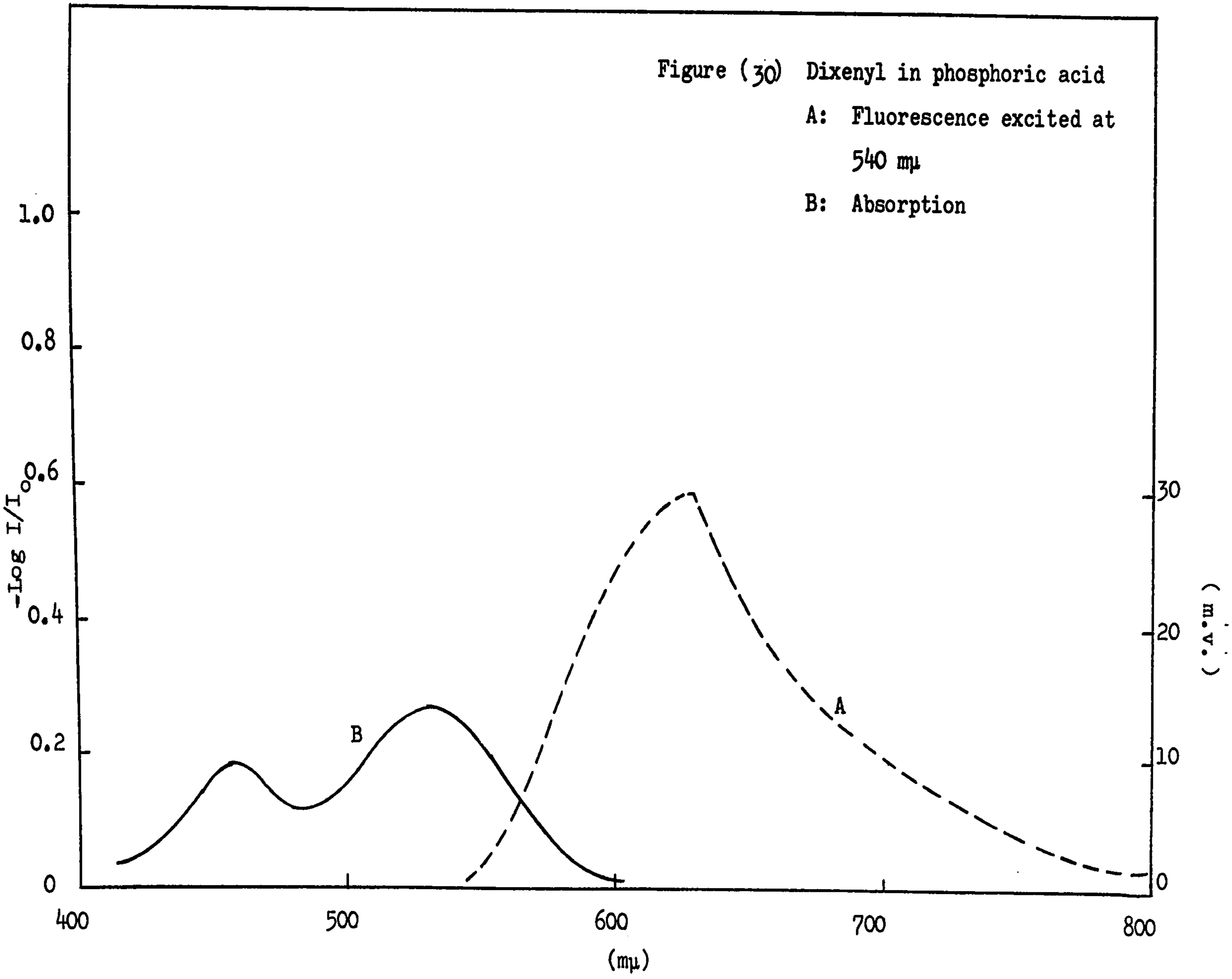


Figure (30) Dixenyl in phosphoric acid

A: Fluorescence excited at 540 mμ

B: Absorption

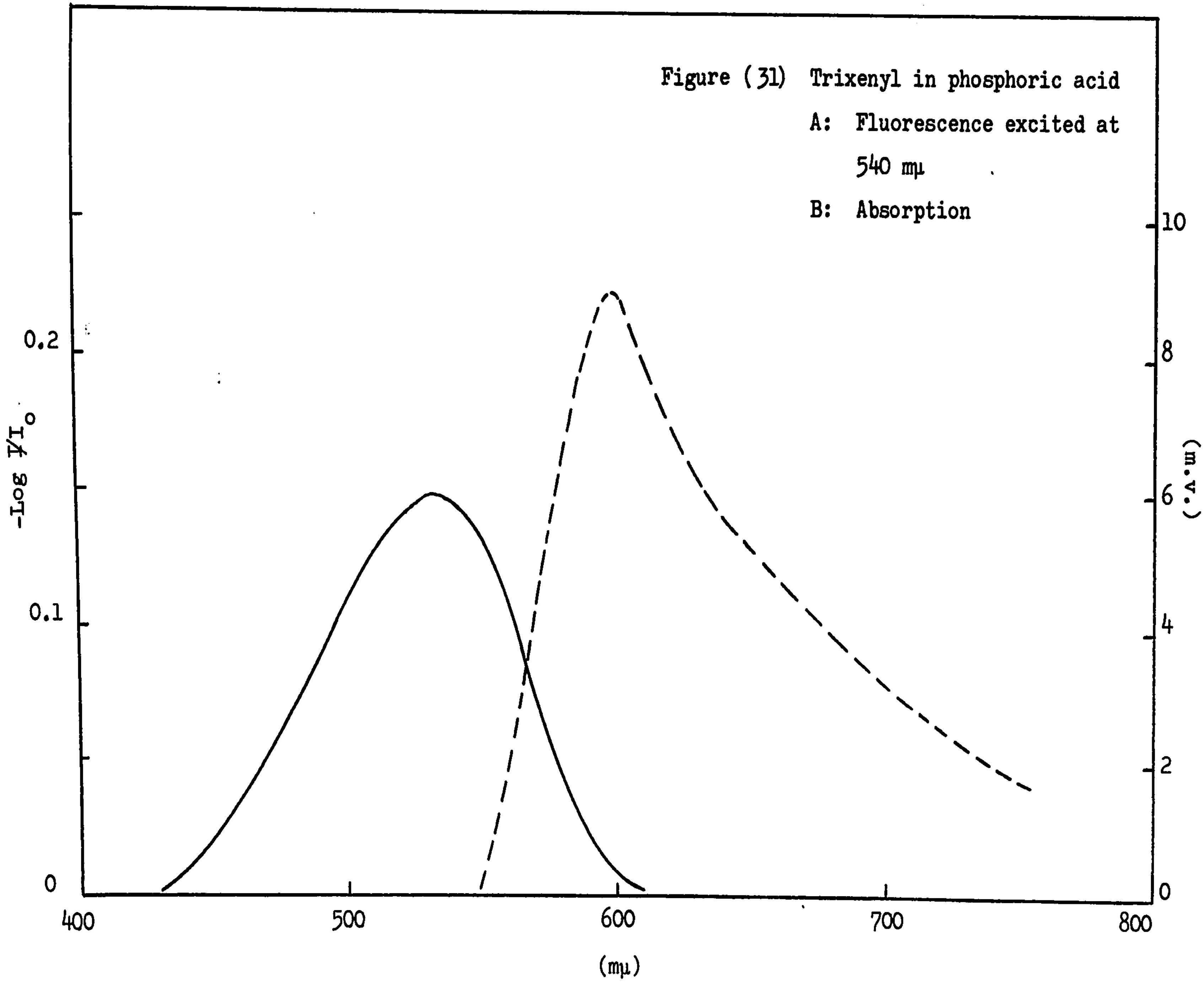


Figure (31) Trixenyl in phosphoric acid

A: Fluorescence excited at 540 mμ

B: Absorption

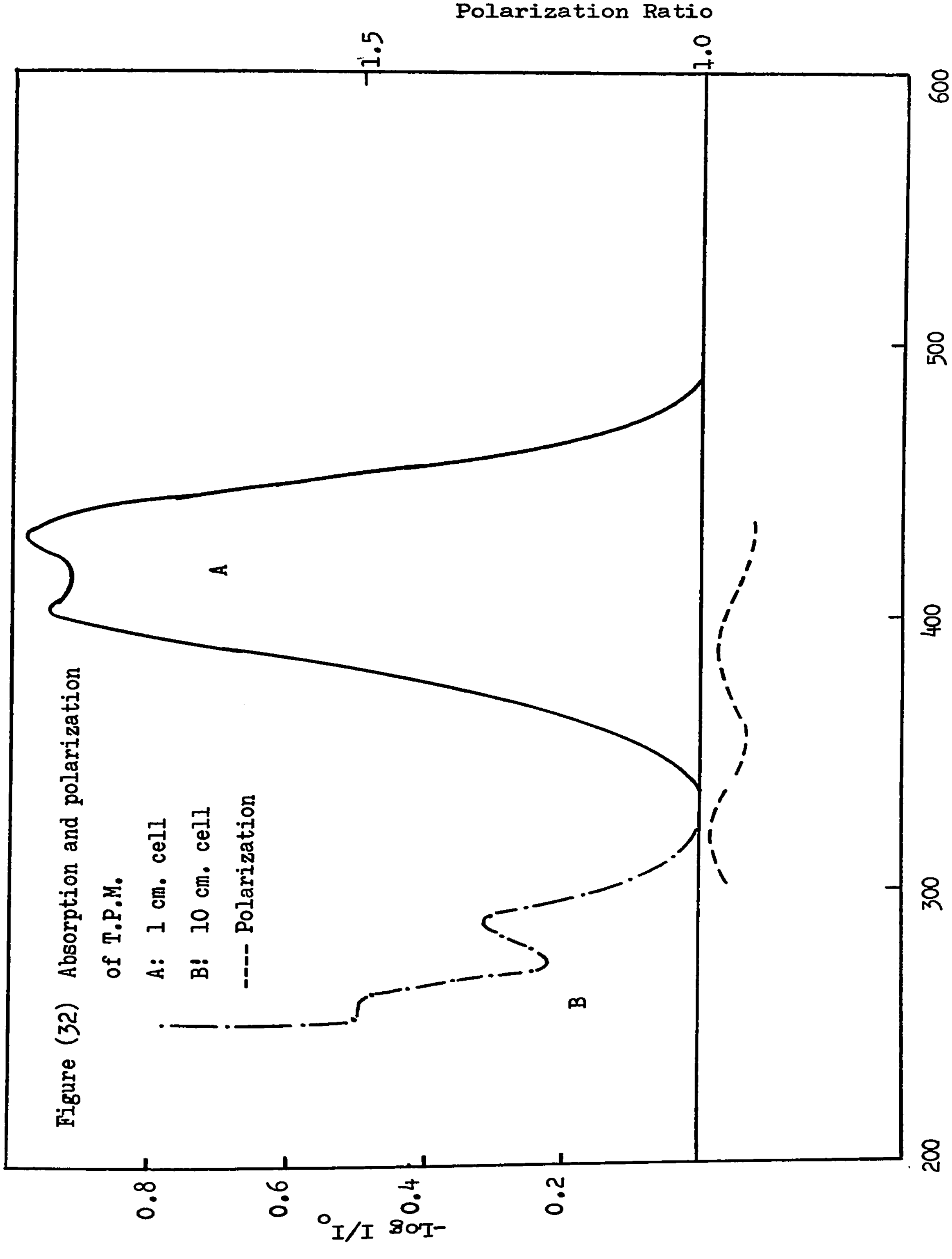


Figure (32) Absorption and polarization of T.P.M.

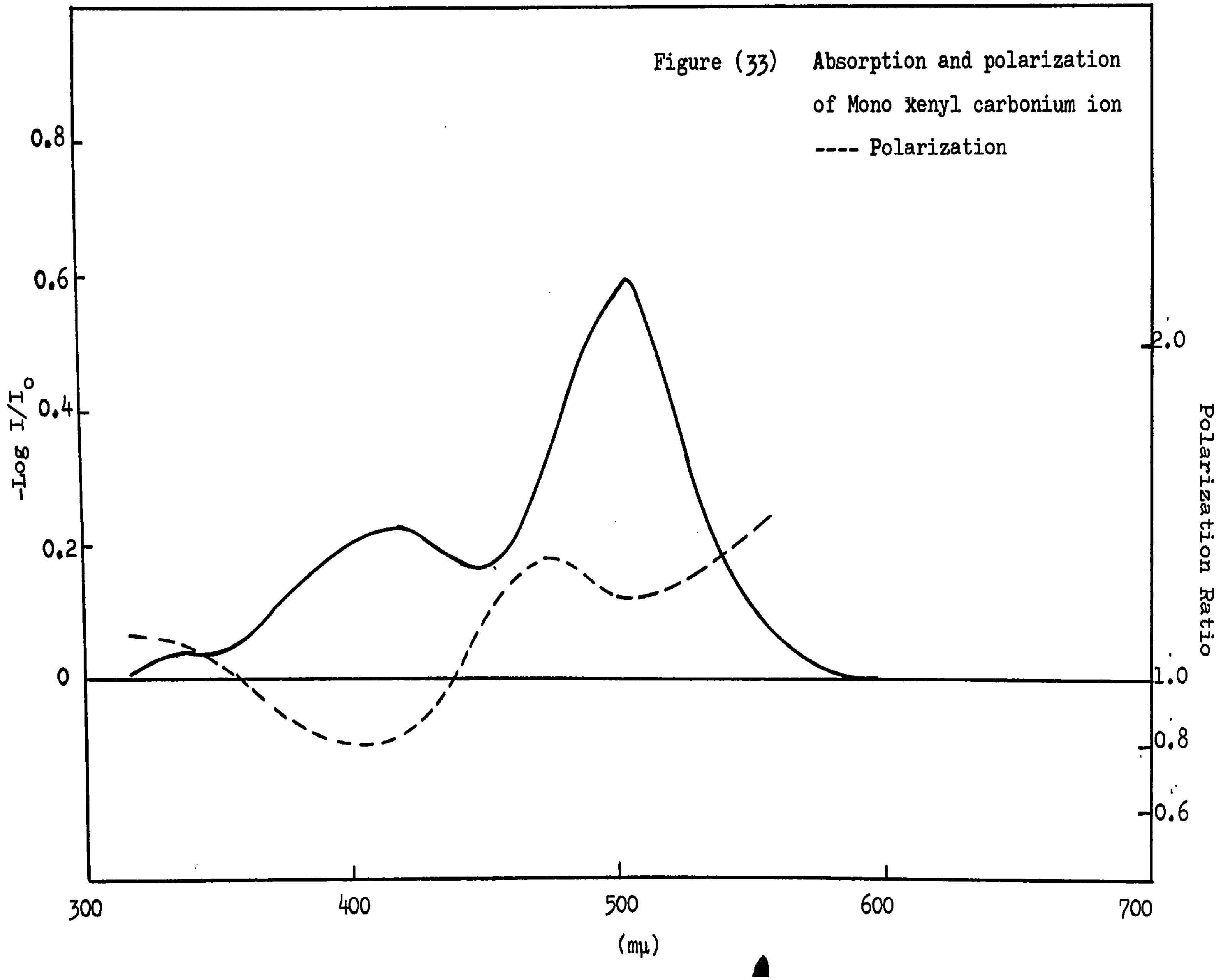


Figure (33) Absorption and polarization of Mono Xenyl carbonium ion

---- Polarization

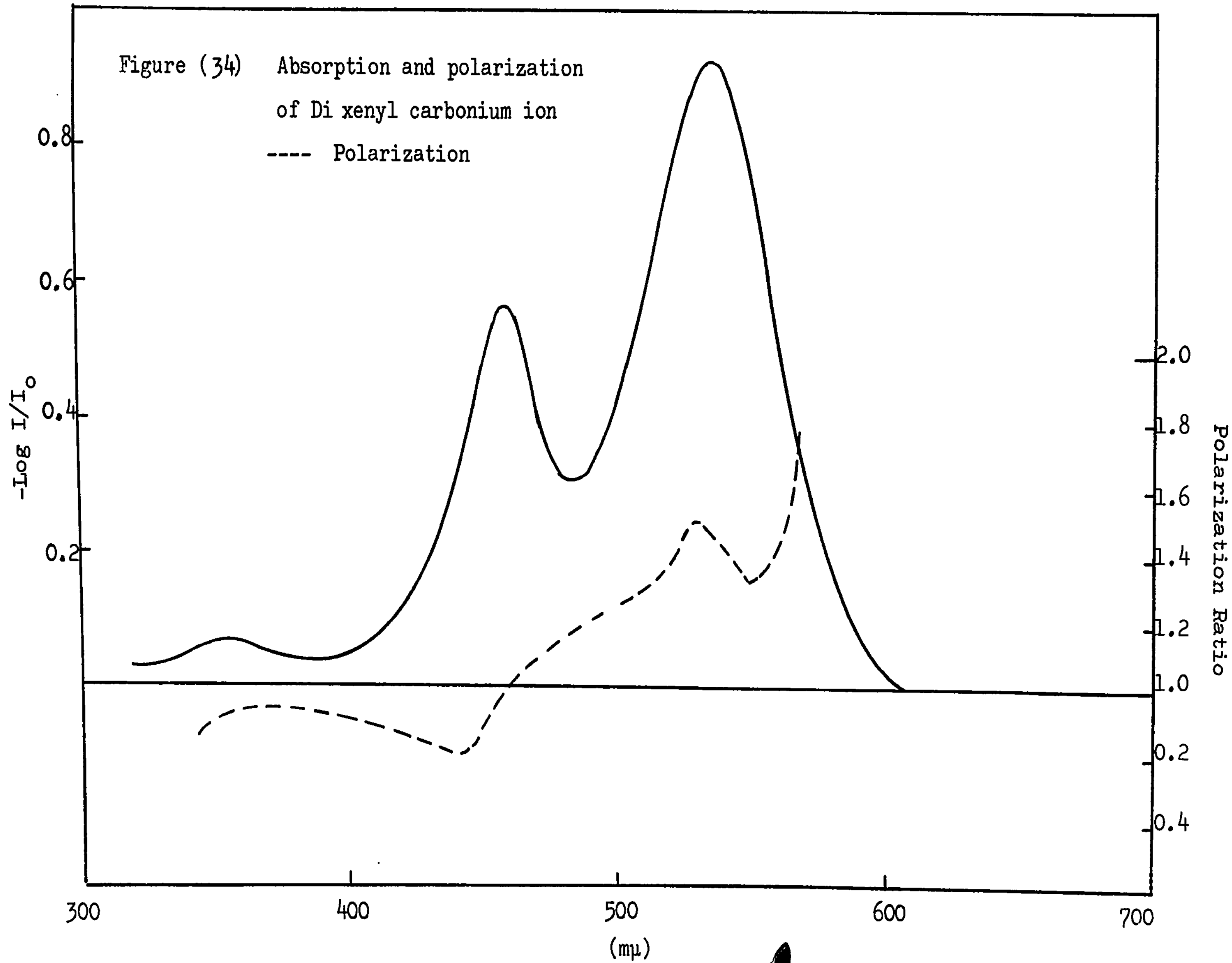


Figure (34) Absorption and polarization of Di xenyl carbonium ion

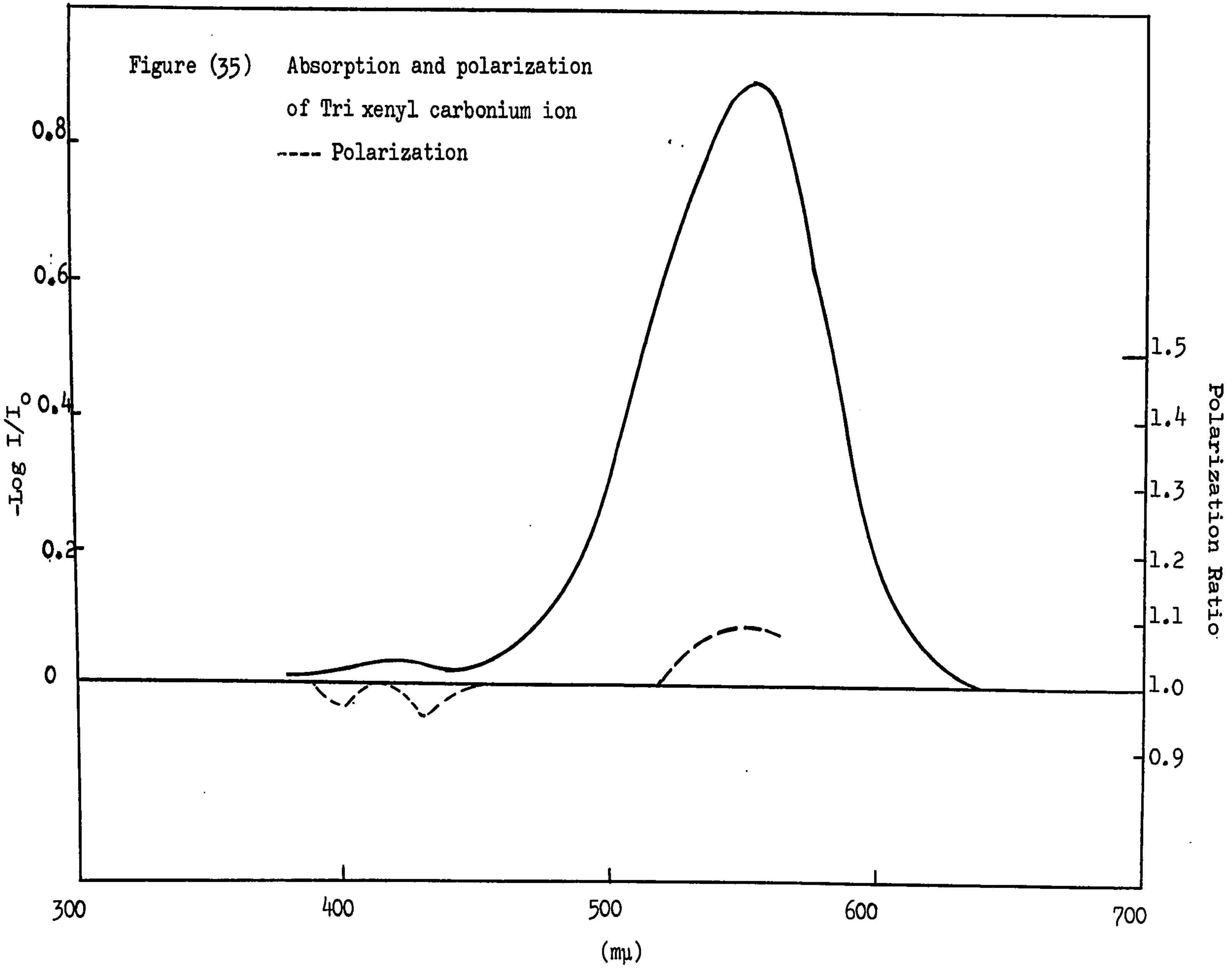


Figure (35) Absorption and polarization of Tri xenyl carbonium ion

(5) Nuclear Magnetic Resonance:

Nuclear magnetic resonance spectra of the carbonium ions were taken with a Varian A-60 and under higher resolution using a Varian HR-100 spectrometer. The carbinols were dissolved in trifluoro acetic acid and trifluoro acetic anhydride mixtures under vacuum. Spectra of the carbinols in 95 % H_2SO_4 and H_2SO_4 - HAc mixtures were also taken. Chemical shifts were measured by the external standard technique using tetramethyl silane as a standard in the Varian A-60, while fields in the HR-100 were measured by the spinning side-band technique. The spectra appear in Figures (36) to (43).

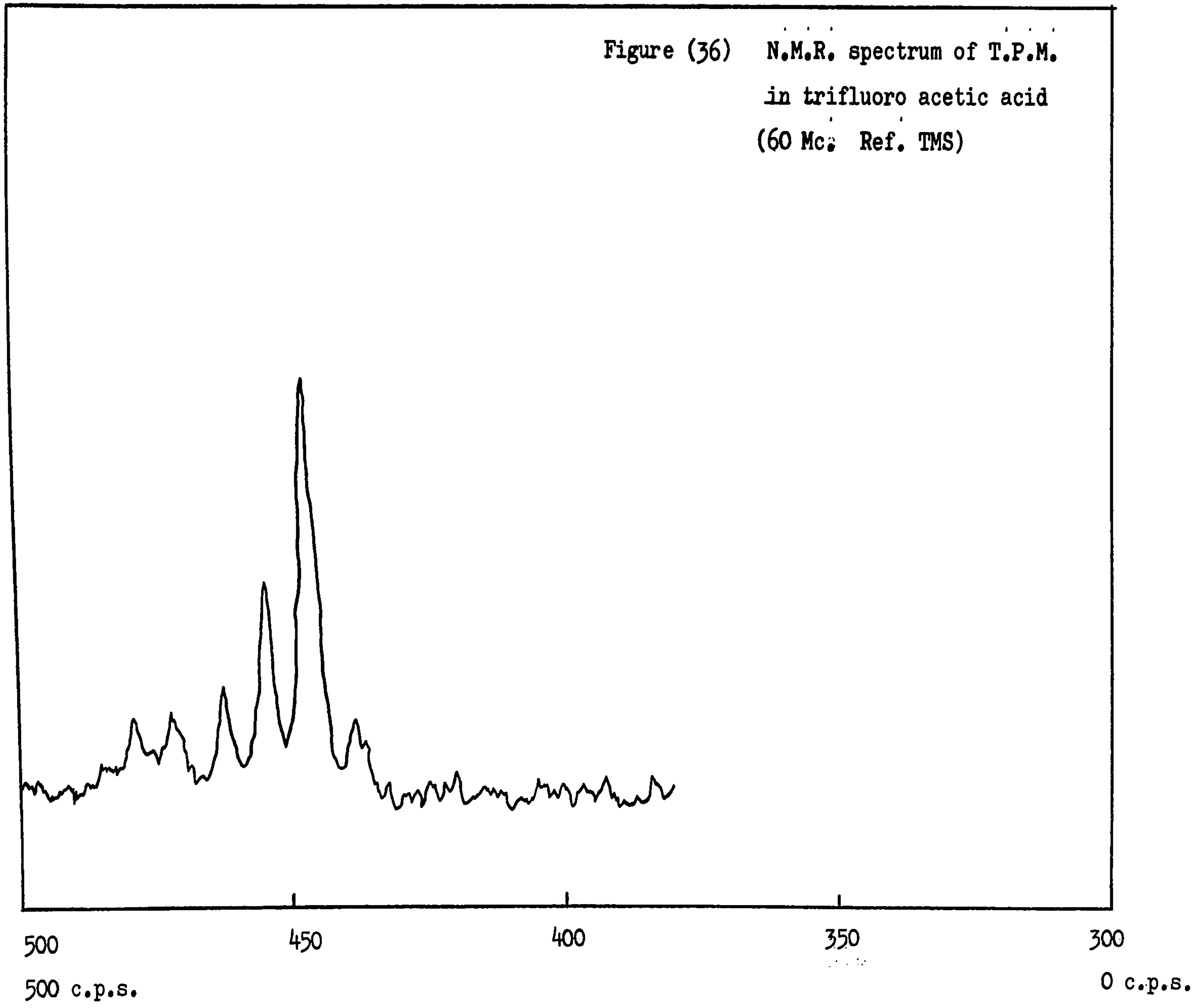


Figure (36) N.M.R. spectrum of T.P.M. in trifluoro acetic acid (60 Mc. Ref. TMS)

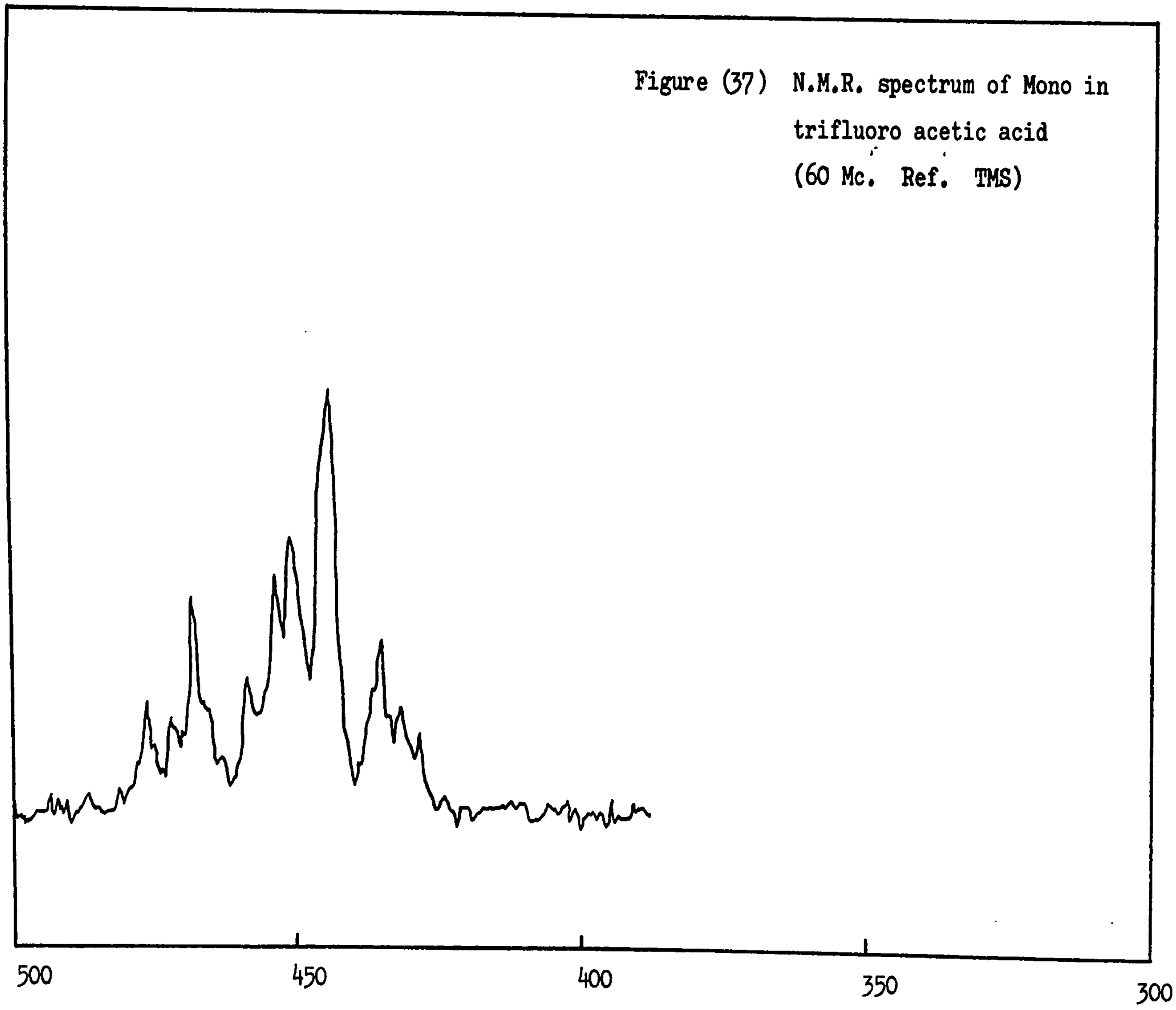


Figure (37) N.M.R. spectrum of Mono in trifluoro acetic acid (60 Mc. Ref. TMS)

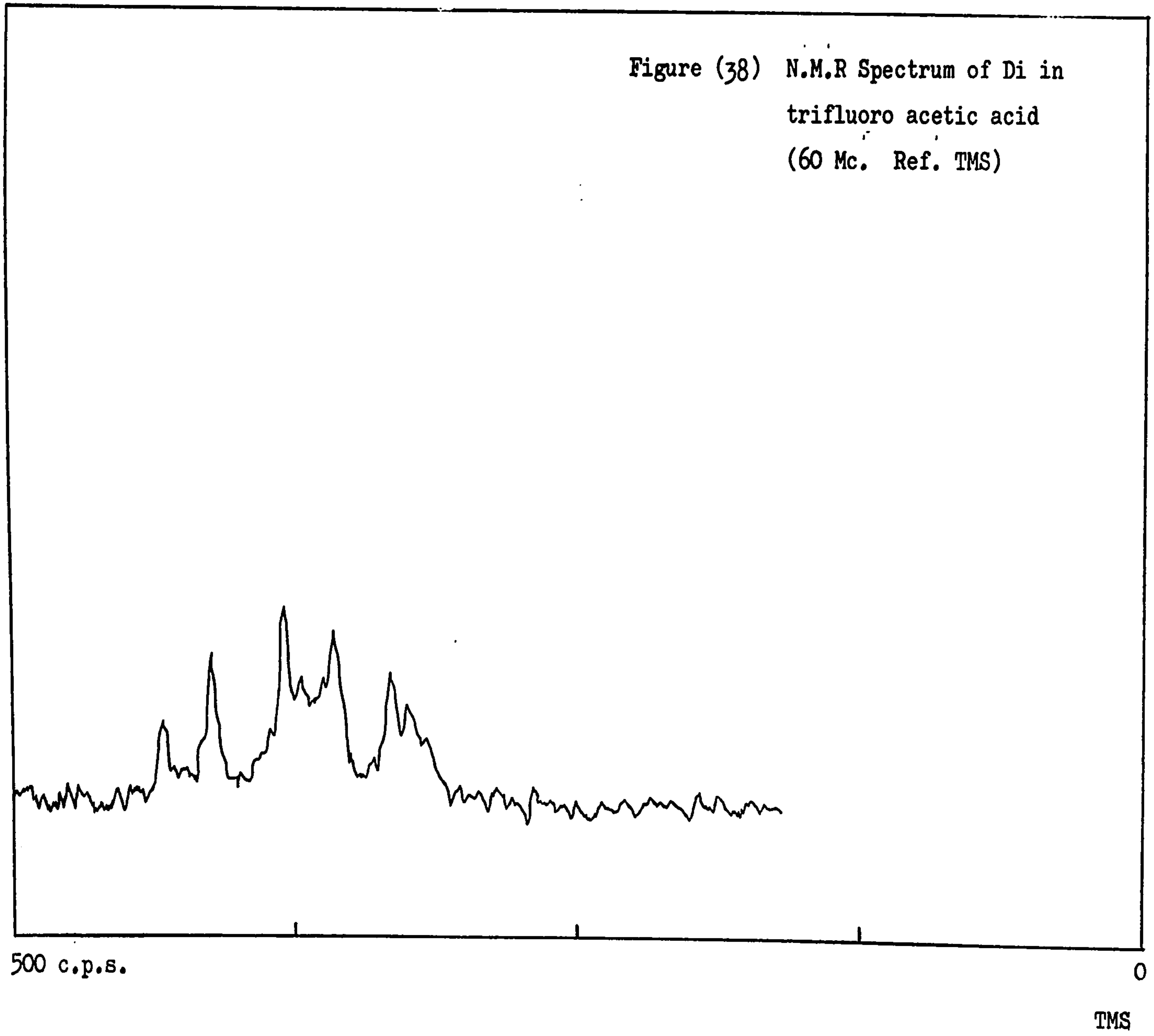


Figure (38) N.M.R Spectrum of Di in trifluoro acetic acid (60 Mc. Ref. TMS)

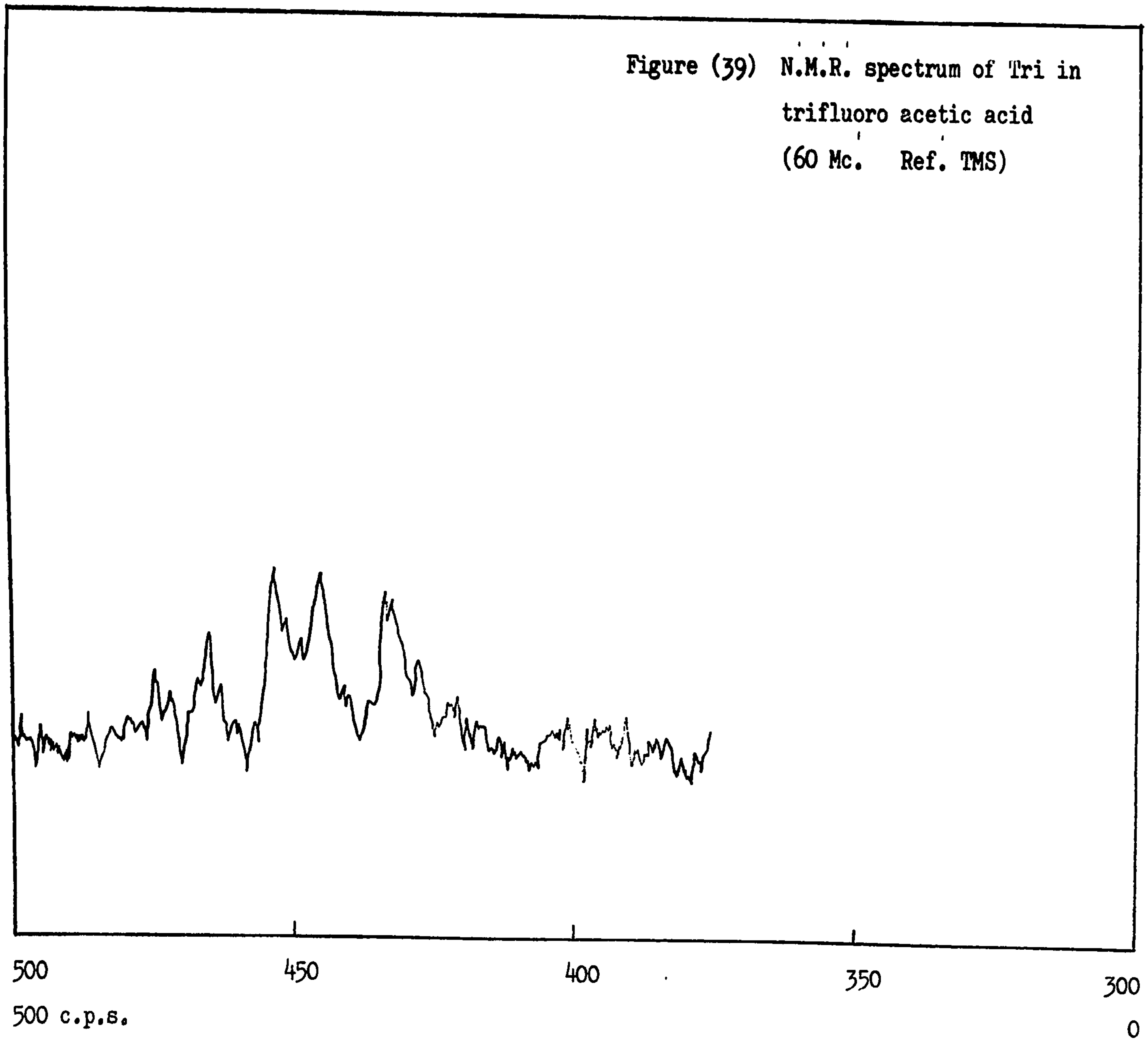


Figure (39) N.M.R. spectrum of Tri in trifluoro acetic acid
(60 Mc. Ref. TMS)

Figure (40) N.M.R. spectrum of T.P.M. in trifluoroacetic acid (100 Mc. Side band technique 1 unit = 2.867 c.p.s.)

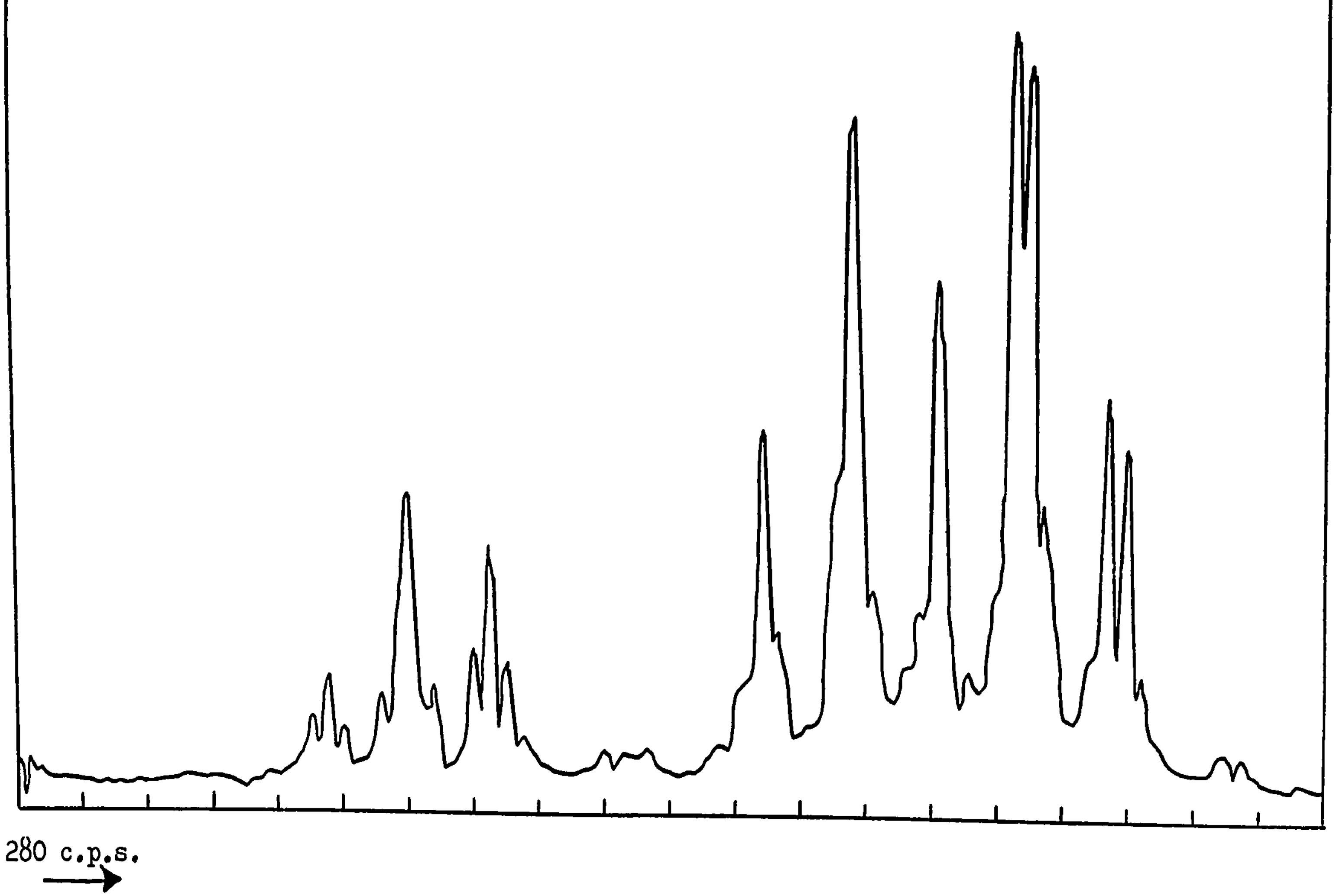
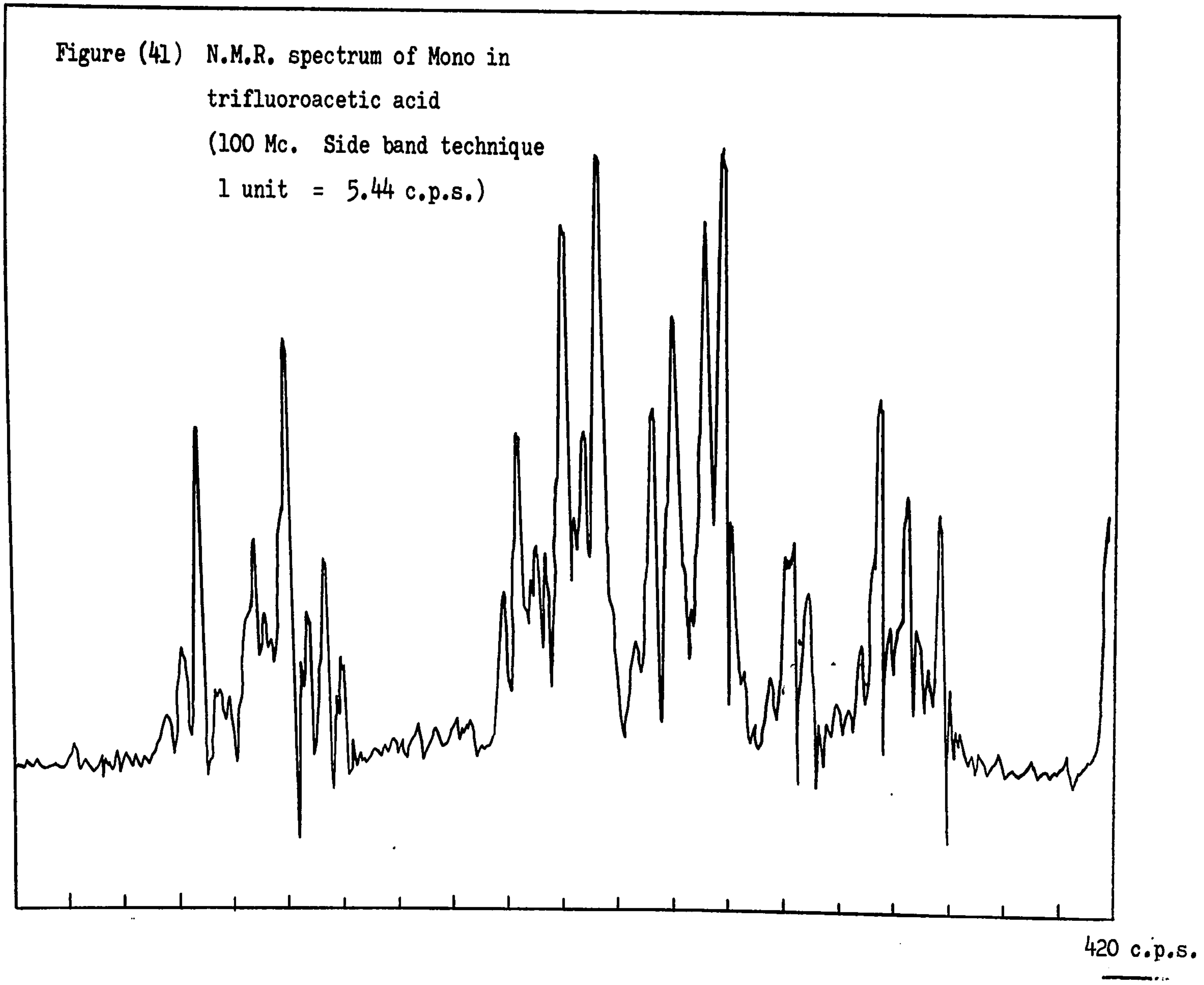


Figure (41) N.M.R. spectrum of Mono in trifluoroacetic acid
(100 Mc. Side band technique
1 unit = 5.44 c.p.s.)



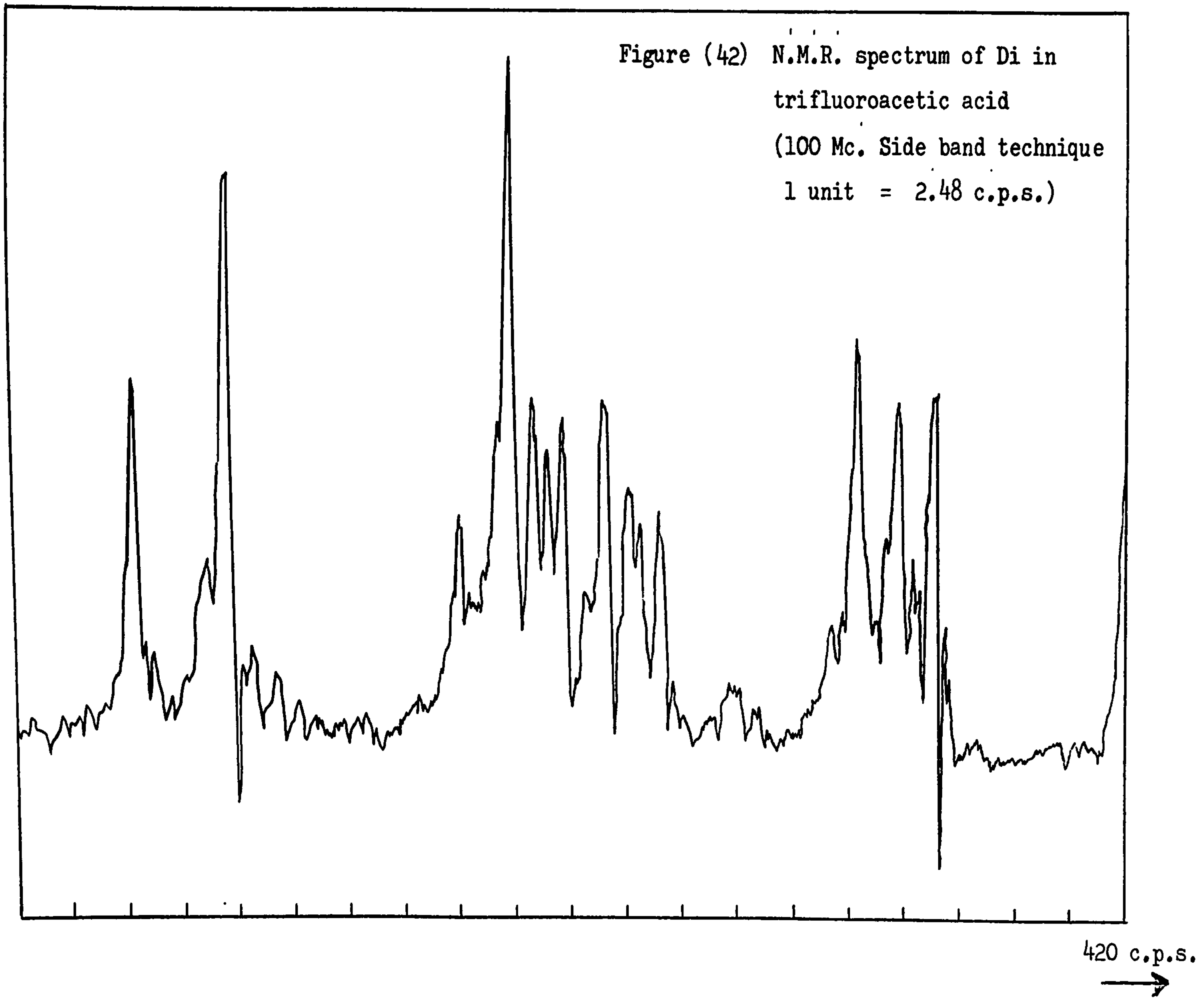


Figure (42) N.M.R. spectrum of Di in trifluoroacetic acid (100 Mc. Side band technique 1 unit = 2.48 c.p.s.)

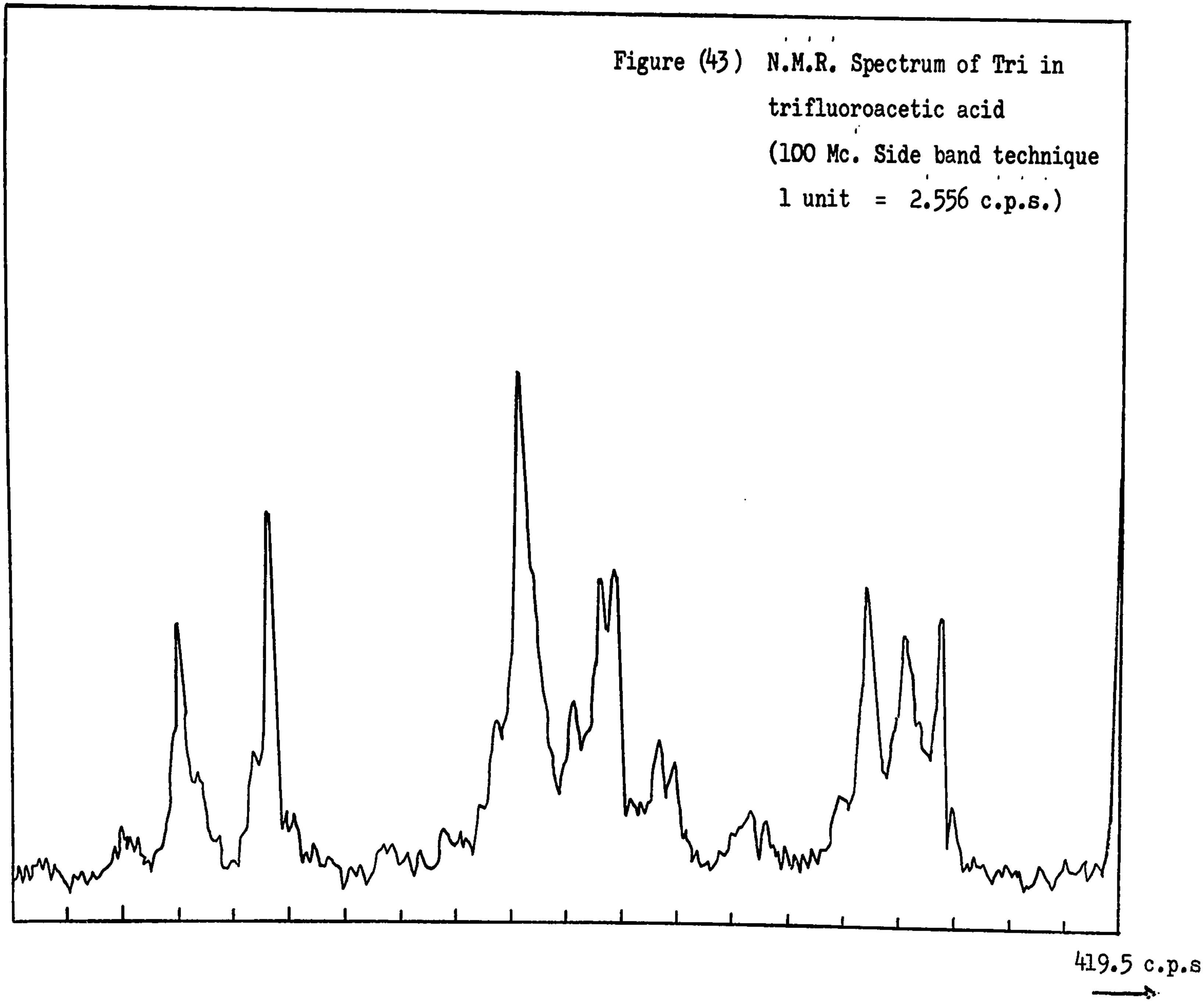


Figure (43) N.M.R. Spectrum of Tri in trifluoroacetic acid
(100 Mc. Side band technique
1 unit = 2.556 c.p.s.)

SYMMETRY ASSIGNMENTS

Part A: Nitrosobenzene:

(1) n $\longrightarrow$ π^* Transition:

It has been generally accepted that in molecules containing heteroatoms such as nitrogen and oxygen, the long wave length optical band is a n $\longrightarrow$ π^* transition. Orgel (3) and Nakamoto (6) have given a theoretical substantiation to this effect.

The electronic spectra of solute molecules has been found to depend on the properties of the solvent media, and this has been used empirically as a criterion in the classification of electronic transitions. A blue shift of the absorption maximum on changing the solvent from non-polar to polar is taken as an indication of a n $\longrightarrow$ π^* transition. Such an effect is explained currently by a hypothesis suggested by McConnell (4), or by a specific hydrogen bonding hypothesis favored by Kasha (66).

McConnell proposed that the blue shift originates from the solvent molecules orienting themselves around the solute molecule to fit in with the ground state charge distribution. On excitation, the charge distribution of the solute molecules changes, but the solvent molecules are unable to follow this change instantaneously. In this sense, the destabilizing effect of the excited state would remain relatively constant regardless of the nature of the solvent. However, because the ground state is more polar than the excited state, it would be expected that a polar solvent would stabilize the ground state more than a non-polar solvent.

Kasha on the other hand insisted that the formation of a hydrogen bond with the n-electrons lowers the energy of the n-orbitals by an amount equal to the energy of the hydrogen bond. In the n $\longrightarrow$ π^* transition, one of the electrons is removed from the n-orbital and goes to an empty anti-bonding π orbital. The remaining n-electron is not sufficient to sustain the hydrogen bond, especially since the atom takes on a formal charge. When the hydrogen bond is broken, the energy of the excited state should be approximately equal to the energy of the same excited state in the absence of a hydrogen bond. In either hypothesis the blue shift is caused by the stabilization of the ground state compared to the excited state. Inspection of Figure (15) for nitroso compounds clearly indicates that such a blue shift was obtained in the spectrum in going from carbon tetrachloride to the solvent water.

A n $\longrightarrow$ π^* transition is also known to be very sensitive to chemical substitution (67). A general conjugation effect is observed in comparing nitrosobenzene and trimethyl nitrosomethane (Figure (9)). More specific to n $\longrightarrow$ π^* transitions is a blue shift observed on substituting electron-donating groups in the benzene ring. In a n $\longrightarrow$ π^* transition, the electron is excited from a localized orbital to an orbital more or less delocalized throughout the molecule, and this implies the movement of charge toward the benzene ring. It is therefore not difficult to see that electron-donating groups should hinder such movement, or raise the excited state energy. On the other hand, an electron-withdrawing substituent should have the opposite effect. This is borne out by noting the spectra of N N-dimethyl nitroso aniline, and 2, 4, 6 tribromo nitrosobenzene, where a blue shift is observed for the former, a red shift for the latter when compared to nitrosobenzene.

It is also observed empirically that n $\longrightarrow$ π^* transitions, even if symmetry allowed, have oscillator strength of the order of magnitude of 10^{-2}. The main cause for this low intensity is poor orbital overlap for the n $\longrightarrow \pi^*$ promotion. A hypothetical intensity calculation of a 2s $\longrightarrow$ 2p transition which is taken to be analogous to a n $\longrightarrow \pi^*$ transition, gives a transition moment length of 0.3Å, as shown in Appendix (I), compared to the observed moment of 0.05Å. Although this calculation is not regorous, it does indicate that it is not unreasonable to assign the 760mμ band in the spectrum of nitrosobenzene as n $\longrightarrow \pi^*$ transition.

The question as to which pair of unshared electrons is involved in the transition is a little more difficult to answer. X-Ray data indicate that in the dimerization process, the nitrogen pairs become involved in bonding, and are not available for n $\longrightarrow \pi^*$ type transitions. This is consistent with the disappearence of the long wave length transition upon dimerization of nitroso compounds. On the other hand, $K_2NO(SO_3)_2$ absorbed at 550mμ, but has no unshared nitrogen pairs. If this is the counterpart of the 760mμ in nitroso benzene, and arises from the oxygen pair, then a second transition of about the same intensity should be found for nitroso compounds. As the infrared spectrum shows, none could be found in this region. It appears then that the 550mμ of $K_2NO(SO_3)_2$ does not correspond to the 760mμ band of nitroso benzene, and that the latter transition involves the nitrogen atom pair.

(2) Multiplicity of Upper State:

In general, the intensity of an absorption process is related to the life time of its excited state by the following expression (68):

$$\int \epsilon \, d\bar{v} = 3.97\text{x}10^8 \left(\frac{1}{\bar{v}_A^2 \; n^2} \right) \left(\frac{g_u}{g_e} \right) k_e \; ,$$

where: $d\bar{v}$ = area under the absorption curve,

ϵ = molar extinction coefficient,

$\bar{v}$ = absorption frequency in wave numbers (cm.$^{-1}$),

$\bar{v}_A$ = absorption maximum in cm.$^{-1}$,

n^2 = square of the refractive index of the medium,

g_u, g_e = multiplicity of upper and ground state, respectively,

k_e = rate constant of the radiative process.

When the emission process alone takes the molecule from the upper to the lower state, the mean life time (τ) of the upper state is then, by definition, the reciprocal of k_e. On the other hand, when there is some competing process such as the thermal dissipation of the energy of the upper state, τ may be considerably less than the life time that would be observed if emission of radiation were the sole process. Assuming a triplet upper state, and inserting the pertinent numerical values into the above equation, one obtains a life time of the upper state of 10^{-6} seconds. This figure is too small for a triplet state which is usually of the order of 10^{-4} to 10 seconds. From the point of view of intensity, a S $\longrightarrow$ T transition, being spin forbidden, is far less intense than a S $\longrightarrow$ S transition, roughly by a factor of 10^{-6}. The extinction coefficient of this 760mμ band is 40 which, though low, appears to be too intense for a genuine S $\longrightarrow$ T transition.

A more serious objection to the identification of this band as a S $\longrightarrow$ T transition arises when the effect of spin-orbital coupling is considered. In addition to the electrostatic interaction between the electrons, there is a magnetic interaction between the orbital motion of the electron and the electron's spin magnetic moment. From the electron's point of view, it is at the centre of things, and the nucleus moves in an orbital around the electron. Since the nucleus and core bear a charge, the electron sees itself encircled by an electric circuit, just as if it were in the middle of a coil of wire carrying a current. This current produces a magnetic field, which at the position of the electron in an isolated atom, is perpendicular to the plane of the orbit. The electron, however, bears a magnetic moment parallel to its axis of spin and its energy will vary depending on the relative directions of this spin magnetic moment and the magnetic field from the orbital motion. Therefore, the energy of a system must depend to some extent on the relative orientation of the spin axes and the orbital angular momentum axes of the electrons in the system.

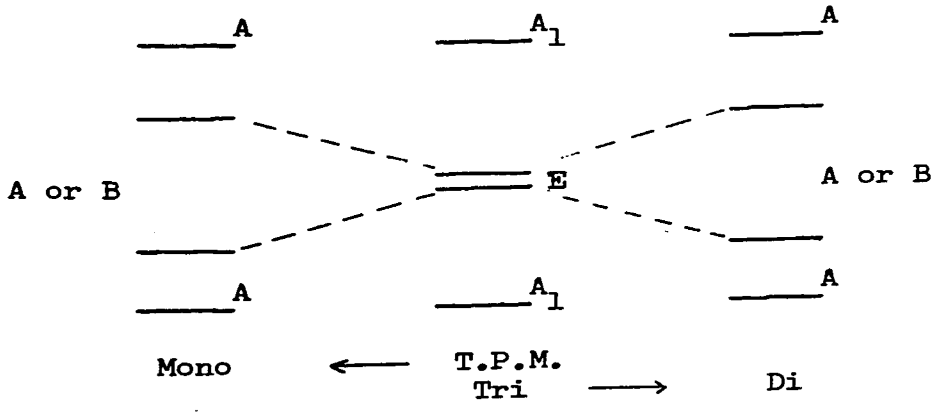
The magnitude of this spin-orbital interaction in an atom is found to depend on the average value of the gradient of the electric field produced by the nucleus (69). It therefore tends to be large with atoms of heavy nucleus and for orbitals that penetrate into the core. Extending this argument to the π orbitals of complex molecules, the perturbation caused by heavy atom substituents should depend on two main factors: (i) the degree of penetration of the π electron into the electric field of the nucleus of the perturbing atom, and (ii) the strength of this electric field (i.e. the atomic number of the substituent). The major effect of this perturbation is to mix the singlet and triplet states so that neither of them will be a "pure" state. As a consequence, the transition probability of the otherwise spin-forbidden S ⟶ T transition is enhanced. This effect has indeed been observed and Kasha (70) reported that such enhancement is observable even when the heavy atom is contained not in the molecule of interest, but in the solvent molecule instead.

Comparing the spectra of nitrosobenzene and tribromo nitrosobenzene in carbon tetrachloride, it is apparent that the expected enhancement is absent. On the contrary, the corresponding absorption is weaker in 2, 4, 6 tribromo nitrosobenzene. Since spin-orbital coupling increases the S —— T transition probability, it must therefore decrease the S → S transition probability. The observed change of intensity is therefore a strong indication that the upper state is not a triplet.

Our experimental evidence therefore indicated that the 760mμ band in nitrosobenzene is a S → S rather than a S → T transition.

Part B: Carbonium Ions:

Since the T.P.M. carbonium ion has an even number of electrons (18), and has C_{3v} group symmetry, it may be assumed that the ground state wave function has symmetry A_1. On purely group theoretical grounds the $A_1 \longrightarrow A_1$ transition is polarized in the z direction which may be taken to be along the threefold axis of the molecule. The next transition would be to a state whose wave function belongs to the symmetry E., This $A_1 \longrightarrow E$ transition would be degenerate and allowed in plane (i.e. x, y). When T.P.M. is perturbed in such a way that the threefold axis of symmetry is lost, the resulting molecule may be considered to belong to the point group C_2, as in Mono and Di. The forbidden transition of T.P.M. is independent of the nature of the perturbation and becomes allowed and is always polarized in the direction of the perturbation. This may be considered the "y" direction of the molecule. On the other hand, in going from the C_3 to C_2 symmetry the doubly degenerate wave function will split into wave functions of lower symmetry A and B. A is symmetric to reflection along the y axis, and B is antisymmetric. Diagramatically, the relationship can be represented as follows:

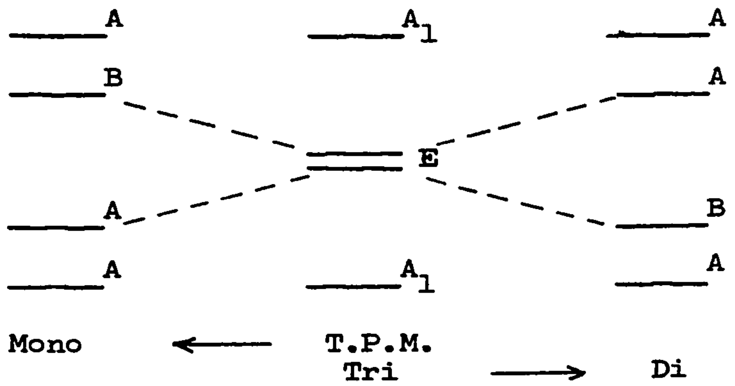


In the C_2 group, the A $\longrightarrow$ A transition is polarized y, and the A $\longrightarrow$ B transition is polarized x. Therefore, it is predicted that T.P.M. and Tri should have two transitions, one allowed and one forbidden, while Mono and Di should have three, all allowed. This prediction is based purely on group theoretical grounds with no recourse to models of any kind. However, group theory cannot predict the actual arrangement of energy levels in the Mono and Di molecule.

The actual identification of the energy levels must be found from experimental data. The spectrum of T.P.M. in various solvents consists of two bands, one in the visible and the other in the U.V. The visible band splits approximately 20mμ apart and is of high intensity. The U.V. band is extremely weak and appears as a shoulder on a much more intense band further in the U.V. The first band is apparently a degenerate pair, split by solvent, or ion-pair effects, perhaps, and the second is probably a forbidden one, most likely allowed through distortions from perfect C_3 symmetry. Very much the same considerations apply to the spectrum of Tri. Therefore, the first transition is, in all probability $A_1 \longrightarrow E$, while the weak band is $A_1 \longrightarrow A_1$.

The molecules of Mono, and Di can be looked upon as perturbed forms of T.P.M. and Tri, resulting from the addition or removal of a phenyl ring, respectively. Their spectra clearly show the three band system as predicted by group theory. The two bands in the visible region may therefore be considered as derived from the doubly degenerate pair and the high energy band the analogue of the forbidden band in their respective parent molecules. It was also predicted that the high energy transition throughout this series of molecules is always polarized "y" with respect to the molecular frame. This realization is the most critical factor in the assignment of the band system in Mono and Di.

In the case of Mono, the relative polarizations as determined by the measured polarization ratios are: parallel, perpendicular and parallel going from long to short wave length. In terms of the molecular frame co-ordinates, this would be interpreted as y, x, and y. It follows therefore, that the transitions are A → A, A → B, and A → A. The final energy level diagram therefore takes the following form:

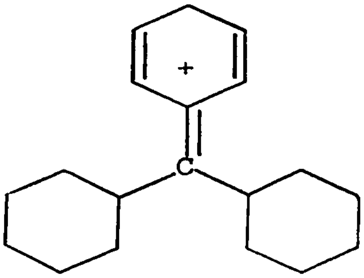


It is apparent that the energy levels cross over, so to speak, in going from Mono to Di. In the language of the triphenylmethyl dye system as investigated by Adam (32), Mono behaves as negative dye relative to T.P.M. and Di as a positive dye relative to Tri.

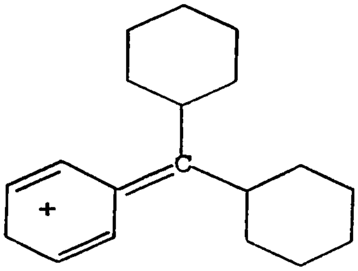
NUMERICAL RESULTS

(A) Structure Representation Method:

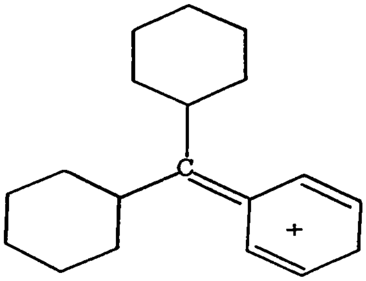
Following the scheme outlined in the section on theory, we assume for the n low energy structures for T.P.M. to be:



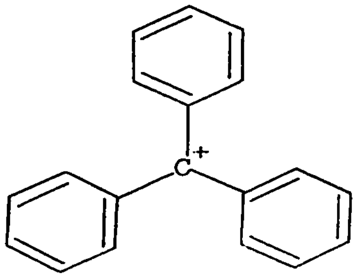
(1)



(2)



(3)



(4)

In this representation, no distinction is made between structures with the positive charge in the ortho and para positions of a benzene ring, and their combined effect is designated simply by putting a positive charge in the respective benzene ring as above. Structures (1), (2) and (3) are equivalent and (4) is distinct. Application of the C_{3v} group operations generates the following non-zero fragments:

$$A_1 \quad \begin{cases} (1) \quad + \quad (2) \quad + \quad (3) \\ (4) \end{cases} ,$$

$$E \quad \begin{cases} 2(1) \quad - \quad (2) \quad - \quad (3) \\ 2(2) \quad - \quad (3) \quad - \quad (1) \\ 2(3) \quad - \quad (1) \quad - \quad (2) \end{cases} .$$

As mentioned before, this is a case, where two linear combinations are necessary to represent states of symmetry A, namely,

$$A_1 \quad \begin{cases} {\dfrac{1 - c^2}{3}}^{1/2} \Big[(1) \quad + \quad (2) \quad + \quad (3) \Big] \quad + \quad c \; (4) \\ \dfrac{c}{\sqrt{3}} \Big[(1) \quad + \quad (2) \quad + \quad (3) \Big] \quad - \quad \sqrt{(1 - c^2)} \; (4) \end{cases}$$

when c is the mixing coefficient. Of the three fragments in the doubly degenerated representation (E), only two are linearly independent. The best linear combination suitable for both C_{3v} and C_{2v} groups are, after normalization,

$$A \quad \left(\frac{2}{3}\right)^{1/2} (1) \quad - \quad \frac{1}{\sqrt{6}} (2) \quad - \quad \frac{1}{\sqrt{6}} (3) ,$$

$$B \quad \frac{1}{\sqrt{2}} (2) \quad - \quad \frac{1}{\sqrt{2}} (3) ,$$

As stated earlier, the columns of the $\underset{\sim}{S}^{-1}$ matrix are the state eigenvectors, so that for T.P.M.:

$$\underset{\sim}{S}^{-1} = \begin{pmatrix} {\frac{1-c^2}{3}}^{1/2} & 0 & {\frac{2}{3}}^{1/2} & \frac{c}{\sqrt{3}} \\ {\frac{1-c^2}{3}}^{1/2} & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} & \frac{c}{\sqrt{3}} \\ {\frac{1-c^2}{3}}^{1/2} & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} & \frac{c}{\sqrt{3}} \\ {\frac{1-c^2}{3}}^{1/2} & 0 & 0 & -(1-c^2)^{1/2} \end{pmatrix}$$

and $\underset{\sim}{S}$ is the transpose of $\underset{\sim}{S}^{-1}$.

The first transition to the degenerate level in T.P.M. occurs experimentally at 2.398 (in units of 10^4 cm.^{-1}) and the forbidden band is found at 3.448. For ease of mathematical manipulation, the first level is chosen as the zero energy for the molecule. The choice is arbitrary and its convenience is suggested by the fact that in going from T.P.M. to Mono, one of the levels remains unperturbed. The E matrix in the Heisenberg representation is then diagonal with the following simple form:

$$\underset{\sim}{E} = \begin{pmatrix} -2.398 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1.05 \end{pmatrix}$$

After performing the transformation into the structure representation, the energy matrix E' has the form :

$$\underset{\sim}{E''} = \begin{pmatrix} x & x & x & y \\ x & x & x & y \\ x & x & x & y \\ y & y & y & z \end{pmatrix}$$

where: $x = \frac{-2.398 + 3.448\, c^2}{3}$,

$$y = -3.448 \left(\frac{1 - c^2}{3}\right)^{1/2} c ,$$

$$z = 1.05 - 3.448\, c^2 .$$

Since the purpose of this investigation was of an exploratory nature, a number of different calculations were carried out, based largely on chemical intuition, and the desire to keep the method as simple as possible. It seems reasonable but by no means essential to suppose that the interaction between structures (1) and (2) is very small (i.e. $E_{12} = 0$). E' for T.P.M. then takes the simple form:

$$E' = \begin{pmatrix} 0 & 0 & 0 & -.9161 \\ 0 & 0 & 0 & -.9161 \\ 0 & 0 & 0 & -.9161 \\ -.9161 & -.9161 & -.9161 & -1.3481 \end{pmatrix}$$

The formalism can then be applied to Mono based on the assumption that:

$$\underset{\sim}{E'}_{\text{Mono}} = \underset{\sim}{E'}_{\text{T.P.M.}} + \underset{\sim}{\delta E'} ,$$

where δE' is the perturbation energy matrix the elements of which can be chosen again with the guidance of chemical intuition. A variety of δE and other conditions have been investigated. The following set of conditions were found to yield meaningful results within the framework of this investigation.

It is apparent that the substitution of a phenyl group in the para position of ring (1) in T.P.M. will most decisively change the energy of structure (1) since now there are six possible low energy resonance structures which may be drawn instead of three. Accordingly, a calculation was carried out varying only this parameter (calculation a). Following this a calculation involving variation in both E_{11} and E_{44} was effected (calculation b). Next higher in the degree of sophistication is where the elements ϵ_{11} and ϵ_{44}, and $\epsilon_{14} = \epsilon_{41}$, were allowed to vary. This may be done in two ways wherein the trace is maintained invariant (i.e. the sum of the diagonal elements = the sum of absorption energies), (calculation c), and wherein it was allowed to vary (calculation d).

Taking as a typical example (calculation b), and using Adam's method (32)

$$\underset{\sim}{E'}_{\text{Mono}} = \begin{pmatrix} \epsilon_{11} & 0 & 0 & -.9161 \\ 0 & 0 & 0 & -.9161 \\ 0 & 0 & 0 & -.9161 \\ -.9161 & -.9161 & -.9161 & -1.3481 + \epsilon_{44} \end{pmatrix}$$

This matrix is diagonalized to match the observed spectrum of Mono. The resulting equation is:

$$\lambda^4 + \lambda^3(1.3481 - \epsilon_{11} - \epsilon_{44}) + \lambda^2\left[\epsilon_{11}\ \epsilon_{44} - 1.3471\ \epsilon_{11} - 3(.9161)^2\right] + \left[2(.9161)^2\ \epsilon_{11}\right] = 0.$$

The observed spectrum of Mono gives the energy matrix as:

$$E_{\text{Mono}} = \begin{pmatrix} -2.404 & 0 & 0 & 0 \\ 0 & -.424 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & .581 \end{pmatrix}$$

which results in the following equation:

$$\lambda^4 + 2.247\lambda^3 - .6237\lambda^2 - .5922 = 0.$$

Equating the coefficiencies leads to:

$$\epsilon_{11} = -.3528 ,$$

$$\epsilon_{44} = -.5461 .$$

Substitution of these values gives E'_{Mono} as :

$$\underset{\sim}{E'}_{Mono} = \begin{pmatrix} -.3528 & 0 & 0 & -.9161 \\ 0 & 0 & 0 & -.9161 \\ 0 & 0 & 0 & -.9161 \\ -.9161 & -.9161 & -.9161 & -1.8942 \end{pmatrix}$$

Once E' is known, the entries of S^{-1} are found in the usual manner by the solution of the simultaneous equations :

$$C_{ij} = (\sum_j E'_{ij} - \lambda_i) = 0 ,$$

and the normalization condition :

$$\sum_j C^2_{ij} = 1 .$$

$\underset{\sim}{S}^{-1}$ obtained this way for T.P.M. and Mono are :

$$S^{-1}_{T.P.M.} = \begin{pmatrix} .3186 & 0 & .8165 & .4815 \\ .3186 & .7071 & -.4083 & .4815 \\ .3186 & .7071 & -.4083 & .4815 \\ .8340 & 0 & 0 & -.5518 \end{pmatrix}$$

$$S^{-1}_{Mono} = \begin{pmatrix} .3652 & .9702 & 0 & .3725 \\ .3116 & .1629 & .7071 & .5987 \\ .3116 & .1629 & -.7071 & .5987 \\ .8117 & .0754 & 0 & -.3797 \end{pmatrix}$$

After finding these matrices which diagonalize $\underset{\sim}{E'}$, it is possible to compute the expectation value of any dynamic variable. From the point of view of spectroscopy, absorption intensities are the most convenient to choose. They also offer a most important criterion to judge the accuracy of the $\underset{\sim}{S}^{-1}$ matrices and to test the ability of the method to make predictions. In the structure representation, the electric moment matrices $\underset{\sim}{x}'$ and $\underset{\sim}{y}'$ are diagonal, while the corresponding transition moment matrices $\underset{\sim}{x}$ and $\underset{\sim}{y}$, in the Heisenberg representation are non-diagonal. These are related by the following transformations:

$$\underset{\sim}{x} = \underset{\sim}{S}\,\underset{\sim}{x}'\,\underset{\sim}{S}^{-1},$$

$$\underset{\sim}{y} = \underset{\sim}{S}\,\underset{\sim}{y}'\,\underset{\sim}{S}^{-1},$$

Prediction of transition intensities may be made by adopting the experimental values of the parent molecules together with the corresponding $\underset{\sim}{S}^{-1}$ determined as above from the transition energies. This procedure was used in previous work of this type (32) and leads to the results that:

$$\overrightarrow{q_x} = 2(C_{21})(.7071)(\overline{X}_{22}),$$

$$\overrightarrow{q_y} = C_{11}\ (C_{21} \text{ or } C_{31})\ \overline{Y}_{11} + 2(C_{21})(C_{22} \text{ or } C_{33})\ \overline{Y}_{22},$$

where: $\overrightarrow{q_x}$, $\overrightarrow{q_y}$ = transition moments in the x and y directions,

C_{ij} = entries of the $\underset{\sim}{S}^{-1}$ matrix of the corresponding molecule ,

$\overline{X}_{ii}$, $\overline{Y}_{ii}$ = experimental values of electric moment of the parent molecule .

The corresponding values of $\overline{X}_{ii}$, $\overline{Y}_{ii}$ for T.P.M. and Tri derived from experimentally observed transition moments are given below:

T.P.M.	Tri
$\overline{X}_{22} = 2.5700\text{Å}$,	$\overline{X}_{22} = 4.0938\text{Å}$,
$\overline{Y}_{11} = 2.9676\text{Å}$,	$\overline{Y}_{11} = 4.7269\text{Å}$,

$\bar{Y}_{22} = 1.4838\text{Å}$, $\bar{Y}_{22} = 2.3635\text{Å}$.

However, with the particular sequence of compounds used in this research it is possible to determine the charge displacement of a given structure since there are no heteroatom substituents to complicate the situation. In fact, if one calculates the charge displacement assuming equal ortho and para carbonium contributions, and using an average of 1.4Å for ring C-C bonds and 1.5Å for the central bonds, one obtains $\bar{Y}_{11} = 2.90\text{Å}$ which compares favorably with 2.9676Å.

The results of the calculations are summarized in Table (2).

(B) H.M.O. Method:

The transition energies, intensities, and polarizations for each of the ions have been calculated by the H.M.O. method, and the values appear in Table (3). Only those transitions of significant intensity in any of the x, y or z directions, and those transitions predicted to have energies less than 40 kk are included, this last being the excitation energy of the B_{2u} transition of an isolated benzene molecule. No corrections have been made for the overlap or non-planar distortions; nor have further improvements such as the ω-technique been cited. The value of $\beta = 26.3$ kk has been chosen for each cation except T.P.M. where the value of $\beta = 24.0$ kk has been used for better agreement. The observed energies are in each case those of vertical transition, since it is clearly impossible to choose the 0-0 vibronic component in any consistent way for all of the transitions.

(C) N.M.R. Spectrum of T.P.M.:

The analysis of the N.M.R. spectrum is based on the method of

TABLE (2)

Results of the Structure Method Calculation

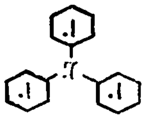
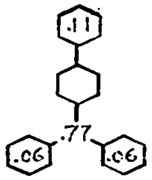
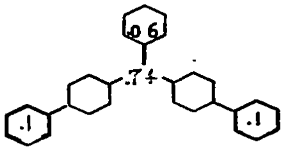
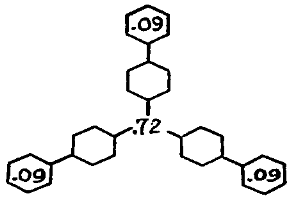
	Intensity (Observed)	Intensity (Calculated)				Charge Distribution In Rings
		(a)	(b)	(c)	(d)	
T.P.M.	q = 1.64Å q_f = .20Å	1.60Å 0				
Mono	q_x = 1.13Å q_y = 1.62Å q'_y = .45Å	.91Å 1.57Å .89Å	q_x 1.13Å q_y 1.52Å 1.20Å	.96Å 1.43Å .97Å	.95Å 1.48Å .93Å	 (d)
Di	q_x = 1.84Å q_y = 1.40Å q'_y = .62Å	1.83Å 1.24Å 1.03Å	1.78Å 1.20Å .99Å	2.16Å 1.08Å 1.13Å	1.80Å 1.20Å .98Å	 (d)
Tri	q = 2.50Å q_f = .58Å	2.30Å 0				

TABLE (3)

Results of H.M.O. Calculations

	Energy				Intensity	
	β	(KK)	Obs.	Symmetry	Calc.	Obs.
T.P.M.	0	0	0	A	---	---
	1.0000	(24)	24.0	E	2.5495	1.64
	1.5060	35.2	34.5	A	0	0.2
Mono	0	0	0	A	---	---
	0.7512	19.8	19.8	A	2.3494	1.62
	1.0000	26.3	24.0	B	1.2394	1.13
	1.2232	32.2	29.8	A	0.5266	0.45
	1.5024	39.6	37	A	1.0946	---
	1.5590	41.0			0.0913	---
Di	0	0	0	A	---	---
	0.7046	18.5	18.6	B	2.6303	1.84
	0.8106	21.3	21.7	A	1.8664	1.40
	1.1361	29.9	28.3	A	0.8110	0.62
	1.3174	34.6	36	B	0.2636	---
	1.4092	37.1		A B	0.8804	---
	1.5152	39.9		B	1.4216	---
Tri	0	0	0	A	---	---
	0.7046	(18.5)	18.6	E	3.6272	2.5
	0.9270	24.4	26.0	A	0	0.58
	1.3174	34.8	37	E	1.7465	---
	1.4093	37.1	40.0	E		
	1.6126	40.0		A	0	---
	1.6316	42.9		E	1.1977	---

moments (71) and the following formulae relating the various moments of a basic multiplet and the chemical shifts:

$$\langle \Delta V \rangle = N^{-1} \sum_i V_i = 0 ,$$

$$\langle (\Delta V)^2 \rangle = N^{-1} \sum_i (\Delta V_i)^2 ,$$

$$\langle (\Delta V)^3 \rangle = N^{-1} \sum_i (\Delta V_i)^3 .$$

where $\langle (\Delta V)^k \rangle$ is the k^{th} moment of the multiplet with respect to the mean frequency of the multiplet, (ΔV_i) is the shift of the "i" group of protons relative to the mean frequency, and N is the total number of protons. Anderson (72) simplified the solution of the above simultaneous equations by defining two new equations:

$$R = \frac{\langle (\Delta V)^3 \rangle}{\langle (\Delta V)^2 \rangle^{3/2}} ,$$

and ,

$$\Omega_i = \frac{\Delta V_i}{\langle (\Delta V)^2 \rangle^{1/2}} .$$

A general functional relationship between R and Ω_i is presented as a graph and the solution is reduced to reading the values of Ω_i corresponding to a definite R value of the system.

The various intensities of the multiplet in T.P.M. were determined by taking the average values of a graphical integration and that of areas measured by a planimeter. R was found to be 0.97, and Ω_i's were read from the graph given by Anderson as:

$$\Omega_B = -0.9 ,$$

$$\Omega_A = 0 ,$$

$$\Omega_C = 1.85 ,$$

where A, B, C correspond to the meta, ortho and para protons in a benzene ring. The relative chemical shifts from the above results are :

$$\delta_{o-m} = .181 \text{ p.p.m.} ,$$

$$\delta_{p-m} = .373 \text{ p.p.m.} ,$$

$$\delta_{p-o} = .554 \text{ p.p.m.} ,$$

which agree with the results of Berry (73).

DISCUSSION

Part A: Nitrosobenzene:

Before discussing the possible reasons for the failure of nitrosobenzene to emit radiation, it is appropriate to recapitulate some of the factors governing absorption and emission phenomena.

The first of these is the Franck-Condon principle. Because of the Born-Oppenheimer assumption, the wave function of a molecule can, to a good approximation be written in the form:

$$\psi = \phi_e \phi_v \phi_r \quad ,$$

where: ϕ_e = function of the position of the electrons and nuclei,

ϕ_v = vibrational wave function, depending on the inter-nuclear distance alone,

ϕ_r = rotational wave function.

Therefore, the inter-nuclear distance occurs in the molecular wave function in two places; in ϕ_v and ϕ_e. In general, ϕ_v varies much more rapidly with inter-nuclear distance than ϕ_e. For purpose of illustration, a simplified potential energy curve is represented as in Figure (44).

For a transition from the ith vibrational level of state I to the jth vibrational level of state II, the transition moment integral is given by:

$$M = \int I_i \left(\Sigma m\right) II_j \; d\Gamma \quad ,$$

which in terms of the separated wave functions becomes:

$$M = \int \left(\phi_e^{I} \; \phi_{v_i}^{I}\right) \Sigma m \left(\phi_e^{II} \; \phi_{v_j}^{II}\right) d\Gamma \quad ,$$

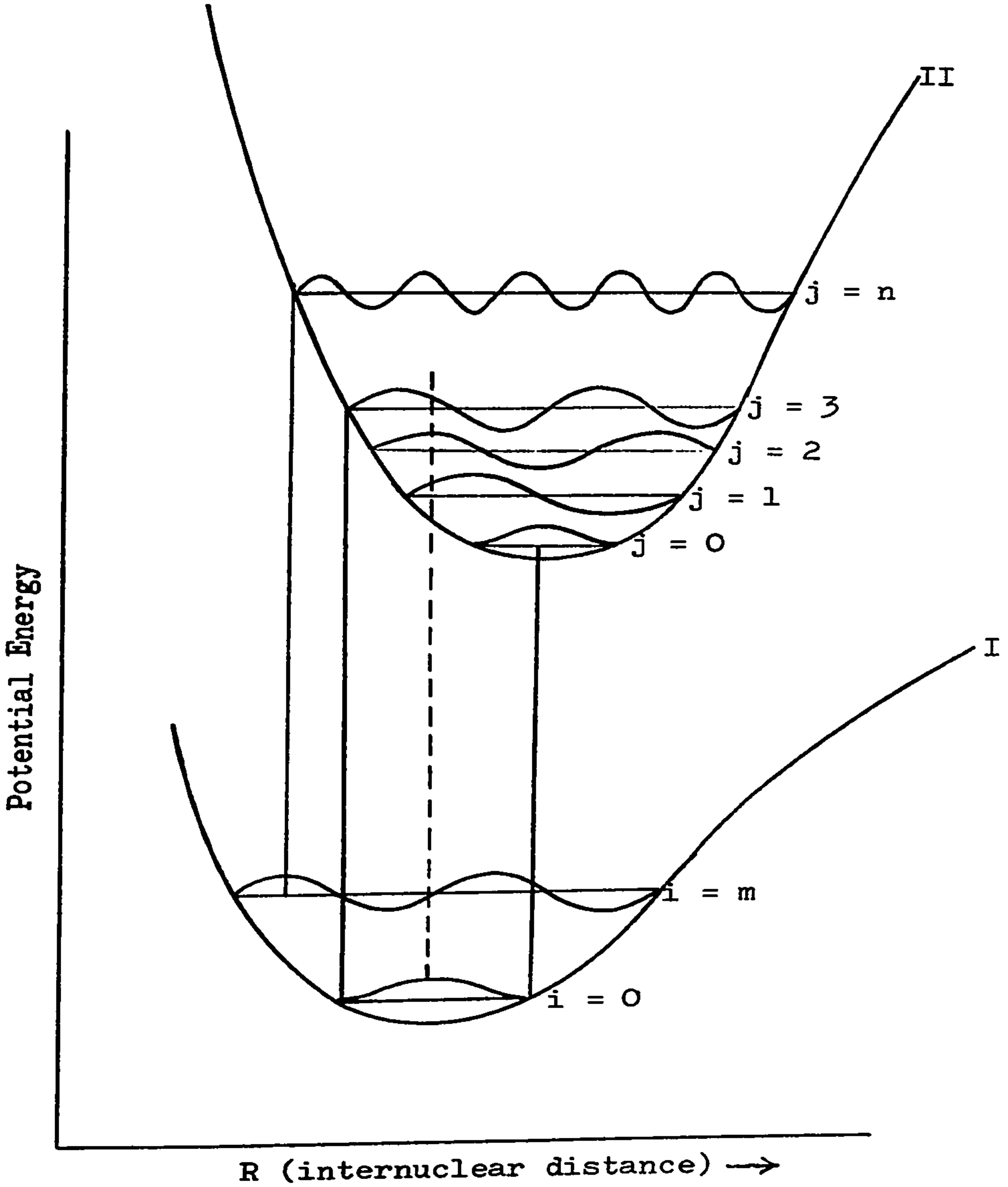


Figure (44)
Franck-Condon Principle

Since the product $\phi^{I}_{v_i}$ $\phi^{II}_{v_j}$ varies so much more rapidly with the inter-nuclear distance, the magnitude of the integral M will depend largely on the value of this product. For a transition from i = 0, to j = 0, in this particular molecule, this product is very small because $\phi^{I}_{v_i}$ is large in regions where $\phi^{II}_{v_j}$ is small. Such a transition is therefore very unlikely. Considering the next transition $\phi^{I}_{i=0} \longrightarrow$ $\phi^{II}_{j=n}$, the overlap of the two functions is large, but $\phi^{II}_{v_{j=n}}$ oscillates rather rapidly in the regions of this overlap. As a result, the product changes its sign frequently as R varies, and the positive part cancels the negative part so that the integral as a whole is small. Finally, the transitions from $i = 0 \longrightarrow j = 3, 4, 5$ represent cases where ϕ^{II}_{v} does not oscillate so much in the regions where ϕ^{I}_{v} is large. Hence, the product will be appreciable and these transitions are more probable. This represents the quantum mechanical arguments leading to the Franck-Condon principle, stating that transitions tend to occur between vibrational levels of two different electronic states which have approximately the same nuclear configuration. In other words, the transitions tend to go vertically as indicated by the solid lines. Consequently, the intensity distribution of an absorption band depends largely on the characteristics of the potential energy surface of the two electronic states involved. A transition is Franck-Condon forbidden when it involves unfavorable nuclear configurations.

The second important factor which has to be considered is the deactivation processes which occur immediately after excitation. Depending on whether the process is intra-, or inter-molecular, the deactivation is referred to as radiationless transition, or quenching, respectively. In either case, these processes are generally extremely efficient with the result that very often emission may be completely suppressed.

Radiationless transitions may occur between levels of the same or different multiplicity. The former is usually called internal conversion and the latter intersystem crossing. Internal conversion is responsible for the fact that there is only one fluorescence band in a molecule regardless of the wave length of the exciting light. When the molecule is excited to a higher level than the first, the system invariably cascades down to the lowest excited level before it emits and the excess excitation energy is given up to the surrounding medium as heat. Thus, infrared dissipation is a more efficient process than fluorescence. Kasha (74) has placed an upper limit of $\leq 10^{-4}$ to the ratio of the rate constant of spontaneous fluorescence to that of radiationless internal conversion,

$$\frac{k_L}{k_{I.C.}} \leq 10^{-4} .$$

Thus, the internal conversion process takes place at least 10^4 times as fast as the spontaneous fluorescence from levels higher than the first. A better idea of the rate for this process may be obtained if the life time of the excited state is taken as 10^{-9} secs. (74). Then the reciprocal rate of the internal conversion process is thus,

$$\frac{1}{k_{I.C.}} \leq 10^{-13}\text{sec.}$$

The process of internal conversion may therefore occur well within the period of vibration.

On the other hand, intersystem crossing refers to radiationless transitions occurring between a triplet and a singlet state. According to the theory of Lewis, this is the process whereby the phosphorescent triplet level is populated. In most organic molecules, particularly the aromatics, there is usually a low-lying triplet level. After the excited molecule has cascaded down to the lowest singlet level by internal conversion, there is a finite probability that the molecule might cross from the singlet to the lower energy triplet level. This probability may be measured by the intersystem crossing ratio, χ, which is defined as the ratio of quantum yields of phosphorescence to fluorescence:

$$\chi = \frac{\Phi_P}{\Phi_F} = \frac{k_{I.S.}}{k_F} .$$

If an arbitrary prohibition factor of 10^6 is applied to $\frac{1}{k_{I.C.}}$ on account of the spin-forbidden character, the reciprocal rate of intersystem crossing would be:

$$\frac{1}{k_{I.S.}} \leq 10^{-7} \text{ sec.}$$

This, together with an assumed life time of 10^{-9} sec. for the fluorescent state will give:

$$\chi = \frac{10^{7}}{10^{9}} = .01 .$$

In addition to the above intramolecular deactivations, those arising from intermolecular processes have to be considered as well. Possible mechanisms for this process are:

(i) chemical reaction with the solvent,

(ii) reaction with dissolved oxygen or other impurities,

(iii) bimolecular deactivation between two excited molecules,

(iv) reaction of excited with normal molecules,

(v) collisional deactivation by the solvent.

Any one of the above processes can deactivate the excited molecule and suppress emission totally or partially.

The proposed existence of the meta-stable triplet state has far-reaching consequences and it has stimulated a great many investigations. Of these, one of the most direct and significant is the work of G. Porter (75) who has studied the triplet state absorption and deactivation of a number of aromatic hydrocarbons by the method of flash photolysis. His results indicate the triplet state of anthracene has a life time of 10^{-3} sec. and that the intersystem crossing between the first singlet and the first triplet is approximately 10^4 times more efficient than that between the first triplet and the ground state. These results are extremely important in the present case of nitrosobenzene.

It is clear from the above that numerous competing pathways are open to the excited molecule. Whether the excited molecule will return to its ground state by radiative process or not will depend on the rate of the competing processes, on the natural life time and on the nuclear configuration of the excited state. In view of this, the failure of nitrosobenzene to emit is, perhaps, not so incomprehensible. However, the fact remains that fluorescence has been observed for many different classes of organic molecules under approximately the same conditions as used in the present research. Possible explanations for the anomaly are:

(1) The nitroso group is free to rotate and on excitation it may take up a different conformation. On the basis of the Franck-Condon principle, emission would be very improbable in such a case. However,

substitution of two methyl groups in positions ortho to the nitroso group has not improved the emitting property of the molecule as the results with 2, 6 dimethyl nitrosobenzene indicate. On the other hand, it is possible that emission occurs with such a low quantum yield that it escapes detection. In our case, this is very unlikely since the sensitivity of our detecting system (1 mv A.C.) is high and it was found entirely successful in the carbonium ion measurements.

(2) It is also possible that on absorption of ultra-violet light, nitrosobenzene decomposes. For some aliphatic nitroso compounds, it has been shown by Hammick and his co-workers (76) that the visible absorption is associated with photodecomposition.

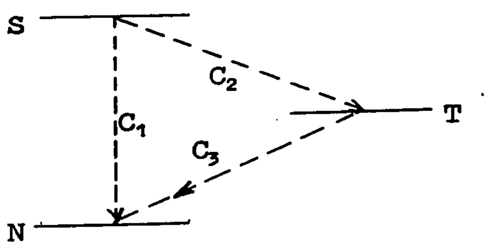
During one emission experiment, the sample tube of para-nitroso dimethyl aniline broke open in such an unusual manner as to indicate the generation of high gas pressure. Nitric oxide was suspected as a possible decomposition product. However, subsequent investigations could not provide definitive evidence.

(3) It is also possible that the more polar excited nitroso group will pick up a proton from the solvent, thus change the characteristics of the emitting species. However, the significant point is that most of the original work of fluorescence, including that of Lewis, was done in alcohol containing solvents and rigid glasses. Furthermore, our use of isopropyl alcohol--isopentane mixture or methyl cyclohexane--isopentane mixture as solvent were equally unsuccessful.

(4) Quenching of fluorescence by foreign substances, such as oxygen, alcohol, halogen atoms and nitric oxide, is often encountered in emission work. Quenching may be accounted for by two different mechanisms: (a) the quencher may form a complex with the fluorescent molecule before it has

absorbed light; and (b) the quencher interacts directly with the fluorescent molecule after it has been excited, forming a complex which may return to the ground state by radiationless transitions. Our sample has been prepared under vacuum, so that oxygen quenching seems very unlikely. However, it has also been found that the fluorescent substances themselves are among the most potent quenching agents. Porter (75) reported a quenching rate constant of $k = 10^{10}$ $mole^{-1}$ $sec.^{-1}$ for nitric oxide for various aryl triplets. The concentrations of our emission samples were varied considerably and the result seemed to indicate that such a "self-quenching" effect is not operative here.

(5) The various radiationless transitions may occur to such an extent that the radiative transition is completely suppressed. Three of these are of particular importance: C_1, the path from the first excited



level to the ground state, C_2, the intersystem crossing from a singlet to a triplet, and C_3, the return from a triplet to the ground state. C_1 is usually of lesser importance compared to the corresponding fluorescence return. However, its importance increases rapidly if the life time of the S state increases on account of the Franck-Condon factor, or if the S and N potential energy surfaces cross. When the system is such that a low-lying T state exists, then C_2 is certianly the most important process. For reasons not well understood yet, C_2 is by far the most rapid process in spite of the spin forbidden character and it seems to be unaffected by the nature of the medium. As mentioned previously, the life time of the T state in most organic molecules is of the order of 10^{-3} sec. which is long compared to the various rate constants of the quenching processes. A molecule in this state has, therefore, a very small probability of returning to N by emission.

Although the existence of a triplet state has not been detected, experimentally as shown by the spectrum of 2, 4, 6 tribromo nitrosobenzene, the analysis of Orgel (3) may well be correct and the triplet state of the compound lies very far in the infrared. In fact, it may well be that the excited singlet state passes readily into a linear configuration analagous to oxygen, and the triplet state so formed is very close in energy to the ground state but considerably different in nuclear configuration.

All considerations seem to point to the conclusion that the complete absence of fluorescence is a unique property of the aromatic nitroso compounds. Of course, the problem of the nitroso group emission and polarization could be pursued by more bulky substitution and by studies in the crystalline state. In the latter case, if it is possible to study the polarization of the N=O transition, it is also possible to determine unambiguously the polarization of the other aromatic transitions. Such a different approach thus deviates too far from the original object of this investigation.

It seems at the present moment that the luminescence obtained by Lewis and Kasha may not have arisen from the nitroso compound as they supposed, but may have been due to some impurity in their system. On the basis of the present findings the only feasible way which could possibly result in an unequivocal determination of the fluorescence of nitroso compounds might be in using a matrix of rare gases rather than the organic solvents used here. This would eliminate the possibility of chemical reactions in the excited states at least, but might not even so produce a successful result for the other reasons cited.

Part B: Carbonium Ions

In the foregoing sections, a low resolution spectroscopic study has been made of a sequence of molecular systems which vary by a similar chemical substitution in adjacent members. The series begins and ends with a molecule of trigonal symmetry and, as such, completes a cycle. The expectations based on two theoretical models, the structure representation and the H.M.O. method, have been compared to the experimentally determined values. This procedure is common to many scientific investigations besides spectroscopy, but the question arises as to how well the theoretical and practical results can be expected to correlate. In this sense then, some of the hazards arising in the correlation of theoretically and spectroscopically determined values bear some mention. There is, for instance, a 'non-crossing rule' in spectroscopy which states that under no circumstances will two energy levels of the same symmetry cross each other under the effect of some perturbation (85). Stated simply, levels of the same symmetry repel each other due to various terms in the Hamiltonian for the system. These terms may not normally be considered in the Hamiltonian for an isolated system, and may arise from solvent effects, ion pairing, and other phenomena. Since we are considering only a very restricted set of the totality of energy levels for any of these molecules, the possibility that some of the energy levels may be displaced due to this effect must be considered. In the carbonium ion sequence this is the most important in the case of T.P.M. where the highest state considered appears only as a shoulder on more intense absorption. One would expect a red shift from its 'true' or unperturbed position. This is one factor to consider. A second is the fact that under no circumstances has vibrational fine structure been observed for the carbonium ions in the highly polar solvents required in these determinations. Since the theoretical models used are for vibrationless molecules, then the significant experimental values to use would be the zero level vibrational components of each energy level, or the 0 - 0 vibronic transition. These are not available in low resolution liquid phase work in general and it is necessary to use instead the wave length of maximum absorption. These positions could be up to 0.1 or 0.2 in our energy units, away from the true 0 - 0 vibronic energies. In this case, one relies entirely upon the fact that the potential function be similar in the two states (i.e. excitation of one of 18 or more bonding electrons does not change the nuclear configuration markedly). Again this effect would be most marked in the higher energy low intensity transition, especially if this transition is allowed through mixing with an antisymmetric vibrational function. In this case the 0 - 0 transition is completely forbidden, and the apparent centre would be shifted to the blue of its true position. One further intramolecular effect which should be considered applies to the molecular species with trigonal symmetry. The Jahn-Teller principle states that it is not possible to have spin-orbital degeneracy in electronic states of a polyatomic molecule, that any minescule perturbation will lower one of the two degenerate levels so that the functions cannot be truly degenerate. This is usually through a vibronic interaction and results in distorted molecules which have changed their nuclear orientation in such a way as to destroy the trigonal symmetry. In the cases at hand, this intramolecular effect is felt to be considerably smaller than intermolecular interaction of the ions with the solvent. Justification for this is that the first absorption band width is much larger in the case of T.P.M. than with Tri, and one would expect similar band width with a pure Jahn-Teller effect. In fact, the most apparent and most difficult factor to be considered is the interaction between the spectroscopic ion and its surroundings. Since Tri does not demonstrate a marked splitting at all, while T.P.M. does, only the latter compound will be considered here. The matter has been discussed in a recent publication based on the present research (86). Briefly, the degeneracy of T.P.M. has been split so that two intense low energy transitions are observed as in Figure (32). This implies that the ions exist in some kind of off-axis perturbing field. Since the splitting is not sensibly dependent upon either solvent or counter-ion, it seems reasonable to suspect that perturbation is due to the charge of the counter-ion alone. Nor does the N.M.R. spectrum show any nuclear splitting which could be ascribed to a counter-ion, even in cases where it should be observed. On the other hand, conductivity experiments have indicated that most of the ions are bound as ion pairs, and the number of free ions is very small. The two-step ionization suggested by these workers is compatible with a rapid exchange of counter-ions between carbonium ions. The rate would have to be rapid compared to N.M.R. frequencies (10^{-2}sec.$^{-1}$) but slow compared to optical frequencies (10^{-8}sec.$^{-1}$) so that, optically speaking, the ions appear as bound. Exactly how much this effect persists with the other ions of the series is impossible to assess. These interactions would, however, shift the energy levels and change the observed intensities relative to the unperturbed ion. For reasons already presented, agreement would be expected to be better between Tri and Di than between T.P.M. and Mono, as was observed to be the case. Even in the most amenable case, however, the frailities of the methods used must be realized, and that the inherent errors in the assumptions that have been used might easily introduce quantitative discrepancies between theory and practice which might amount to appreciable fractions of the total. On the other hand, the qualitative features of the spectra should be accurately predicted by any acceptable model.

In choosing a system for theoretical study, a compromise is usually made between theoretical interest and practical considerations. In this respect, the present system seems about as convenient as is reasonably possible. For instance, as was pointed out in the previous section, one of the complicating factors is the change of geometry on excitation. When this happens, the theoretical model becomes less applicable. Distortion of this nature is expected to be small when a large number of bonding electrons is involved and optical excitations do not materially change this number. This does not apply so truly in the case of smaller systems and the proliferation of excited states makes the situation for larger condensed aromatic systems more susceptible to questionable assignments. A further simplifying condition is the fact that the sequence of compounds studied contains only hydrocarbons, so that the complications associated with heteroatoms, such as in the equivalent studies on dye molecules, are completely avoided.

The experimental results were in complete agreement with the predictions based on H.M.O. and the structure representation methods. Qualitatively, both theories predict one intense absorption in the optical region for T.P.M. and Tri, while there should be two strong and one weak absorption for Mono and Di. In the cases of Mono and Di, the theories further predict that all three transitions are allowed in the molecular plane. The shortest wave length band is polarized in the 'y' direction in both molecules, while in Mono, the longest wave length transition is polarized in the 'y' and the second in the 'x' direction. This polarization relationship is reversed in the case of Di. These theoretical considerations are verified by the results presented in this research. For T.P.M. and Tri, however, the spectra consist of an intense band in the optical region and a weak band in the ultraviolet. As far as molecules with trigonal symmetry are concerned, the weak band is assumed to gain intensity through distortion from the perfect symmetry. This is particularly obvious in the case of T.P.M. where distortion has actually split the degenerate E state. Nevertheless, the demonstration that these off-axis perturbations exist is not, in itself, sufficient to prove that the forbidden transition has gained sufficient intensity to correlate with the assignment given, even though it gains intensity with departure from C_3 symmetry. A considerably more convincing test is to be found through the calculation of the transition intensities. As explained in the numerical section, these calculated intensities depend upon the transformation matrix $\underset{\sim}{S}^{-1}$ which in turn depends upon the relative magnitudes of the transition energies. The intensity of the forbidden band will always be zero, since the $\underset{\sim}{S}^{-1}$ matrix incorporates the requirements of perfect symmetry. However, a faulty choice for the value of one of the transition energies, in this case, the normally forbidden band in T.P.M. and Tri, will result in a gross difference between the observed and calculated intensity for the first absorption. This calculation gives the results already cited, namely 1.60Å and 2.30Å in the case of T.P.M. and Tri, respectively. These compared very favorably with the observed values of 1.64Å and 2.50Å, respectively. By substituting other values for the forbidden band, as for instance for transitions further in the ultraviolet this good agreement vanishes.

Further reliance in the method of structures is evident from the spectra of sulphonated carbonium ions. It is reasonable to expect an increase in the energy of a sulphonated xenyl ring compared to a non-sulphonated one because the strongly deactivating sulphonic group would repel the positive charge in that ring. Thus the effect of added conjugation would be partly compensated by this charge repulsion effect. It would be expected, then, that the lowering of the energy of a carbonium xenyl ring would not be as marked in the case when this ring is sulphonated. Accordingly, the sulphonated Mono derivatives should have a spectrum more similar to T.P.M. than to Mono, depending upon how large the effective cancellation is found to be. As can be seen from Figure (20), the spectrum of monosulphonate shows less degenerate splitting than the spectrum of Mono.

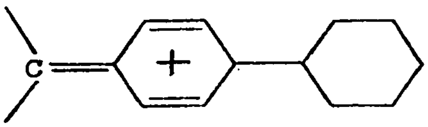
These considerations must be compared to the assignments suggested by Chu and Weissman who apparently overlooked the key fact that the low intensity transitions were polarized in the 'y' direction for both Mono and Di. These authors based their analysis upon the fact that biphenyl absorptions are found near 2600Å in the carbinols and assumed that these transitions were transposed to the 3000Å region on the formation of the carbonium ions. Further assumptions were required regarding the polarization of the long wave length transition of biphenyl. On the basis of the present considerations, it would appear that these assumptions are not warranted, and that the xenyl transitions do not in fact suffer this large displacement to the red. The absorptions under consideration appear unique to the carbonium ions, and not to the parent carbinol.

Whereas these qualitative aspects of the problem seem unequivocal, the main concern of this research lies in the direction of quantitative agreement. In this respect, inspection of Table (3) indicates that the agreement with H.M.O. calculations is satisfactory with regard to the transition energies and the state symmetries. It is significant to note that H.M.O. predicts the occurrence of a band in T.P.M. with the same energy as the A ⟶ B transition of Mono. This is due to the fact that m.o.'s of symmetry B have nodes in the perturbation direction and therefore the orbital energies do not change in going from T.P.M. to Mono, and because the lower transitions each involve the non-bonding m.o. with zero energy. By the same token, Tri is predicted to have a band occuring with the same energy as the A ⟶ B transition in Di. These conclusions are positively verified and the results agree with the predictions of Grinter and Mason (87) based on similar H.M.O. considerations. In the present case, the identification of the bands has been experimentally proven by the polarization determination.

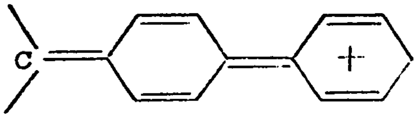
When intensities of transitions are considered, values calculated by H.M.O. are generally much higher than those observed. This can be attributed to the limitation of the H.M.O. method with regard to intensity calculation and further refinement, such as the ω -technique, would probably improve the agreement but increase the labor expended. On the other hand, the method of structures gives much better assessment of the experimental intensity values as shown in Table (2). It should be borne in mind that this agreement does not depend upon the

the use of a parent compound to obtain the tranistion moment magnitudes as was necessary in the case of the earlier dye studies. These intensities were based on a reasonable estimate made from the classical nuclear configuration.

Within the framework of the structure representation method, attempts have been made to improve the predicted intensity values. Two major changes were effected in the calculation. One of these was to use an expanded secular determinant to take into account extra structures, for example, in the case of Mono, a structure of the following type:



in addition to



This results in a higher order of secular determinant but more seriously introduces phantom states whose existence cannot be experimentally demonstrated. Another attempt was to include overlap integrals in the determinant to account for any non-orthogonality between structures. A series of calculations was also carried out where attempts were made to correct for the possibility that the interaction beween the central atom and a xenyl ring (i.e. ϵ_{14}) might change the interactions involving phenyl rings (i.e. ϵ_{24}, ϵ_{34}). Refinements of this nature, though theoretically justifiable, were found to be quite involved mathematically and as a result deter from the general idea of a simple, workable theory.

Accordingly, the work reported was confined to the simpler methods of calculation based on the work of Adam (32). In the case of trigonal molecules, such as T.P.M. and Tri, the calculated intensities based on the $\underset{\sim}{S}^{-1}$ derived from the structure method together with the electric moments estimated through a classical valence picture, are in excellent agreement with the observed values. In the original application of this method to dye molecules, this procedure was not possible because of the uncertainties in treating the heteroatoms. That such good agreement is obtained in the present case may certainly be looked upon as positive indication of the soundness of the structure representation. Furthermore, the agreements in the cases of Mono and Di are also very reasonable, and are within 15 % of the observed values as shown in Table (2). This certainly represents a considerable improvement over the H.M.O. results where some of the predicted intensities are out by 100 % or more.

The elements in the perturbation matrix have been chosen in a variety of ways as mentioned in the numerical section. The most uniform agreement was found when only one parameter, namely ϵ_{11}, was used. In fact, starting with Tri as the parent molecule, it was possible to successfully reproduce the spectra of Di, Mono, and T.P.M., in this order, treating one molecule as the parent of the other. Agreement of this nature is gratifying when the simplicity of the method is kept in mind. However, when more constraints are put on the matrix elements, for instance varying ϵ_{11}, $\epsilon_{14} = \epsilon_{41}$ and ϵ_{44} at the same time, the agreement obtained, though still reasonable, is poorer.

Not so reasonable were the results of the magnetic resonance spectra. The original purpose for studying the N.M.R. spectra of these carbonium ions was to provide independent information concerning the ground state wave functions of these species. This should have been achieved through the currently proposed empirical relationship between proton chemical shift and excess charge in the carbon atom attached to the proton under investigation. This charge distribution in the ion is also reflected in the elements of the $\underset{\sim}{S}^{-1}$ matrix. In this way, information from N.M.R. could have provided an independent check on the theoretical model and vice versa.

Qualitatively, the spectra of T.P.M. consists of a para proton triplet, and a meta proton triplet overlapped in part by an ortho proton doublet. Chemical shifts derived from the spectrum agree satisfactorily with literature values as mentioned in the numerical section. The spectra of Mono, Di and Tri are less susceptible to quantitative analysis due to their great complexity. Nevertheless, certain aspects of these spectra may be dealt with qualitatively. It appears that when a xenyl ring is present in the ion, certain new bands arise as can be seen from Figures (40) to (43). These consist of a doublet and a triplet. Each gains in relative intensity as the number of xenyl rings increases. In the case of Mono, a tentative assumption would be that the para proton triplet in T.P.M. goes up field and is submerged under the doublet which appears characteristic of the xenyl ring. This would suggest a decrease in charge in the phenyl ring. The triplet characteristic of xenyl rings, however, remains relatively constant in position in going from Mono to Di and Tri. These qualitative aspects are in agreement with the structure calculations as shown in Table (2).

The quantitative aspects of the spectrum of T.P.M. require further attention since the charge distributions obtained from N.M.R. analysis (88) disagree with those expected from the structure method and from calculations based on the optical intensities. Furthermore, the N.M.R. results indicated that the meta position carries more positive charge than the ortho position. This is clearly contrary to classical chemical thought. However, it must be remembered that chemical shift is the combined effect of many factors. In the present case, the most important complications would result from ion-pair formation, anisotropy of the charged central carbon atom, and the ring current due to the nearby phenyl rings. Unless these factors can be differentiated from the simple effect due to charge distribtuion in the ring, chemical shift data will give erroneous conclusions. Apparently, the technique of N.M.R. at the present stage is still not entriely competent in treating cases as complicated as the present system. Although Pople's S.C.F. calculations (89) seem to substantiate the N.M.R. results without inclusion of these other complicating factors, the fact that ion-pairing appears to exist in the case of T.P.M. casts some doubt on the reliability of these sophisticated calculations. Furthermore, the optical intensities calculated using the S.C.F. charge distribution and the structure representation wave functions give very poor agreement with those obtained experimentally.

CONCLUSIONS

As shown in the present research, the structure representation method is an extremely convenient tool in studies of the π electron systems. The calculations based on this method agree substantially with the results of the H.M.O. method but are in much better agreement with the experimental results in the question of intensities. The method is in essence a semi-empirical perturbation technique. Mathematical difficulties which tend to limit the usefulness of most non-empirical methods are avoided by the use of matrix algebra. Electron interactions are included as matrix elements derived from observed quantities. In this respect, it is superior to some non-empirical methods and is capable of treating complex systems.

The fact that excellent accounting of intensities in T.P.M. and Tri is given by the structure representation, together with classical valence theory, gives much weight in the justification of the fundamental assumption that structures $\langle 1 \rangle$ are equivalent to structures $\langle 2 \rangle$. Furthermore, the agreement demonstrated in the present research with regard to choice of energy levels, lends strong support to Simpson's scheme of classifying the π electronic levels into 'N' and 'E' states, namely, that the number of N states is the same as the number of low energy structures. This theorem should be modified somewhat, since in the present case, the Kekulé structures themselves have been neglected, and further, the ortho and para structures have been lumped together and considered as a single entity. There are in fact forty-four of these structures, but even so, the method works by consideration of only four composite strucutres. The grouping was of course dictated by chemical intuition but is probably justified best by the fact that the interactions within a given structure are more or less constant and do not appear explicitly in the general formulation. These interactions are probably much stronger than those which appear as matrix elements in the E' matrix and the reduction is probably only justified by their constancy. However, this result may be of some use in the consideration of other systems, such as naphthalene negative ion, where many such valence bond structures can be drawn. Judicious reduction may be possible even in this difficult case.

Certain mathematical difficulties are apparent when attempts are mde to obtain better agreement with the experimental results. As was seen, these arise when added constraints are put into the computational scheme. When the calculations are so restricted, complex energies are sometimes found and these have no significance in this or any other system. The best results were obtained in the present case when only a single parameter was used. Further refinements, however justified, gave some deterioration in the agreement with experiment,. It may be that the principle source of quantitative disagreement may in fact lie with the uncertainties in interpretation which have been mentioned with respect to the quantities which have been measured in the laboratory.

It may be of some advantage in the future to carry out a similar study under conditions of higher resolutions, and where vibrational analyses are available for the compounds, to remove some of those uncertainties. At present, it seems unlikely that this will be possible with organic carbonium ions since their existence seems limited to high dielectric solvents where such resolution is at best difficult.

Within the framework of low resolution spectroscopy, the structure method has been shown to have some advantage in simplicity and in accuracy, and in another context may be used to predict N.M.R. spectra on the basis of optical data alone.

APPENDIX (I)

The n electron was initially in a sp^2 orbital of the nitrogen atom and excited to a p_z orbital.

$$\therefore \quad \Psi_i = \Psi_{sp^2} \qquad \Psi_f = \Psi_{p_z}$$

$$\Psi_{sp^2} = \frac{1}{\sqrt{3}}\,\Psi_{2s} + \frac{\sqrt{2}}{\sqrt{3}}\,\Psi_{p_{xy}}$$

The only contribution expected from ΣM is that of z, hence the important part of Ψ_{sp^2} is $\frac{1}{\sqrt{3}}\,\Psi_{2s}$

$$\vec{q} = \int \Psi_i \,\Sigma M\, \Psi_f \, d\tau$$

$$Z = r\cos\theta$$

$$\Psi_i = \Psi_{sp^2} = \Psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}(2-\rho)\,e^{-\frac{\rho}{2}}$$

$$\Psi_f = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}\rho\, e^{-\frac{\rho}{2}}\cos\theta$$

$$\rho = \left(\frac{Z}{a_o}\right)r$$

$$\therefore \quad \vec{q} = \int\left[\frac{1}{\sqrt{3}}\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}(2-\rho)\,e^{-\frac{\rho}{2}}\right]\left[r\cos\theta\right]\left[\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}\rho\, e^{-\frac{\rho}{2}}\cos\theta\right]d\tau$$

$$d\tau = r^2\sin\theta\, dr\, d\theta\, d\phi$$

$$\therefore \quad \vec{q} = \frac{1}{32\pi\sqrt{3}}\int_{\rho=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left(\frac{a_o}{Z}\right)e^{-\rho}\cos^2\theta\, d(\cos\theta)\, d\phi\,(2\rho^4-\rho^5)\,d\rho$$

$$= \frac{1}{16\sqrt{3}}\,\frac{a_o}{Z}\int_{\rho=0}^{\infty}(2\rho^4-\rho^5)\,e^{-\rho}\,d\rho\int_{\theta=0}^{\pi}\cos^2\theta\, d(\cos\theta)$$

$$= -\frac{1}{16\sqrt{3}}\left(\frac{a_o}{Z}\right)\left(\frac{\cos^3\theta}{3}\right)_{\theta=0}^{\pi}\int_{\rho=0}^{\infty}(2\rho^4-\rho^5)\,e^{-\rho}\,d\rho$$

$$\therefore \quad \vec{q} = \frac{2a_0}{3\sqrt{3}\,16Z}\left(2\cdot 4! - 5!\right)$$

$$= \frac{a_0}{3\sqrt{3}} \cdot \frac{9}{Z}$$

Z is equal to the nuclear charge of 7 minus the screening effect of the remaining 6 electrons. Taking 0.85 for the 2π electrons and 0.35 for the four inner electrons,

$$Z = 7 - \left[(2 \times .85) + (4 \times .35)\right]$$

$$Z = 3.9$$

$$a_0 = 0.53\ \text{Å}$$

$$\therefore \vec{q} = 0.3\ \text{Å}$$

However, as shown by the calculation of McEwen (90), there is indication that the N_{sp^2} and O_{p_z} electrons form bonding moleculer orbitals. This will reduce the above intensity by approximately a factor of two.

BIBLIOGRAPHY

(1)	B.G. Gowenlock, W. Luttke	Quarterly reviews, Vol XII, p321 (1958).
(2)	G.N. Lewis	J. Am. Chem. Soc., 67, 994 (1945).
(3)	L.E. Orgel	J. Chem. Soc., 1276 (1953).
(4)	H. McConnell	J. Chem. Phys., 20, 700 (1952).
(5)	J. Mason	J. Chem. Soc., 3904 (1957).
(6)	K. Nakamoto	J. Chem. Phys., 20, 197 (1952).
(7)	Y. Matsunaga	Bull. Chem. Soc., Japan, 29, 969 (1956).
(8)	M.S. Welster	J. Chem. Soc., 2841 (1956).
(9)	A.I. Jitaigorodskii	"Organic Chemical Crystallography", Consultants Bureau Enterprises, Inc., New York, pp. 399 (1955).
(10)	B.P. Wladen	Ber., 35, 2018 (1902).
(11)	A Maccoll	"The Transition State", p160, Special publication No. 16, The Chemical Society, London (1962).
(12)	M.C.R. Symons	Mo. Phys., 3, 205 (1960).
(13)	N.C. Deno	J. Am. Chem. Soc., 86, 1745 (1964).
(14)	M.C.R. Symons	J. Chem. Soc., 1 (1961).
(15)	G. Dallinga	Mol. Phys., 1, 123 (1958).
(16)	C. MacLean	Mol. Phys., 1, 247 (1958).
(17)	W.P. Weijland	Ph.D. thesis, Vrije Univesiteit te Amsterdam (1958).
(18)	P.H. Van Der Meij	Private Copy, Vrije Univesiteit te Amsterdam (1958).
(19)		Technical Information, Varian Associates.
(20)	L.P. Hammett	J. Am. Chem. Soc., 55, 1900 (1933).
(21)	V. Gold	J. Chem. Soc., 2102 (1951).

(22) N.N. Licktin J. Am. Chem. Soc., 73, 5530 (1951).

(23) Y. Pocker J. Chem. Soc., 240 (1958).

(24) J.L. Cotter J. Chem. Soc., 2988 (1959).

(25) R. Stewart Can. J. Cehm., 39, 1849 (1961).

(26) N.C. Deno J. Am. Chem. Soc., 73, 3644 (1951).

(27) A. Streitwieser, Jr. J. Am. Chem. Soc., 74, 5288 (1952).

(28) V. Gold J. Chem. Soc., 3944 (1956).

(29) G.N. Lewis J. Am. Chem. Soc., 64, 1774 (1942).

(30) S. Weissman J. Chem. Phys., 22, 21 (1954).

(31) D.W.A. Sharp J. Chem. Soc., 678 (1957).

(32) F.C. Adam Ph.D. thesis, University of Washington, (1957).

(33) A.A. Morton J. Am. Chem. Soc., 60, 284 (1938).

(34) A. Streitwieser, Jr. "Molecular Orbital for Organic Chemists", John Wiley and Sons, Inc. (1961).

(35) G.W. Wheland J. Chem. Phys., 17, 264 (1949).

(36) A. Streitwieser, Jr. J. Am. Chem. Soc., 82, 4123 (1960).

(37) R.S. Mulliken J. Am. Chem. Soc., 76, 4770 (1954).

(38) C.C.J. Roothaan Rev. Mod. Phys., 23, 69 (1951).

(39) J.A. Pople Trans. Faraday Soc., 909 (1954).

(40) L. Pauling J. Chem. Phys., 1, 280 (1933).

(41) J.W. Linnett J. Chem. Soc., 1035 (1962).

(42) W.T. Simpson J. Am. Chem. Soc., 75, 597 (1953).

(43) W.T. Simpson J. Am. Chem. Soc., 76, 6285 (1954).

(44) W.T. Simpson J. Am. Chem. Soc., 76, 6293 (1954).

(45) W.T. Simpson J. Am. Chem. Soc., 73, 5363 (1951).

(46) W.T. Simpson J. Am. Chem. Soc., 77, 6164 (1955).

(47) A. Saika J. Chem. Phys., 22, 26 (1954).

(48) J.A. Pople — Proc. Roy. Soc., A 239, 541 (1957).

(49) P.L. Corio — J. Am. Chem. Soc., 78, 3043 (1956).

(50) W.G. Schneider — J. Am. Chem. Soc., 80, 3497 (1958).

(51) T. Schaefer — Can. J. Chem., 41, 966 (1963).

(52) P. Pringsheim — "Fluorescence and Phosphorescence", Interscience Pulishers, Inc., New York (1949).

(53) S. McClure — J. Chem. Phys., 22, 1668 (1954).

(54) S. Silverman — Rev. Sci. Instr., 12, 212 (1941).

(55) P. Pringsheim — "Fluorescence and Phosphorescnece, p 383 Interscience Publishers, Inc., New York (1949).

(56) R.M. Hochstrasser — Can. J. Chem., 39, 1776 (1961).

(57) L, Gattermann — "Laboratory Methods of Organic Chemistry", MacMillan and Co., Ltd., London, p 179 (1938).

(58) R.R. Homes — J. Am. Chem. Soc., 3454 (1960).

(59) E.J. Bowen — "The Chemical Aspects of Light", Oxford, 2nd Edition (1946).

(60) L.F. Fieser — "Experiments in Organic Chemistry", D.C. Heath and Company, New York, p 183 (1941).

(61) W. Schlenk — Ann., 295 (1909).

(62) S.T. Bowden — J. Chem. Soc., 306 (1939).

(63) A.A. Morton — J. Am. Chem. Soc., 53, 4028 (1931).

(64) K.M. Harmon — J. Org. Chem., 25, 1442 (1960).

(65) L.J. Bellamy — "The Infrared Spectra of Complex Molecules", John Wiley and Sons, Inc., New York, p 350 (1958).

(66) M. Kasha — J. Am. Chem. Soc., 77, 4463 (1955).

(67) G.W. Wheland "Resonance in Organic Chemistry", John Wiley and Sons, Inc., New York (1955).

(68) C. Reid "Excited States in Chemistry and Biology", Butterworth's Scientific Publications, London (1957).

(69) W. Kauzmann "Quantum Chemistry", Academic Press, Inc., New York (1957).

(70) M. Kasha and H.J. Bernstein J. Am. Chem. Soc., 67, 994 (1945).

(71) W.G. Schneider and J.A.Pople "High Resolution Magnetic Resonance", McGraw Hill, Toronto (1959).

(72) W.A. Anderson J. Chem. Phys., 26, 1501 (1957).

(73) R.S. Berry J. Chem. Phys., 34, 1460 (1961).

(74).M. Kasha Dis. Faraday Soc., No. 9, p 15 (1950).

(75) G. Porter Dis. Faraday Soc., No. 17, (1954).

(76) D.L. Hammick J. Chem. Soc., 1679 (1935).

(77) J.R. Platt J. Opt. Soc. Amer., 43, 252 (1953).

(78) V. Gold J. Chem. Soc., 3944 (1956).

(79) W.G. Schneider Can. J. Chem. 41, 966 (1963).

(80) V.R. Sandel J. Am. Chem. Soc., 85, 2328 (1963).

(81) J.A. Pople Trans. Faraday Soc., 901 (1954).

(82) G.N. Lewis J. Am. Chem. Soc., 67, 994 (1945).

(83) K. Ingold J. Chem. Soc., 173 (1924).

(84) D.L. Hammick J. Chem. Soc., 2358 (1930).

(85) G. Herzberg "Molecular Spectra and Molecular Structure", I. Spectra of Diatonic Molecules, D. Van Norstrand Company,Inc., New York, p 295 (1950).

(86) F.C. Adam and E. Ng Can. J. Chem., 42, 810 (1964).

(87) R. Grinter and S.F. Mason Proc. Chem. Soc., 386 (1961).

(88) T. Schaefer and W.G. Schneider Can. J. Chem., 41, 966 (1963).

(89) J.A. Pople J. Phys. Chem., 61, 6 (1957).

(90) L. McEwen J. Chem. Phys., 34 547 (1961).