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MAGNETIC CIRCULAR DICHROISM STUDIES OF ELECTRON-DONOR-ACCEPTOR COMPLEXES IN SOLUTION

by

GRACE MICKEVICIUS

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment
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Doctor of Philosophy, The City University
of New York.

1974

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

MAGNETIC CIRCULAR DICHROISM STUDIES
OF ELECTRON-DONOR-ACCEPTOR
COMPLEXES IN SOLUTION

by

Grace Mickevicius

Adviser: Professor Angelo V. Santoro

In this investigation magnetic circular dichroism (MCD) was applied to an especially difficult structural problem, namely the structure determination of electron-donor-acceptor (EDA) molecular complexes in solution. The complexes selected for study had to satisfy certain criteria with respect to solubility, wavelength region of absorption, symmetry considerations and intensity of MCD bands. Consequently the aromatic hydrocarbons chosen as donors were triphenylene, benzene, mesitylene (1,3,5-trimethyl benzene), naphthalene, phenanthrene, and anthracene. The acceptors selected were iodine, tetracyanoethylene (TCNE), mellitic trianhydride (MTA), and 1,3,5-

trinitrobenzene (TNB).

The results obtained in this study were the first reported instances of MCD spectra of electron-donor-acceptor molecular complexes in solution. The MCD CT band of the triphenylene·iodine complex was found to be an A-term, of the benzene·iodine complex a set of overlapping A-terms, of the mesitylene·iodine complex a broad A-term, and of the others B-terms. Furthermore two B-terms were detected for the two CT bands of the triphenylene·tetracyanoethylene complex. Consequently strong evidence was obtained for the structure of the aromatic hydrocarbon·iodine complexes where the iodine axis lies perpendicular to the plane of aromatic hydrocarbons, and in addition the iodine seems to be always centrally located with respect to the aromatic ring. Also the existence was confirmed of the complexes between iodine and the solvents p-dioxane and ethanol by the detection of B-terms in the MCD spectrum.

This investigation also contributed additional information for elucidation of the absorption spectrum of iodine. The originally hidden band in the absorption spectrum of iodine due to the $^1\pi_{1u} \leftarrow {}^1\Sigma_g^+$ transition was revealed clearly as a positive B-term at 470 mu in the MCD spectrum. This is an example of the capability of MCD to uncover hidden absorption bands. The other negatively signed B-term at 530 mμ is due to the $^3\Pi^+_{ou} \leftarrow {}^1\Sigma^+_g$ transition. Another dramatic result was the discovery of the broad positive B-term at 665 mμ due to the $^3\Pi_{1u} \leftarrow {}^1\Sigma^+_g$ transition, which is extremely difficult to detect in the absorption spectrum since it is a barely perceptible shoulder. This is an illustration of the utilization of MCD as a tool for detecting otherwise weak bands in the absorption spectrum. Another band was also found at higher concentrations of iodine at 280 mμ which has been attributed to the $I_2 \cdot I_2$ dimer complex.

In addition a technique was developed for the experimental determination of the equilibrium constant. The absorption band of iodine in the visible region was utilized for this purpose. Knowledge of the equilibrium constant was necessitated due to the presence of uncomplexed material in the equilibrium mixture .

ACKNOWLEDGEMENTS

I wish to express my appreciation to my adviser Professor Angelo Santoro for his valuable direction throughout the course of this project. Also I am grateful to the members of my committee, Professor William Berkowitz and Professor Louis Massa, for their helpful suggestions.

I sincerely thank Mr. David Snyder for all the illustrations, and my family for their constant encouragement and understanding.

CONTENTS

TABLES

FIGURES

Page

I. INTRODUCTION

Electron-Donor-Acceptor (EDA) Complexes

Classification of Donors and Acceptors

Preceding any discussion of the formation of the above complexes, a classification of the donor and acceptor types is imperative. They have been characterized excellently by Mulliken. His classification is most explicit as presented in tabular form.[1] (See tables 1 and 2).

Increvalent donors may be described approximately as "lone" pair (n) donors. For example an electron is donated from nitrogen in ammonia, $:NH_3$, and an odd electron remains which can form an additional valence bond (this is the origin of the term increvalent). However it must be realized that the "lone" pair on nitrogen occupies a molecular orbital which also extends somewhat over the neighboring atoms. Similarly, increvalent acceptors are "vacant" orbital (v) acceptors. Thus an electron is accepted into the "vacant" orbital of,

TABLE 1

Types of Donors

Number of electrons	Functional type	Structure type	Examples[a]
Odd	Free radical	R	C_2H_5, NO, NO_2
Even	Increvalent	n	R_2X, RCN, R_2S, R_2CO
	Sacrificial	σ	Aliphatic hydrocarbons
		π	Aromatic and unsaturated hydrocarbons

[a] R = H, alkyl or other group; X = F, Cl, Br, I.

TABLE 2

Types of Acceptors

Number of electrons	Functional type	Structure type	Examples[a]
Odd	Free radical	Q	X, OH, NH_2
Even	Increvalent	v	BX_3, AlX_3
	Sacrificial	σ	X_2, HX, RX
		π	Aromatic and unsaturated hydrocarbons especially if polycyclic containing electron-withdrawing groups. (TCNE, quinones, maleic anhydride.)

[a] R=H, alkyl or other group; X=F, Cl, Br, I; TCNE=tetracyanoethylene.

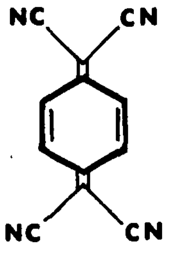
for example, boron in BCl_3 which can form an additional valence bond. But in this instance also the "vacant" orbital is a molecular orbital which may extend to a degree over the other atoms.

Sacrificial donors involve donation from a bonding molecular orbital, so that such a donor entering a complex weakens the bonding within itself. This results in an increase of bond lengths and a decrease in the corresponding vibrational frequencies within the donor. In sacrificial acceptors the acceptance of an electron is into an antibonding molecular orbital with resulting weakening of bonding within the acceptor. Sacrificial donors and acceptors may be further classified as σ and π with respect to the type of molecular orbital involved. Both σ and π acceptors are prevalent, but σ donors are weak and only π donors are usually encountered.

Examples of Types of Complexes

From the classification of donors and acceptors various types of possible complexes may be exemplified. An illustration of the $b\pi \cdot a\sigma$ type is aromatic hydrocarbon·iodine. This notation indicates that an electron is transferred from a bonding π orbital of the donor, aromatic hydrocarbon, to an antibonding σ_u orbital of the acceptor, iodine. Consequently iodine is a sacrificial acceptor and the bond between the atoms is weakened upon acceptance of an electron. Similarly in the aromatic hydrocarbon·TCNE (tetracyanoethylene) complex which is an example of the $b\pi \cdot a\pi$ type, an electron is transferred from a bonding π orbital of the aromatic hydrocarbon to an antibonding π orbital of the acceptor, TCNE.

The dioxane·halogen complexes may be described as $n \cdot a\sigma$ types. Furthermore, $NH_3 \cdot BF_3$ illustrates an $n \cdot v$ addition compound involving an increvalent donor and an increvalent acceptor. Most of the R-Q types between radical donors and acceptors encompasses compounds with ordinary chemical bonds. In addition to all these types, complexes between radicals and radical ions such as $(TCNQ)^{-2}$ have also been investigated.[2] TCNQ (-7, 7, 8, -8 - tetracyanoquinodimethane) has the following structure:



It must be remembered that a substance may act as an acceptor or a donor depending on the other substance which is entering the complex formation. Also no generalization may be made upon the strength of complexes but there seems to be a tendency for those to be strongest in which both are sacrificial. This must be interpreted with caution since there are numerous examples which are contrary to this statement.[3-5]

The name "EDA complexes" utilized by Briegleb is a broad descriptive term encompassing various types of complexes.[6] Mulliken has also adopted this inclusive term in preference to the name "CT (charge transfer) complexes". He states that CT forces are probably predominant in strong $n \cdot v$ and $n \cdot \sigma$ complexes. On the other hand electrostatic forces are probably to a large extent the main factor in $\pi \cdot \pi$ and other rather weak complexes.[3] However, it must be pointed out that in most of the literature and in this study, a new absorption band which appears after the formation of a complex is referred to as the CT band.

The benzene·iodine complex

It is of interest to consider the benzene·iodine complex in more detail since much controversy has existed concerning this complex.[7-12] Originally Mulliken (1952) proposed three possible models.[13] (See figure 1.)

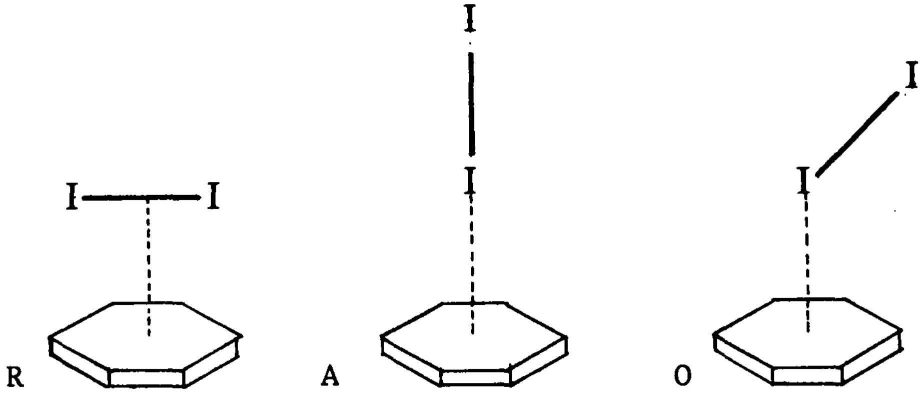


Fig. 1 The R (resting), A (axial), and O (oblique) models of the benzene·iodine complex.

Recently Fredin and Nelander (1974) reached the conclusion from infrared and ultraviolet spectra of nitrogen matrices at 20°K containing benzene and iodine that the structure is axial,[14] which is consistent with the results in this study. Their work seems to be well-founded although it is still open to some question whether the geometries predicated are valid outside of a nitrogen matrix.

It is of interest to note that Mulliken and Person have shown that two CT states must be considered in describing the benzene·iodine complex by employing second order perturbation theory. These results and the unpublished approximate calculations which include overlap-integral calculations of Chiu and Person (University of Florida) support the axial structure. For a detailed discussion see reference 3.

The benzene·chlorine and the benzene·bromine complexes

Other benzene halogen complexes have been studied. For example Collin and D'Or have reported the existence of a benzene·chlorine molecular complex on the basis of infrared spectra of solutions of chlorine in benzene. They concluded that the halogen is asymmetrically located on benzene, that is not axially.[15] Other infrared studies of bromine and iodine benzene complexes indicated axial orientation.[10, 16, 17] However, the recent infrared and ultraviolet data obtained by Fredin and Nelander indicate that in nitrogen matrix at 20°K the chlorine and bromine complexes of benzene are oblique.[14] On the other hand Ferguson and Matsen have indicated that interpretation of infrared spectra of benzene·halogen molecular complexes is quite complicated and suggested a possible explanation for infrared intensity changes which would apply for either the axial or resting model.[18-20]

X-ray diffraction studies of the benzene·chlorine and benzene·iodine complexes in the solid state suggest the axial structure consisting of alternating benzene-halogen molecules. Each halogen molecule is aligned along the six-fold axis of a benzene neighbor molecule and the halogen is perpendicular to the benzene ring.[21,22] However, infrared studies on the benzene·bromine crystal formed at low temperature (-200°C) show that centers of symmetry are not present in the complex.[23] It must be noted that results found for crystals cannot be absolutely extrapolated to solutions except for particularly stable complexes whose crystal structure contains only one type of molecule per unit cell.

It is obvious from the above discussion that the structures of benzene·halogen complexes is still open to question.

Simplified Resonance-Structure Theory

To describe complexes quantum mechanically Mulliken originally presented a simplified resonance-structure theory. This theory involves resonance between no-bond structures of the acceptor and donor (A,D) and the dative structures (A^-, D^+). It predicts electronic absorption spectra characteristic for the A·D complex. They are referred to as CT spectra and the forces causing complex formation as CT forces.[24]

The derivation will not be presented but only the results given.[3] In this theory only one Charge Transfer (CT) state is assumed and only two resonance structures (ψ_0 and ψ_1). Utilizing first order perturbation theory, the following equations are obtained:

$$W_N = W_O - \frac{\beta_0^2}{\Delta} + \text{small correction terms} \quad (1)$$

$$W_V = W_1 + \frac{\beta_1^2}{\Delta} + \text{small correction terms} \quad (2)$$

These equations are true if $(\Delta/2)^2 \gg \beta_0\,\beta_1$, and $S_{o1}^2 \ll 1$. This is expected for weak complexes. Subtracting (2) from (1) yields:

$$h\nu_{CT} = \Delta + \frac{\beta_0^2+\beta_1^2}{\Delta} + \cdots\cdots \quad (3)$$

An illustration of the perturbation-theory equations (1) (2) and (3) may be represented in terms of an energy diagram. (See figure 2.) The above results may also be obtained from second order perturbation theory.

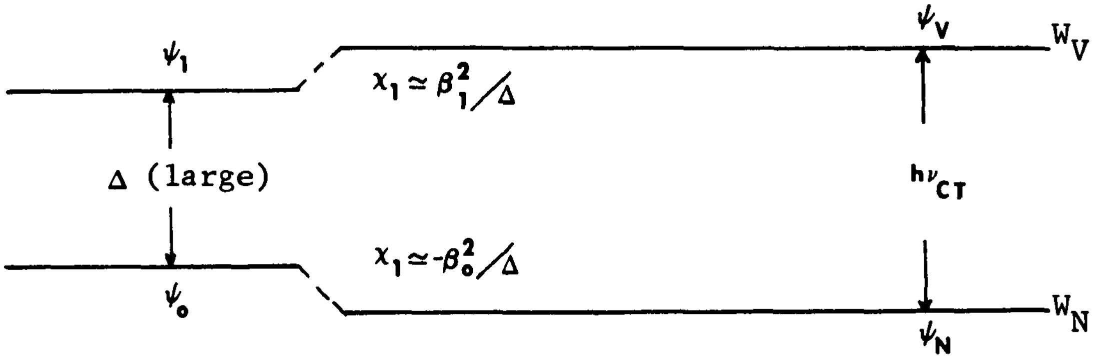


Fig. 2 Energy diagram illustrating equations 1 through 3.

The meanings of the symbols that represent wavefunctions are:

ψ_N = Wavefunction for the ground state of the complex

ψ_V = Wavefunction for the charge transfer state

$\psi_0(D,A)$ = Wavefunction for the no-bond structure

$\psi_1(D^+ - A^-)$ = Wavefunction for the dative structure

S_{01} = Overlap integral between ψ_0 and ψ_1

The meanings of the symbols referring to the energy of the complex are:

CT = charge transfer

W_N = The energy of the complex in the ground state

W_V = The energy of the complex in its charge transfer state

W_o = The energy of the "no-bond" structure of the complex

W_1 = The energy of the "dative" structure

Δ = The energy difference between dative and the "no-bond" structure

$\beta_i = W_{o1} - W_i S_{o1}$; $i = 0$ or 1

χ_o, χ_1 = The CT resonance energies (= $-\beta_o^2/\Delta$ or β_1^2/Δ, respectively)

Spectrophotometric Methods for Experimental Determination of the Equilibrium Constant, K

Various spectrophotometric methods are available for determing the equilibrium constant, K, of complex formations. However, preceding a discussion of the methods a general equation for the formation of a 1:1 complex will be presented. The reaction between a donor (D) and acceptor (A) may be expressed as follows:

$$D + A \rightleftarrows DA$$

Consequently the equilibrium constant expression for the above reaction is represented as follows:

$$K = \frac{(c_{DA})}{(c_D^o - c_{DA})\ (c_A^o - c_{DA})} \qquad (1)$$

c_A^o = initial concentration of the acceptor

c_D^o = initial concentration of the donor

c_{DA} = concentration of the complex

All concentrations are expressed in moles liter^{-1}.

The absorbance A_{DA} due to the complex is expressed in terms of Beer's law:

$$A_{DA} = (\epsilon)\ (c_{DA})\ (1) \qquad (2)$$

ϵ = molar absorpitivity

1 = length of path in centimeters

The classical Benesi-Hildebrand spectrophotometric method employs the following equation:[8]

$$\frac{1c_A^o}{A_{DA}} = \frac{1}{K\epsilon} \cdot \frac{1}{c_D^o} + \frac{1}{\epsilon} \qquad (3)$$

It is derived assuming low initial concentrations of donor and acceptor, the existence of only one equilibrium in solution, a small K, and the relative insolubility of the acceptor. The final form of the Benesi-Hildebrand equation is obtained by rearranging equation (1) as follows:

$$\frac{1}{K} = \left(\frac{c_D^o c_A^o}{c_{DA}} - c_D^o\right) - c_A^o + c_{DA} \qquad (4)$$

Then equation (4) is combined with Beer's law (2) assuming that $c_D^o \gg c_A^o > c_{DA}$. It is important to note that for strong complexes when $c_A^o \simeq c_{DA}$, no terms may be neglected and thus this equation is not applicable. Furthermore its utilization is limited by the assumption that absorbance, A_{DA}, at the CT band wavelength is entirely due to the complex. Often a correction must be made due to overlapping absorption of two species. The concentration of acceptor is kept constant while the concentration of donor is varied. Thus it is assumed that the absorption due to the uncomplexed acceptor is independent of the presence of donor. It is important to consider this for weak complexes since the concentration of donor must be large in order to produce sufficient concentration of the complex for study.

In order to avoid extrapolation to concentrated solutions as is often necessary in the Benesi-Hildebrand treatment a modification has been proposed by Scott:[25]

$$\frac{(c_D^o)\ (c_A^o)}{A_{AD}} = \frac{c_D^o}{\epsilon^{AD}} + \frac{1}{K\ (\epsilon^{AD})} \qquad (5)$$

This modification is still not satisfactory since most of the problems associated with the Benesi-Hildebrand treatment are still applicable.

A more recent analysis of K was made by Maguire and Banewicz (1972) using a modified version of the Scott equation on the propionitrile·iodine complex from spectral data in the visible region.[26] They were unable to use the CT band because the nitrile absorbed strongly in the ultraviolet region. Therefore, the visible region was used where the iodine absorption appears. Here the absorption due to the donor is assumed to be zero and the concentration of the complex comparatively small. The difference between the iodine/nitrile solution absorbance (A) and that of the absorbance (A_o) of the reference solution containing the same total iodine concentration is measured in the visible region. The equation is as follows:

$$c_D^o + c_A^o = (\epsilon^{cx} - \epsilon^A) \left[\frac{(c_D^o)\ (c_A^o)}{A-Ao} \right] - \frac{1}{K} \qquad (6)$$

c_D^o = initial concentration of the donor (nitrile)

c_A^o = initial concentration of the acceptor (iodine)

ϵ^{cx} = molar absorptivity of the complex

ϵ^{A} = molar absorptivity of the acceptor (iodine)

Plotting the above equation one may obtain K from the intercept and $(\epsilon^{cx} - \epsilon^{A})$ from the slope. When the concentration of the complex becomes appreciable a term is added to the right side of the equation, (6):

$$- \frac{(A-A_0)}{(\epsilon^{cx} - \epsilon^{A})}.$$

Other methods have been developed for specific needs. For example, Rose and Drago have found a method applicable to those cases where scatter of data is substantial.[27] And Liptay has developed a technique directly compatible with computers.[28]

If the complex is of the 1:1 type measurement of the equilibrium constant, K, should be independent of wavelength. However, it has been noticed by Johnson and Bowen that for some TCNE complexes the determination of experimental K varies with wavelength.[29] They indicate that this could be due to the presence of 2:1 complexes. Briegleb, however, states that this behavior is due to deviation of the system from the assumption that the molar absorptivities

(ϵ_A, ϵ_{DA}, ϵ_D) are identical in the pure inert solvent as in the solvent containing excess donor.[6] Another possibility is the existence of experimental error. Presently skepticism and controversy concerning K and ϵ value of complexes is quite evident in the literature.

Circular Dichroism

Natural Circular Dichroism (CD)

In order for natural circular dichroism (CD) to be exhibited a substance must be optically active. This type of substance has unequal refractive indices for left and right circularly polarized light. The result of this circular birefringence is an unequal rate of propagation of left and right circularly polarized rays. If the right circularly polarized ray E_R travels faster than the left E_L the result will be $\alpha = +$, therefore the medium is dextrorotatory. If E_L travels faster than E_R the result will be $\alpha' = -$, therefore the medium is levoratatory. The resultant wave will still pulsate in a plane, that is, it will be plane polarized but the plane of polarization will no longer be the x-plane but will make an angle α' with x-plane. Thus the circularly birefringent medium has rotated the plane of polarization by an angle α'.

Refer to figure 3 and note that the plane-polarized wave travels away from observer along the axis passing through centers of circles. The angle of rotation per unit path length is defined as,[31]

$$\alpha = \frac{(n_L - n_R)\pi}{\lambda}$$

λ = vacuum wavelength of light

n_L = refractive index for left circularly polarized light

n_R = refractive index for right circularly polarized light

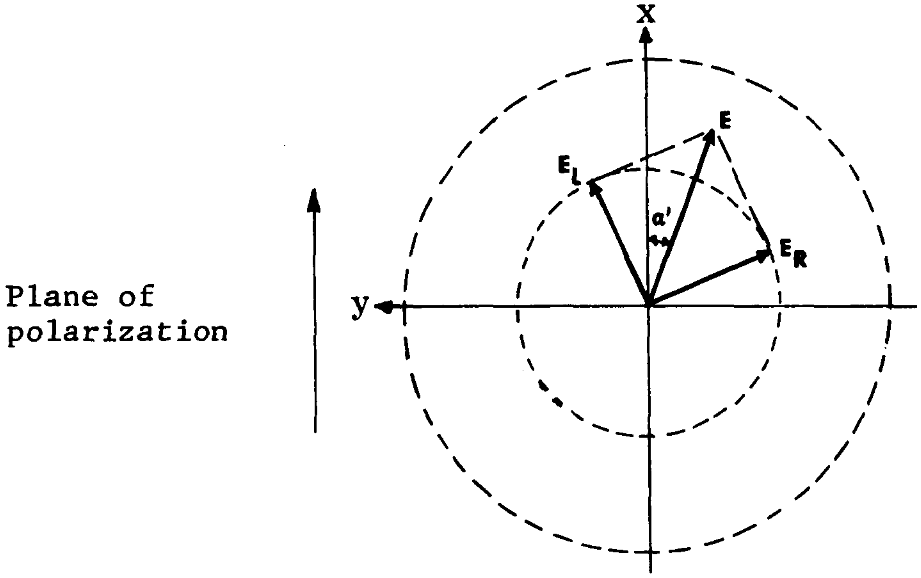


Fig. 3 Optical rotation as a result of circular birefringence. (Per reference 30.)

A dissymetric medium has different n's and absorptivity coefficients (E). Thus E_L and E_R vectors are of unequal length and their resultant instead of increasing and decreasing in a given plane (the plane of polarization) actually sweeps out in an elongated ellipse. The plane-polarized light passing through a dissymmetric medium therefore becomes elliptically polarized, the major axis of the ellipse taking the place of the plane of polarization. This phenomenon is called "circular dichroism."[32]

Magnetic Circular Dichroism (MCD)

Magnetic circular dichroism (MCD) or the "Faraday Effect" on the other hand is exhibited by all substances when they are placed in a magnetic field. Michael Farady observed this phenomenon in 1845. He and others have shown that the plane of polarization of linearly polarized light is rotated upon passing through any substance placed in a magnetic field with non-zero component in the direction of the light beam. Thus a longitudinal magnetic field makes all substances appear optically active.

The "Faraday Effect" was first expressed in quantitative terms by Verdet:[33]

$$\alpha = (\delta)\ (l)\ (H)\ (\cos\phi)$$

α = magnetic rotation

δ = Verdet constant (characteristic at a given α of a particular substance; for H_2O $\delta = 0.13$)

1 = path length of light

H = magnetic field strength

ϕ = angle between magnetic lines of force

Since H and the light beam are usually parallel, cos $\phi = 1$. One sign convention for it is as follows: (+) is used for a case where light travels along the direction of applied field or magnetization and rotation of polarization vector is clockwise like a right-hand screw.

To begin a theoretical discussion of MCD it is advantageous to use a simplified diagram. (See figure 4.)

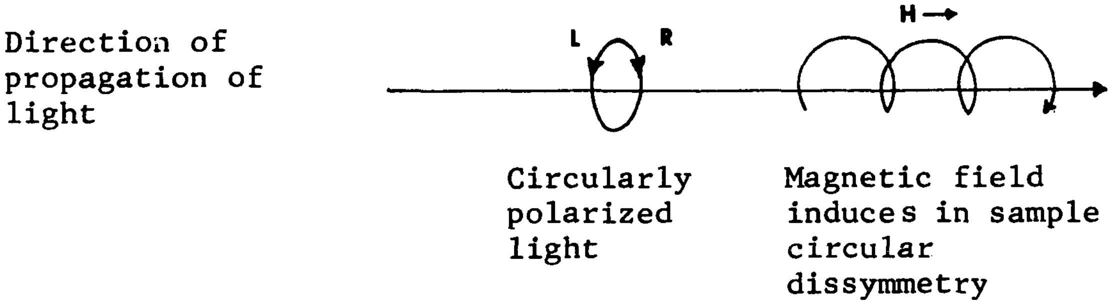


Fig. 4. Illustration of the Faraday effect principle. (Per reference 34.)

Magnetic field (H) is applied along the direction of propagation of the light beam. Circular dissymmetry will be produced in a substance causing differing responses from right and left circularly polarized light components because of the magnetic field's helical symmetry. This results not only in different refractive indices (n_L and n_R) but also in molar absorptivities (ϵ_R and ϵ_L). Thus

$n_L - n_R$ is proportional to α which is named Magnetic Optical Rotatory Dispersion (MORD). And θ or $\Delta\epsilon$ is proportional to $\epsilon_L - \epsilon_R$ which is named Magnetic Circular Dichroism (MCD).[34] MORD has not been used as extensively because of certain experimental difficulties. These result from the fact that in MORD measurements, not only the solute, but also the solvent and cell windows contribute significantly to the total rotation. On the other hand in MCD measurements, dispersion is significant only in the region of absorption. Therefore, one need not be concerned with solvent or cell window contributions if they do not absorb in the same region as the solute. Thus a baseline is obtained using only solvent and then a spectrum of the solution is run. Because of this highly practical advantage, MCD is used almost exclusively.

The normal Zeeman effect is characterized by splitting of spectral lines by a magnetic field into left and right circularly polarized components. The Faraday effect (MCD) may be treated theoretically when dealing with a degenerate state by considering the longitudinal Zeeman effect in absorption.[35]

Serber's (1932) nomenclature for describing the three types of terms observed in MCD is summarized by Buckingham and Stephens.[36, 37] These terms are described as follows:

1) A-term: results from splitting of a degenerate excited state by the magnetic field.

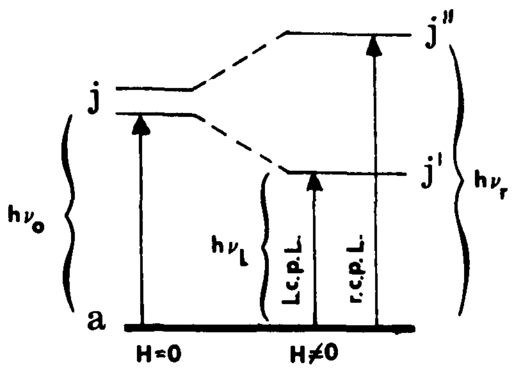
2) B-term: results from mixing of non-degenerate excited levels with the ground state by the magnetic field.

3) C-term: results from splitting of a degenerate ground state and is associated with a change in electronic population of this split ground state. It is the only term that is temperature dependent.

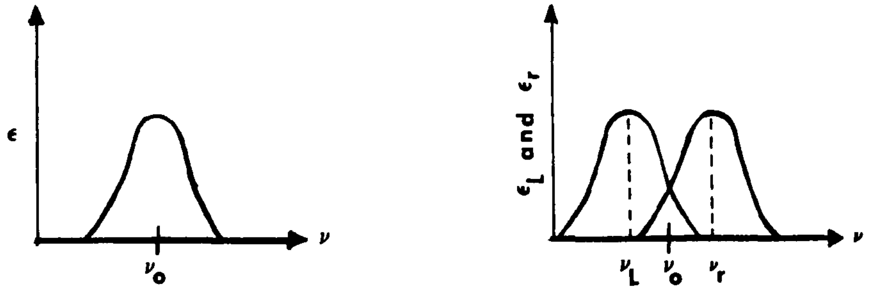
Djerassi's diagrammatic representation of each of the above terms as modified from Schatz and McCaffery's illustrations[38, 39] are given in figures 5, 6 and 7.

A-term

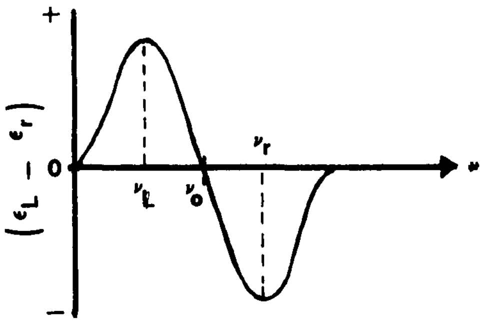
Consider the electronic transition in which an electron is promoted from ground state (a) to excited state (j). (See figure 5.) In order for a molecule to show an A-term there must be at least one degenerate excited state (j) or ground state (a) with a non-vanishing magnetic moment. In order for degeneracy to exist the molecule must possess at least a three-fold



(a) Energy Level Diagram
(l.c.p.l. = left circularly polarized light
r.c.p.l. = right circularly polarized light)



(b) Absorption for H=0 (c) Absorption for H≠0



(d) Resultant A-term

Fig. 5. The MCD A-term.

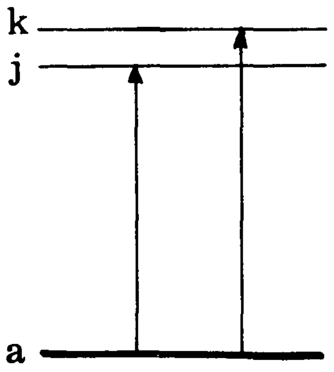
axis of symmetry. In non-zero magnetic field this degeneracy of (j) is removed yielding levels j' and j" which are symmetrically located about the zero-field level j. The strength of the magnetic field and the magnetic moment determine the degree of splitting. The resultant sinusoidal MCD band has a mid-point corresponding to ν_0. Since the left and right circularly polarized light components are selectively absorbed with equal probability for both transitions, the oppositely signed curves should be of equal magnitude.[38] The diagram shown is for a degenerate excited state. A similar diagram can be drawn for a degenerate ground state.

B-term

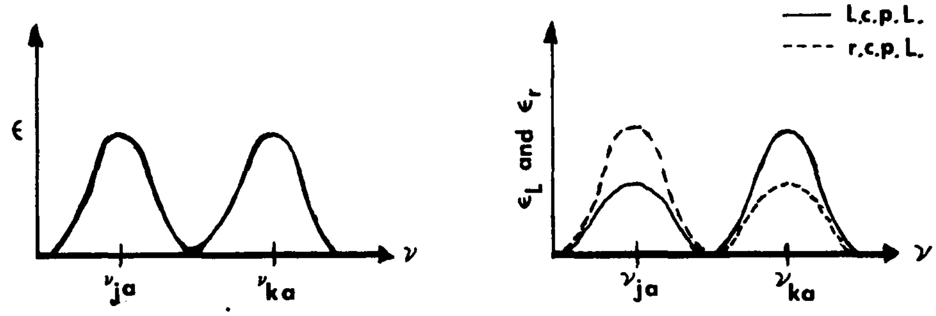
Since many organic molecules are of low symmetry they are non-degenerate in either the ground or excited state. In such cases mixing of the ground and excited state wavefunctions leads to the appearance of a B-term. This B-term can appear as either a positive or negative Gaussian curve. (See figure 6.)

C-term

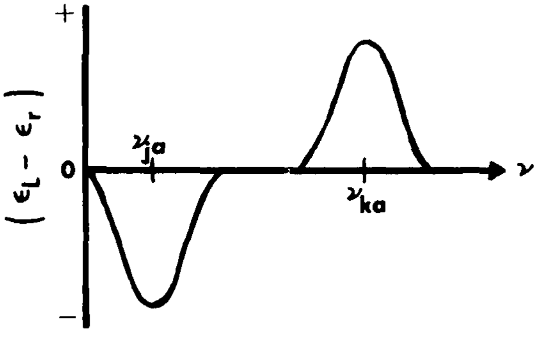
The C-term occurs when there exists a degeneracy



(a) Energy Level Diagram

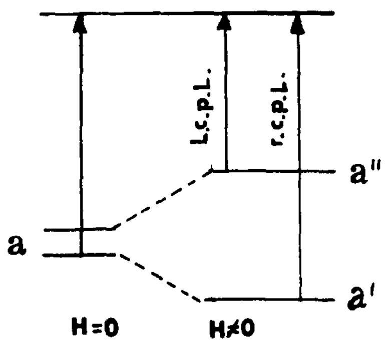


(b) Absorption for H=0 (c) Absorption for H≠0

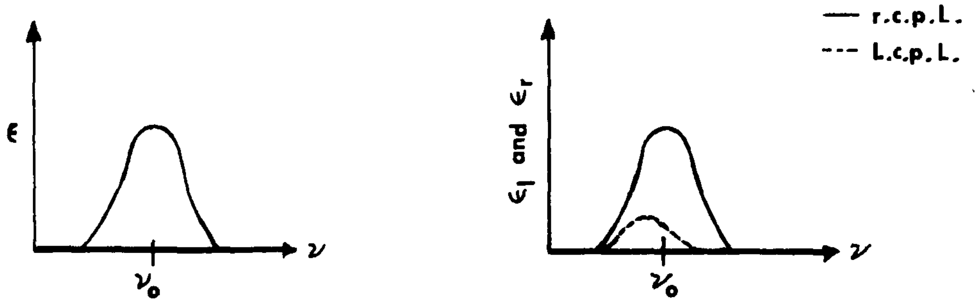


(c) Resultant B-term

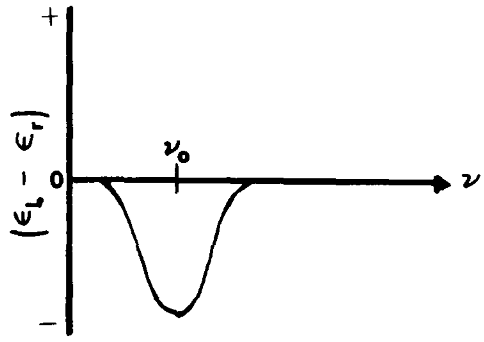
Fig. 6. The MCD B-term.



(a) Energy Level Diagram



(b) Absorption for H=0 (c) Absorption for H≠0



(d) Resultant C-term

Fig. 7. The MCD C-term.

in the ground state. An A-term type of dispersion is expected, but is usually so small that it is hidden under the C-term.[39 - 41] However, there is another feature which must be considered, namely the unequal population of states a' and a". Due to this the resultant dispersion will appear as shown in figure 7. Since the population of the ground state is governed by the Boltzmann distribution, the C-term is temperature dependent. The small A-term which is also present is not shown in figure 7.

Quantum mechanical expressions for the three Faraday term

Although the complete derivations for the quantum mechanical expressions will not be presented here, the final results for the A-B-and-C-terms will be given. For example the quantum mechanical expression for the B-term is:[42]

$$B(a \rightarrow j) = \frac{1}{d_a} \sum_{a \rightarrow j} \operatorname{Im} \left\{ \sum_{k \neq a} \frac{\langle k | \vec{\mu} | a \rangle \cdot \langle a | \vec{m} | j \rangle \times \langle j | \vec{m} | k \rangle}{h\nu_{ka}} + \right.$$

$$\left. + \sum_{k \neq j} \frac{\langle j | \vec{\mu} | k \rangle \cdot \langle a | \vec{m} | j \rangle \times \langle k | \vec{m} | a \rangle}{h\nu_{kj}} \right\} \quad (1)$$

$h\nu_{ka} = E_k - E_a$

$h\nu_{kj} = E_k - E_j$

d_a = degeneracy of a

$\vec{\mu}$ = magnetic dipole operator

$\vec{m}$ = electric dipole operator

Im = imaginary part

An assumption made when arriving at the above result is that the second summation is most important. The numerator in the second summation is the product of three vectors: 1) magnetic moments between j and k; 2) electric dipole moment between the ground state and the excited state j; 3) electric dipole moment between the ground state and the excited state k. The denominator contains energy differences between j and k. For an ideal case the two resulting oppositely signed bands should have the same intensity independent of the absorption band. Furthermore the greater the difference between the energy levels the smaller the B-term and vice versa. It must be noted that non-resolution of the two bands closely resembles sinusoidal A-term. Furthermore since the numerator is in the form of a scalar triple product, the MCD is the largest when the transition moments are orthogonally oriented with respect to each other. For example as the angle between the electric dipole moments decreases, the MCD bands will also decrease. Also, if the moments are parallel no MCD will be exhibited. Another assumption for B-term derivation is the consideration of only three levels (a, k, and j). In the absence of a magnetic field the promotion of an electron from a to j and k is independent of the state of polarization of the incident light. That is the molecule must be optically inactive and the absorption observed is as indicated in figure 6. But if there are off-diagonal matrix elements in $\vec{\mu}$ between states j and k, then the states are mixed by the magnetic field, H. In other words H induces each state to acquire some of the characteristics of the other. Consequently there will be different absorption of left and right circularly polarized light with the resultant B-term. (See figure 6). As can be seen the preferred absorption of left and right circularly polarized light will be different from the two transitions and as a result a +MCD is at ν_{ka} and - MCD at ν_{ja}.

The quantum mechanical expression for the A-term is given as follows:[42]

$$A(a \rightarrow j) = \left(\frac{1}{2d_a}\right) \cdots$$

$$\cdots \sum_{a \rightarrow j} \left[\langle j | \vec{\mu} | j \rangle - \langle a | \vec{\mu} | a \rangle \right] \cdot \mathrm{Im} \left\{ \langle a | \vec{m} | j \rangle \times \langle j | \vec{m} | a \rangle \right\} \tag{2}$$

Finally the quantum mechanical expression for the C-term is given by:[39]

$$C\ (a \rightarrow j) = \frac{1}{2d_a} \cdots$$

$$\cdots \sum_{a \rightarrow j} \langle a | \vec{\mu} | a \rangle \ \mathrm{Im} \left\{ \langle a | \vec{m} | j \rangle \times \langle j | \vec{m} | a \rangle \right\} \tag{3}$$

A convenient expression for magnetic molar ellipticity, $(\theta)_M$ is the following:[39]

$$(\theta)_M = -21.3458 \left\{ f_1 A + f_2 \left[B + C/kT \right] \right\} \tag{4}$$

$(\theta)_M$ = molar ellipticity/unit magnetic field =

$$= \frac{(\text{degree-deciliter})}{(\text{decimeter-mole-gauss})}$$

A = units of (D^2) (β) = square Debye x Bohr magneton

B + C/kT = in units of (D^2) (β) /cm^{-1}

f_1 and f_2 = functions of resonance frequency ν_0, the frequency of incident light beam ν, and half-band width Γ. They describe the shapes of MCD bands. (See equations 5 and 6.)

$$f_1 = \frac{4\,\nu_o\,\nu^3\,(\nu_o^2 - \nu^2)\,\Gamma}{h\left[(\nu_o^2 - \nu^2)^2 + \nu^2\,\Gamma^2\right]^2} \qquad (5)$$

$$f_2 = \frac{\nu^3\Gamma}{(\nu_o^2 - \nu^2)^2 + \nu^2\,\Gamma^2} \qquad (6)$$

h = Planck's constant

Γ = half-band width

It should be pointed out that the sign convention used here is opposite to that described in this text. Conversion from one sign convention to another is obvious.

Applications

Generally the MCD spectrum may yield various types of informative data. For example, it is used to assign excited states to specific electronic transitions, to determine the magnetic moment in excited states, and sometimes to uncover hidden bands in the absorption spectrum.[43 - 51] Indeed in this study hidden bands become apparent in the MCD spectrum. It is a superior technique for extracting information concerning excited states when compared to EPR or Zeeman effect measurements.

The latter measurements are usable only if very sharp lines are obtained, for example, gas or crystal at low temperature. EPR on the other hand yields very limited excited state information. Furthermore since A and/or C terms are predicted to be non-zero if the molecules or complex ions have at least a three-fold axis of symmetry, their appearance may be utilized to elucidate geometrical configurations.[43] In addition some studies have yielded structural information from MCD spectra containing only B-terms.[52, 53]

Purpose of this Investigation

It is obvious from the previous discussion that MCD can be a useful tool for the elucidation of chemical structures especially in combination with other available methods. The purpose of this investigation was to apply the MCD technique to a particularly difficult structural problem, namely molecular complexes in solution. For such complexes other standard techniques have not resulted in unambiguous structural assignments. It is proposed that MCD data will yield information for structural elucidations of these complexes. Although numerous MCD studies are available for inorganic CT complexes, none have been done with molecular complexes.[54 - 66]

II. INSTRUMENTATION

ORD/CD Spectropolarimeter

The ORD/UV-5 Durrum-Jasco Model J-20 spectropolarimeter was utilized in this study. It has both ORD and CD capabilities.

Specifications for the
Durrum-Jasco Model J-20

Wavelength range - 185 to 800 mμ

Wavelength reproducibility - 0.1 mμ

Light Source - 450 watt high pressure Xenon arc lamp

Source Power Supply - 500 watt with continuous monitoring of lamp current

Source housing - water cooled with safety switch for turning off lamp in case of insufficient water flow

Polarizer - quartz Rochon prism

Monochromator - Czerny-Turner type quartz prism double monochromator

Modulation - Pockels cell

Measuring system - gain modulation

Sensitivity scale - .001° ellipticity per cm to .02° per cm displayed over a 20 cm scale

Slit widths - .005 to 2.0 mm with logarithmic scale automatically or manually programmed

Time constant - 1, 4, 16, and 64 seconds

Stability - less than .002° drift/10 hours

Accuracy - .02% of full scale except where limited by noise

Reproducibility - 1/3 millidegree except where limited by noise

Scanning speeds - 1 mμ per minute to 100 mμ per minute with 15 intermediate steps

Linearity - 0.2% of full scale

Baseline flatness - .002° between 200 - 700 mμ

Cell compartment - 11" long x 5" wide x 6" high

Magnet for MCD - 10 Kilogauss permanent magnet accomodating a quartz cell of maximum 1 mm path length

Operational Description of the CD Mode

The circular dichroism mode may be described as follows: It is a null system utilizing gain modulation to continuously balance and record CD signals. The light exiting from the monochromator after collimation is passed through a Rochon polarizing prism and on to the Pockels cell. Before entering the Pockels cell, the extraordinary polarized light is blocked off so that only the ordinary polarized light passes through the P. C. modulator. The modulator is supplied with an alternating voltage which is adjusted by the wavelength drive so that the output of the P.C. modulator is alternately left and right circularly polarized light. The circularly polarized light passes through the sample and on to the photomultiplier. When the sample is not optically active, the intensity of the light is constant and the photomultiplier output is unmodulated D. C. A sample exhibiting circular dichroism will differentially absorb the right and left circularly polarized light causing the photomultiplier output to be modulated with an AC component of the excitation frequency. The gain of the photomultiplier is then adjusted in synchronism with the excitation frequency so as to cancel the AC component. The amount of gain adjustment required to null the system is directly proportional to the CD and is then recorded as the circular dichroism of the sample.

UV-VIS Spectrophotometers

Both the Cary and Bausch & Lomb Spectronic 505 Spectrophotometers were utilized in this study.

III. EXPERIMENTAL

Procedure

In order to achieve maximum resolution it was found necessary to operate in the sensitivity ranges of 1 or 2 (.001 ^{o} per cm), a time constant of 4 seconds and scanning rates ranging from 1.1 to 5.5 mμ per minute. The concentrations of solutions used were dictated by the above conditions and were determined by trial and error until a spectrum in the wavelength region of interest was of reasonable intensity. The resulting MCD spectrum consists of the MCD of the complex, the free donor and the free acceptor, all of which are present and in equilibrium with each other. In order to obtain the MCD spectrum of the complex one must subtract both the MCD spectrum of the free donor and the free acceptor from the total spectrum. In order to correct for the presence of free donor and acceptor one would obviously need to know their concentration in the equilibrium mixture, that is the equilibrium constant, K. The MCD spectra of donor and acceptor separately at these concentrations can then be determined experimentally and their contributions subtracted from the total spectrum. The approximate concentration of iodine in the equilibrium mixture was obtained by determining the visible absorption spectrum of iodine (515 mμ) utilizing the double beam spectrophotometer. The reference solution consisted of a known concentration of iodine. The concentration was adjusted until the resulting spectrum showed no overcompensation in the absorption region of iodine. This concentration was taken to be the concentration of iodine in the equilibrium mixture. It is obvious that once the concentration of iodine is known, one can calculate the concentration of the complex and the equilibrium constant, K. The MCD spectra of the donor and iodine at the concentrations calculated from the above procedure are then experimentally determined and subtracted manually from the total spectrum of the equilibrium mixture. The resultant spectrum is called an MCD difference spectrum.

A comparison of available equilibrium constant values in the literature indicates good agreement. For example, for the naphthalene·iodine complex the equilibrium constant determined experimentally was 0.76 liter-mole^{-1} in chloroform, which is identical to that reported by de Maine and Peone in the same solvent.[67] Of all the iodine complexes studied, it is the only one for which the equilibrium constant has been determined by other investigators in chloroform. On the other hand for the phenanthrene·iodine complex the experimentally determined equilibrium constant is 0.79 liter $mole^{-1}$ in chloroform. In carbon tetrachloride Person[68] found a value of 0.45 liter-$mole^{-1}$ in contrast to Basu[69] who found a value of 1.06 liter-$mole^{-1}$.

Choice of Solvent

The choice of solvent is rather critical in MCD measurements of this type. The ideal solvent must meet the following requirements:

1) Both donor and acceptor must have an appreciable solubility in the solvent.

2) The complex generated must have an appreciable solubility in the solvent.

3) No competitive complexation between solvent and either acceptor or donor must occur.

4) The solvent should not exhibit any absorption in the wavelength region of interest, preferrably over the entire ultraviolet and visible region.

Chloroform, ethanol, p-dioxane and to a limited extent carbon tetrachloride (borderline solubility) meet criteria (1), (2) and (4) cited above. Ethanol is unacceptable as a solvent since it tends to complex with iodine and exhibits an absorption band due to this complex at approximately 243 mμ.[70] Similarly p-dioxane complexes with iodine and shows a band at approximately 264 mμ.[71] The existence of these complexes is confirmed by the presence of B-terms in MCD spectra of solutions of iodine in p-dioxane and ethanol. For iodine in p-dioxane a B-term occurs at 260 mμ corresponding to the absorption at 264 mμ; while iodine dissolved in ethanol shows a B-term in its MCD spectrum at 240 mμ corresponding to the absorption at 243 mμ. It is obvious that there is good agreement between the MCD B-terms and the literature values for absorption. Since one would not anticipate that these complexes would have a three-fold axis of symmetry, B-terms are expected. In fact these were the first instances of the measurement of the MCD spectra of molecular complexes.

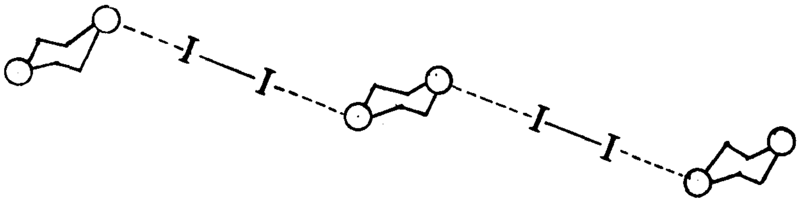


Fig. 8. The structure of the p-dioxane·iodine complex. (Per reference 72.)

It was found by Hassel that complexation in the case of dioxane does occur at the oxygen which acts as an n-type donor. The structure of consists of a chain of dioxane and iodine molecules in which both iodine atoms participate equally in the intermolecular bonding with the four atoms immediately concerned being collinear.[72]

Chloroform, however, does not seem to complex with iodine or any of the donors utilized in this study, therefore was the solvent of choice.

Choice of Complexes for Study

In selecting a complex to be studied the following criteria must be satisfied:

1) The solubility of the complex must be appreciable.

2) There must exist an MCD term in the ultraviolet or visible region.

3) The magnitude of the MCD terms must be

sufficiently large.

4) It is desirable but not necessary for the complex to exist in a structure with at least a three-fold axis of symmetry. However, if it does have this three-fold axis the appearance of an A-term would give considerable structural information.

Donors

It is well-known that aromatic hydrocarbons are very effective donors in molecular complexes. The following aromatic hydrocarbons have been utilized in this study: triphenylene, phenanthrene, naphthalene, anthracene, mesitylene and benzene. Of all these the only ones which could reasonably form molecular complexes with a three-fold axis of symmetry are triphenylene (T ϕ), mesitylene and benzene. (See figure 9.)

I

II

Fig. 9. The structures of mesitylene (I) and triphenylene (II).

Consequently they are of more interest structurally than the others. All of these hydrocarbons did, however, satisfy criteria (1) through (3).

Acceptors

The following acceptors were chosen after a careful review of aromatic hydrocarbon molecular complexes: iodine, tetracyanoethylene (TCNE), mellitic trianhydride (MTA), and 1, 3, 5 - trinitrobenzene (TNB).

1,3, 5 - trinitrobenzene (TNB)

TNB was the initial choice because of its three-fold axis of symmetry. Presumably the most reasonable structure expected upon complexation with donors also possessing a three-fold axis of symmetry, for example, triphenylene, would be of the "sandwich-type" with the respective three-fold axes of symmetry being coincident. The resultant structure of the molecular complex would then also possess a three-fold axis of symmetry. However, the complexes formed are extremely insoluble in the solvents mentioned earlier. In fact, the complex was easily isolated, since it crystallized slowly from these solvents and could be filtered off in rather pure form. Because of the possible symmetry advantage an attempt was made to obtain the MCD spectrum of the complex in the form of a KBr pellet. However, all attempts to produce a completely transparent pellet failed and because of light scattering the resolution of the MCD bands was extremely poor. This is consistent with studies found in the literature on absorption spectra of TNB complexes.[73 - 75]

Mellitic trianhydride (MTA)

Mellitic trianhydride (MTA) very obviously has the same symmetry advantage as TNB, however, it presented unexpected, additional difficulty.

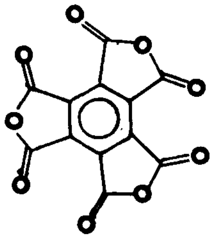


Fig. 10. The structure of mellitic trianhydride.

Upon addition of the aromatic hydrocarbons colored solutions were immediately formed due most likely to the formation of the molecular complexes. These solutions with the exception of triphenylene turned out to be unstable and became colorless in a matter of a few minutes. Degassing of the solutions prior to formation of complex did not eliminate this instability. This instability may be attributable to a reaction occurring between mellitic trianhydride and the aromatic hydrocarbons. The only exception, namely the complex formed with triphenylene, was too insoluble in all the solvents used.

Iodine and tetracyanoethylene (TCNE)

Both tetracyanoethylene and iodine were found to be suitable acceptors presenting no solubility problems and yielding good MCD CT bands. Iodine was particularly suitable because it is of $D_{\infty h}$ symmetry.

Source of Chemicals

The solvents utilized in this study were of spectrophotometric quality. Some of the solids were recrystallized, while others were used directly. The suppliers of the chemicals are as follows:

1) Mallinckrodt: chloroform, carbon tetrachloride and tetrahydrofuran (all spectrophotometric grade).

2) Matheson-Coleman and Bell (MCB): p-dioxane and benzene (spectroquality), mesitylene (99+%), phenanthrene, anthracene (99.9%).

3) K and K Labs: triphenylene and 1, 3, 5 - trinitrobenzene.

4) Eastman Organic Chemicals: tetracyanoethylene

and iodobenzene.

5) Aldrich Chemical Co.: mellitic trianhydride and naphthalene (gold label - 99.9%).

6) CSC: gold shield alcohol (ethanol 100%).

7) J. T. Baker Co.: acetic anhydride, iodine (100%).

IV. RESULTS

The MCD bands of iodine and aromatic hydrocarbons before and after complexation are tabulated with respect to concentration of solutions in chloroform expressed in moles liter^{-1}. The wavelengths of the listed bands are only approximate. For example, in all the tables the band at 515 mμ actually refers to two bands of opposite sign at approximately 470 mμ and 530 mμ. The graphical representation (exhibiting exact wavelengths) and detailed descriptions of the spectra are presented in the discussion of results, which includes types of bands, their intensity, and shifts that are sometimes observed.

TABLE 3

MCD Bands of Iodine

Concentration x10^4	Number of runs	MCD Bands (mμ)		
1.00 to 13.2	2		none	
45.0 to 68.0	2		515	
100 to 177	9		515	665
182 to 600	21	280 (weak)	515	665
700 to 136	7	280 (moderate)	515	665

TABLE 4

MCD Bands of Triphenylene

Concentration $x10^3$	Number of runs	MCD Bands (mμ)					
		1		2	3		
0.020	1		265				
0.041 to 0.049	2	255	265				
0.054 to 0.100	8	255	265	290			
1.00	1	a	a	290			
6.20 to 50.0	4	a	a	a	320	328	333
100 to 200	3	a	a	a	a	a	333
saturated	1	a	a	a	a	a	333

[a] Too intense to be measured.

TABLE 5

MCD Bands of Triphenylene (TØ) and Iodine (I_2)

Concentration x10^3		Number of runs	MCD Bands (mμ)				
TØ	I_2						
0.020 to 0.063	0.040 to 0.125	5	255	265	290		
0.082	11.0	1	255	265	290	515	665
0.100	0.167	1	255	265	290		
0.265 to 0.600	40.0 to 70.0	6	a	a	290	515	665
0.100	85.0 to 100.0	2	a	a	290	515	665

TABLE 5 - Continued

Concentration x10^3		Number of runs	MCD Bands (mμ)								
Tφ	I_2										
0.100 to 0.244	11.0 to 70.0	9	255	265	290					515	665
2.26	1.92	1	a	a	a	320	328	333		515	
5.30	4.50	1	a	a	a	320	328	333	360[b]	515	
10.0 to 50.0	10.0 to 60.0	9	a	a	a	320	328	330	360	515	665
68.0 to 500	55.0 to 100	8	a	a	a	a	a	a	360	515	665

TABLE 5 - Continued

Concentration $\times 10^3$		Number of runs	MCD Bands (mμ)								
Tϕ	I_2										
200 to 500	excess	4	a	a	a	a	a	a	360	515	665
excess	50	1	a	a	a	a	a	a	360	515	665

[a] Too intense to be measured.

[b] CT band.

TABLE 6

MCD Bands of Phenanthrene

Concentration x10^3	Number of runs	(MCD Bands (mμ)							
0.094	1	260	276						
0.850 to 1.25	2	a	276	280	294				
2.50	1	a	276	280	294	312	340		
9.50 to 9.70	2	a	a	a	294	312	340		
10.0 to 12.3	2	a	a	a	a	312	340		
15.0 to 36.5	5	a	a	a	a	312	340	357	
42.0 to 500	10	a	a	a	a	312	340	357	376
1,000	1	a	a	a	a	a	a	a	376

[a] Too intense to be measured.

TABLE 7

MCD Bands of Phenanthrene and Iodine

Concentration $x10^3$		Number of runs	MCD Bands (mμ)							
Phen.	I_2									
0.0068 to 0.094	0.0066 to 0.0092	2	260							
0.0285 to 0.094	11.0 to 15.0	2	260	276	280	294			515	
0.047 to 0.094	22.0 to 60.0	4	260	276	280	294			515	665
0.33	0.0323	1	260	276	280	294				
1.50	0.650	1	a	276	280	294	312	340		

TABLE 7 - Continued

Concentration x10^3		Number of runs	MCD Bands (mμ)										
Phen.	I_2												
1.25	11.1	1	a	276	280	294	312	340				515	
2.32	1.25	1	a	a	a	294	312	340					
2.50	22.0	1	a	a	a	294	312	345				515	665
4.65 to 10.0	2.50 to 60.0	6	a	a	a	a	312	345	357			515	665
10.0	0.970	1	a	a	a	a	312	340	357				
10.0	89.0	1	a	a	a	a	a	340	357			515	665
12.3 to 22.4	11.0 to 24.0	3	a	a	a	a	312	340	357	376	390[b]	515	665

TABLE 7 - Continued

Concentration $\times 10^3$		Number of runs	MCD Bands (mμ)										
Phen.	I_2												
24.5	2.17 to 2.38	2	a	a	a	a	312	340	357				
28.0	30.0	1	a	a	a	a	312	340	357		390	515	665
36.5 to 56.0	33.3 to 89.0	6	a	a	a	a	312	340	357	376	390	515	665
			a	a	a	a	312	340	357	376	390	515	665
42.0 to 100	3.40 to 11.0	7	a	a	a	a	312	340	357	376	390	515	
100 to 125	8.00 to 11.0	2	a	a	a	a	312	340	357	376	390	515	

TABLE 7 - Continued

Concentration x10^3		Number of runs	MCD Bands (mμ)										
Phen.	I_2												
200 to 275	16.0 to 60.0	6	a	a	a	a	a	340	357	376	390	515	665
300	24.0	1	a	a	a	a	a	a	357	376	390	515	665
380 to 500	31.0 to 40.0	2	a	a	a	a	a	a	a	376	390	515	665
870 to 1,000	70.0 to 89.0	2	a	a	a	a	a	a	a	c	a	515	665

[a] Too intense to be measured.

[b] CT band.

TABLE 8

MCD Bands of Naphthalene

Concentration $\times 10^3$	Number of runs	MCD Bands ($m\mu$)				
4.30	1	258	268	278	285	
5.00	1	258	268	278	285	308
10.0 to 50.0	2	a	a	a	a	308

[a] Too intense to be measured.

TABLE 9

MCD Bands of Naphthalene and Iodine

Concentration x10^3		Number of runs	MCD Bands (mμ)							
Napth.	I_2									
0.386	0.0618	1	(258	268	278	285)[b]				
2.90	0.463	1	258	268	278	285	308			
4.30 to 5.00	25.6 to 70.0	4	258	268	278	285	308		515	665
5.00	0.80 to 2.15	2	258	268	278	285	308			
50.0 to 58.0	4.10 to 9.30	2	a	a	a	a	308	350[c]	515	

TABLE 9 - Continued

Concentration $\times 10^3$		Number of runs	MCD Bands (mμ)							
Napth.	I_2									
30.0 to 700	14.0 to 60.0	9	a	a	a	a	a	350	515	665
785 to 1,000	63.0 to 80.0	2	a	a	a	a	a	a	515	665

[a] Too intense to be measured.

[b] Broad and small.

[c] CT band.

TABLE 10

MCD Bands of Anthracene

Concentration x 10^3	Number of runs	MCD Bands (mμ)					
0.033 to 0.100	2	256					
0.850 to 11.0	14	a	308	326	342	358	374
100	1	a	a	a	a	a	b

[a] Too intense to be measured.

[b] Cuts off at 370 mμ.

TABLE 11

MCD Bands of Anthracene and Iodine

Concentration $\times 10^3$		Number of runs	MCD Bands (mμ)							
Anthracene	I_2									
0.033	35.4	1	256						515	665
0.665	17.7	1	256				358		515	665
2.50 to 5.00	2.00 to 4.00	3	a	308	326	342	358	374	515	
2.50 to 3.33	15.0 to 78.0	5	a	308	326	342	358	374	515	665

TABLE 11 - Continued

Concentration $\times 10^3$		Number of runs	MCD Bands (mμ)								
Anthracene	I_2										
5.00 to 10.0	5.00 to 100	12	a	308	326	342	358	374	420[b]	515	665
10.0 to 100	16.0 to 900	8	a	a	a	a	a	a	420	515	665

[a] Too intense to be measured.

[b] CT band.

V. DISCUSSION OF RESULTS

Iodine

The MCD spectrum of iodine has not been reported previously. However, from this investigation the salient features of the MCD spectrum may contribute additional information concerning the assignment of specific excited electronic states to certain transitions. The total MCD spectrum consists of three maxima at 280, 470 and 665 mμ, and a minima at 530 mμ. The bands at 280 mμ and 665 mμ are obviously B-terms. It has been reported that iodine at higher concentrations does exhibit a weak absorption at 280 mμ (ϵ_{max} = 70) which has been attributed at least partially to the presence of the $I_2 \cdot I_2$ dimer complex.[75] In addition, a very weak band (ϵ_{max} = 25) attributed to the ${}^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ electronic transition has been reported by Ham to occur near 690 mμ in heptane.[77] It should be pointed out that the MCD band at 665 mμ in chloroform is very intense even though the absorption band is barely perceptible. This is an excellent example of the distinct advantage in some instances of the MCD

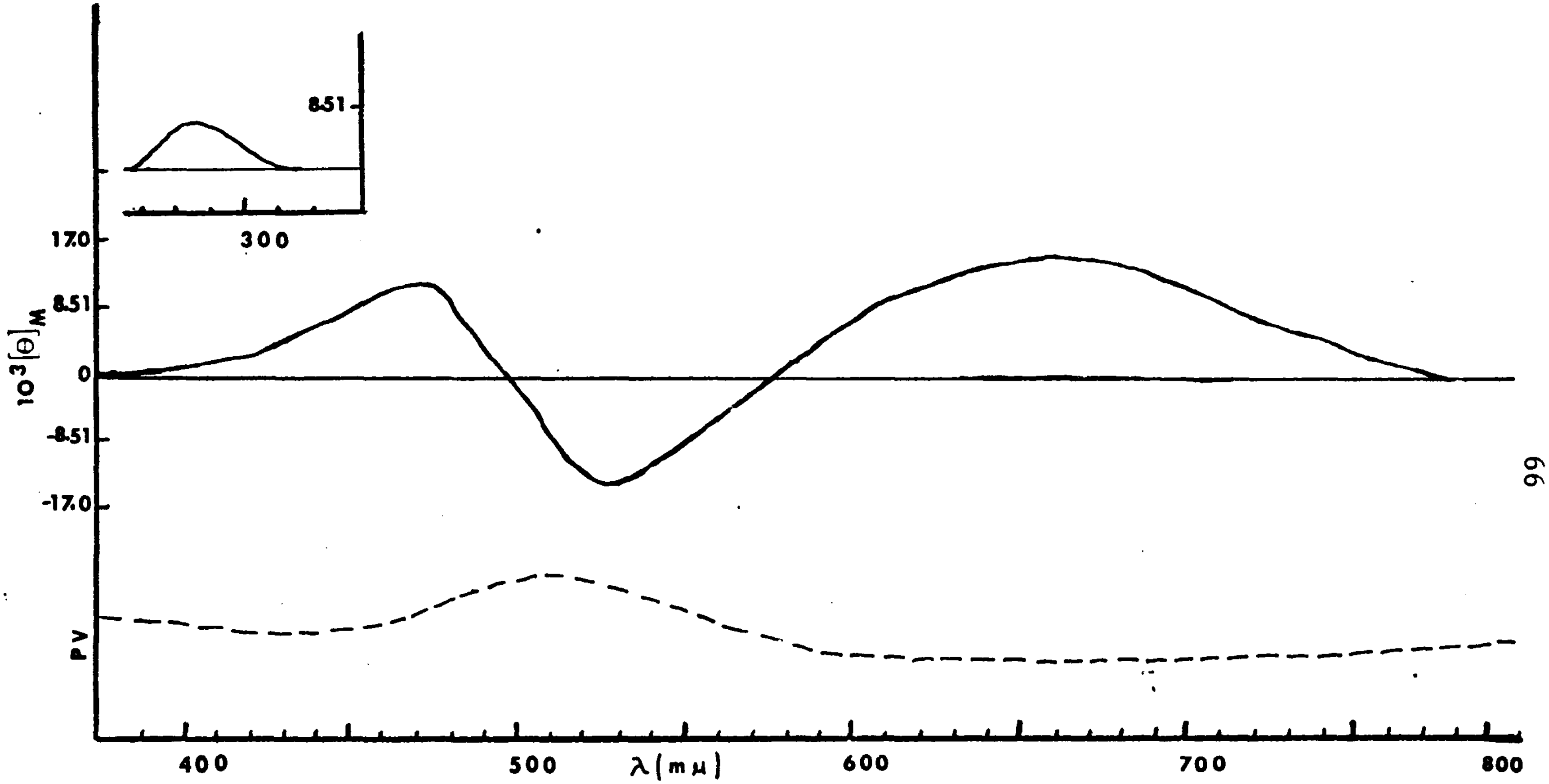


Fig. 11. MCD spectrum (——) of iodine. $[\Theta]_M$ is in units of deg dl dm^{-1} $mole^{-1}G^{-1}$. Photomultiplier voltage, PV, (---) corresponds to the absorption spectrum (ϵ_{280} = 75, ϵ_{515} = 800, ϵ_{665} = 25). Solvent: Chloroform.

TABLE 12

Correlation of Absorption and MCD Bands of Iodine with Electronic Transitions

Wavelength (mμ)	Absorption Band	MCD Band	Electronic Transition
180	very strong	a	$^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$
280[b]	very small	(+) B-term (small)	c
470	-	(+) B-term (large)	$^1\Pi_{1u} \leftarrow {}^1\Sigma_g^+$
515	broad[d]	-	e
530	-	(-) B-term large	$^3\Pi_{0u}^+ \leftarrow {}^1\Sigma_g^+$
665	barely perceptible	(+) B-term large	$^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$

[a] Not detectable because of instrumental limitations.

[b] Apparent at higher concentrations.

[c] Attributed partially to the $I_2 \cdot I_2$ dimer complex.

[d] Broad band ranging from approximately 440 mμ to 590 mμ with a maximum at 515 mμ.

[e] Attributed to the $^3\Pi_{0u}^+ \leftarrow {}^1\Sigma_g^+$ transition and the hidden $^1\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ transition.

technique in yielding strong bands whereas the absorption spectrum exhibits weak bands. (See figure 11 and table 12.)

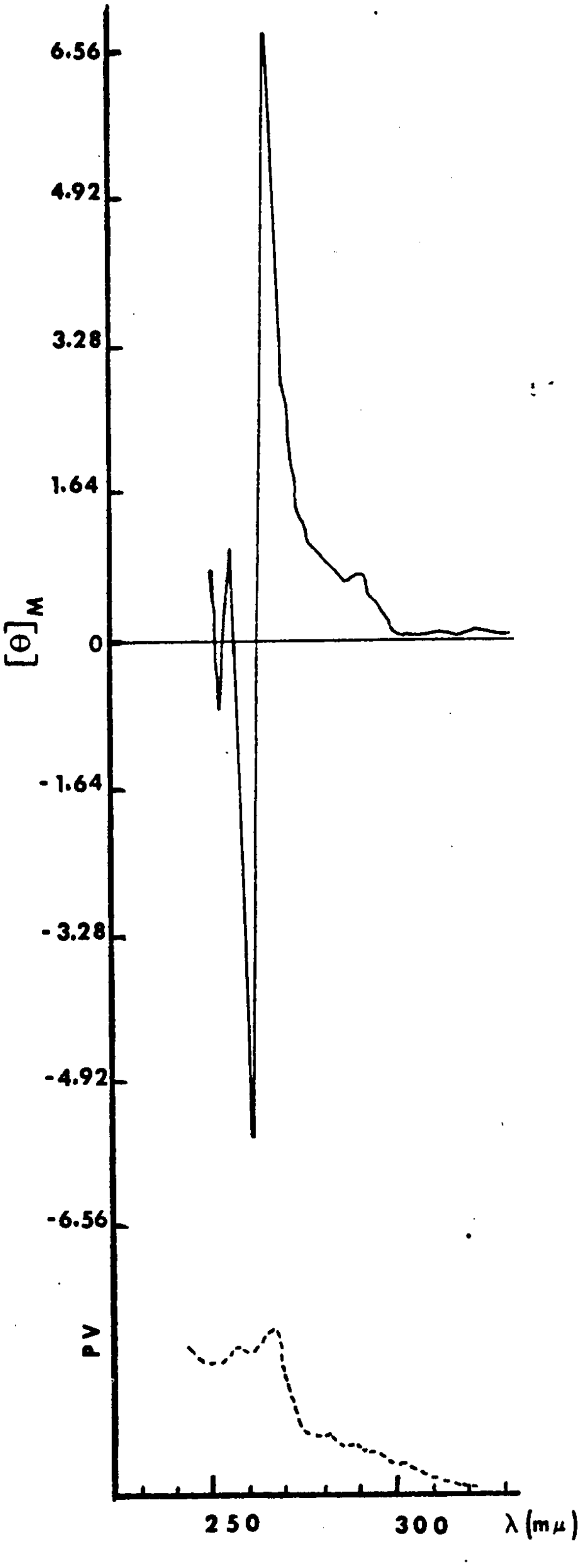
The MCD bands at 470 and 530 mμ are not as easily interpreted. It could be an A-term corresponding to an absorption in the visible region with a maximum at 515 mμ or two B-terms of opposite sign corresponding to absorption maxima at 470 and 530 mμ. Iodine shows a strong broad absorption maximum at 515 ($\epsilon_{max} = 800$) in chloroform attributed to the electronic transition $^3\Pi_{ou}^{+} \leftarrow {}^1\Sigma_g^{+}$.[78] This band correlates well with the minima appearing at 530 mμ in the MCD spectrum. If the band at 530 mμ is interpreted as a B-term, then the band at 470 mμ must necessarily be also a B-term and, therefore, there should be a corresponding absorption in the visible spectrum. The experimental visible absorption spectrum of iodine, however, shows only a broad band ranging from approximately 440 mμ to 590 mμ. It is conceivable and indeed theoretically predicted that a weak absorption corresponding to the $^1\Pi_{1u} \leftarrow {}^1\Sigma_g^{+}$ transition is hidden in the broad iodine absorption band.[74, 78] It is then concluded that the MCD band at 470 mμ is indeed a B-term corresponding to this hidden transition. This is a good example of the ability of the MCD technique to detect hidden absorption bands.

It has also been reported that the absorption spectrum of the iodine vapor exhibits a very strong band with a maximum at 180 mμ which corresponds to a transition to the $^1\Sigma_u^+$ state.[3] However, no MCD spectrum could be obtained because of instrumental limitations.

Triphenylene

The MCD spectrum of triphenylene may be described in terms of three main band categories. (See figures 12, 13 and table 13.) The first band consists of two very closely spaced A-terms. The band at 265 mμ is the large one, and the band at 255 mμ is much smaller. C-terms may be ruled out in this entire study since not only triphenylene but the other aromatic hydrocarbons do not have a degenerate ground state. As previously stated in the theoretical discussion of MCD the prerequisite for a C-term is a degenerate ground state. The band at 290 mμ is a possible B-term but one may not rule out A-terms since it is broad and with some fine structure. The bands at 330 mμ are a complex set similar to that of benzene. They are either B-terms or a closely spaced set of overlapping A-terms.

Fig. 12. MCD spectrum (——) of triphenylene. PV (---) corresponds to the absorption spectrum (ϵ_{265} = 1.6 x 10^5, ϵ_{290} = 6.3 x 10^3). Solvent, PV, and $[\theta]_M$ as in fig. 11.


6.56
4.92
3.28
1.64
0
- 1.64
- 3.28
-4.92
-6.56
[θ]M
PV
250
300
λ (mμ)

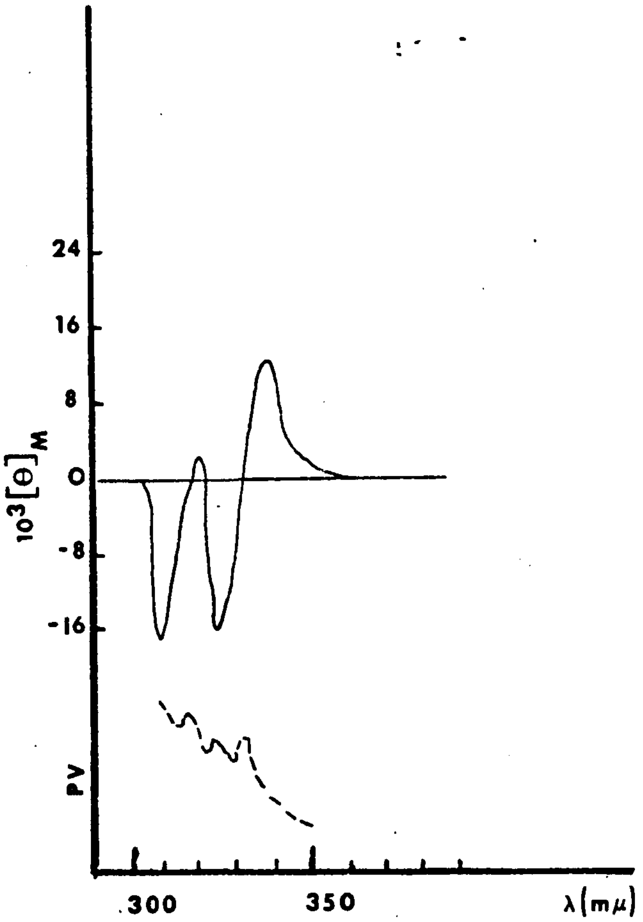


Fig. 13. MCD spectrum (——) of triphenylene. PV (---) corresponds to the absorption spectrum (ϵ_{318}= 800, ϵ_{325}= 1000, ϵ_{333}= 708. Solvent, PV and $[\theta]_M$ as in fig. 11.

TABLE 13

Correlation of MCD Bands of Triphenylene with Electronic Transitions*

Wavelength (mμ)	MCD Band	Electronic Transition
265	A-term	$(^1B_b \leftarrow {}^1A)$**
290	B-terms or overlapping A-terms	$(^1L_a \leftarrow {}^1A)$***
330	Complicated set of bands - could be A or B-terms	$(^1L_b \leftarrow {}^1A)$***

*The electronic states are designated in terms of Platt's notation. (See appendix.)

**Allowed transition.

***Forbidden transition.

Stephens, and others, indicated that an existence of an A-term proves the transition to a degenerate excited state.[79] Furthermore since triphenylene is of the D_{3h} symmetry and has a three-fold axis of symmetry it fulfills another requirement for exhibiting an A-term. The results obtained are in good agreement not only with those of Stephens but also of Schooley and others.[80] However, the sign convention is opposite to theirs. The convention utilized in this study was originally used for Farady measurements and has been adopted, for example, by Foss and McCarville.[81]

Upon complexation with iodine several notable changes in the MCD spectra of triphenylene and iodine are observed. (See figure 14.) There is a marked enhancement in intensity of the triphenylene bands and an appearance of a new CT band. The increase in intensity is expected in the absorption spectrum upon complexation due to mixing of the new CT state with the other existing states. The MCD band of free triphenylene and iodine partially overlapped the CT band, and consequently a difference MCD spectrum had to be plotted. (See the experimental section and figure 15.)

The comparison of the visible absorption spectrum

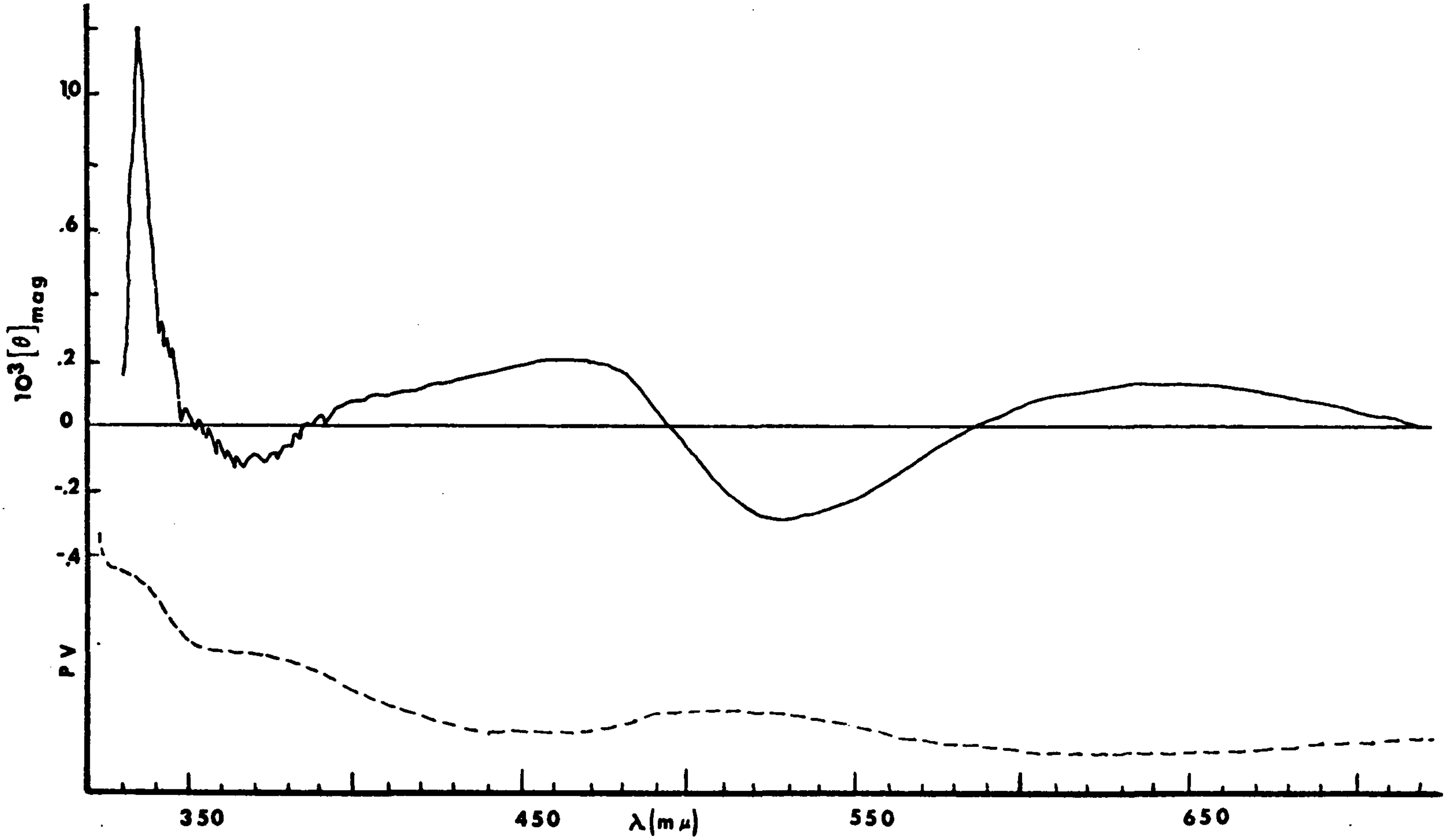


Fig. 14. MCD spectrum (——) of triphenylene plus iodine. Photomultiplier voltage, PV (---) corresponds to the absorption spectrum. $[\theta]_{mag}$ is in units of deg dl dm^{-1}G^{-1}. Solvent: CHCl$_3$. Triphenylene = 2.00 x 10^{-1}M, I$_2$ = 2.20 x 10^{-2}M.

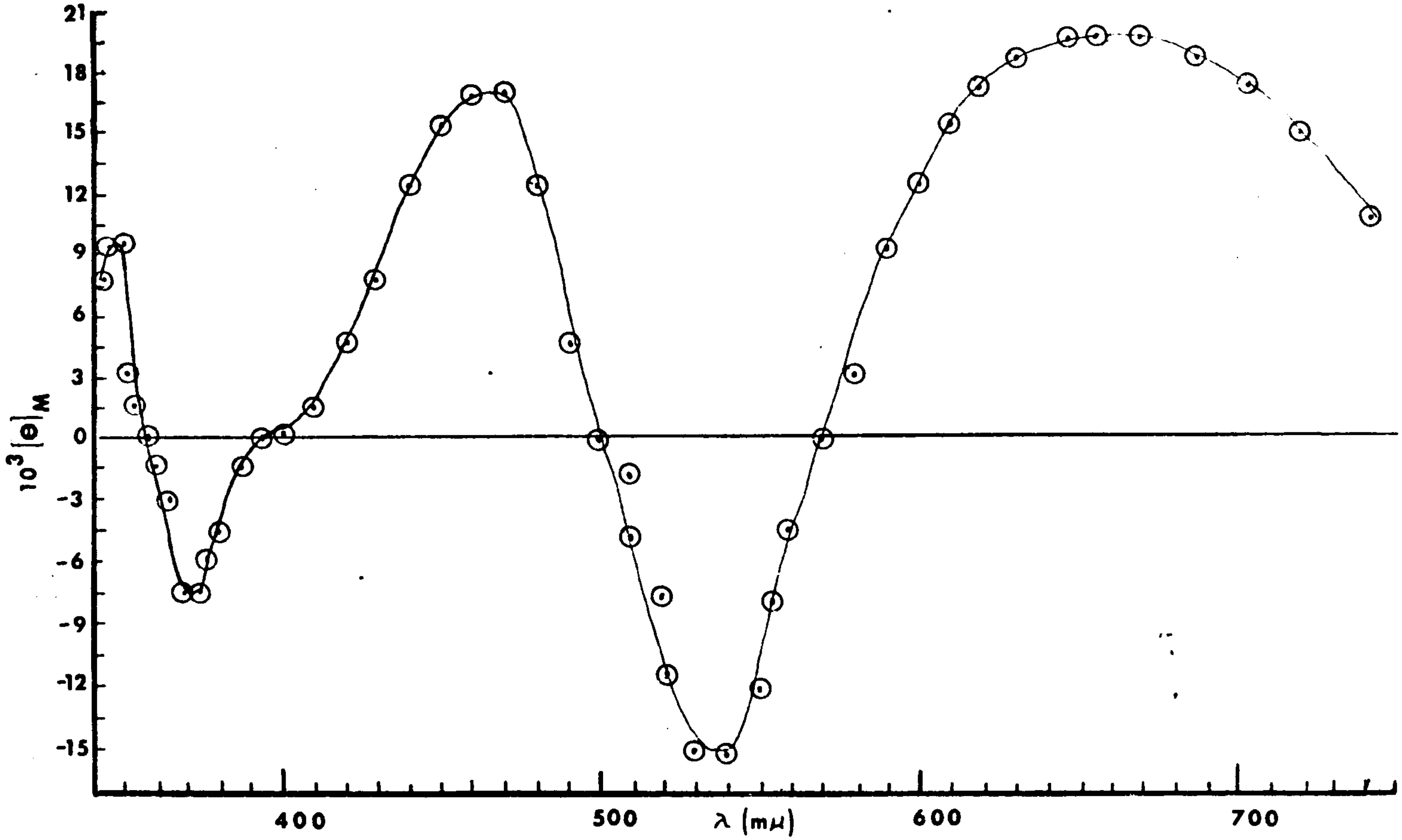


Fig. 15. MCD difference spectrum of triphenylene plus iodine. Solvent and $[\theta]_M$ as in fig. 11.

of iodine in chloroform (maximum at 515 mμ) and that of triphenylene plus iodine indicates a slight blue shift to 510 mμ and overall broadening. This shift to lower wavelengths is peculiar to iodine. A possible explanation of this phenomenon is given by Mulliken.[82] He states that the σ_u antibonding molecular orbital (MO) which contains the electron excited by the absorption of light in the visible band, must be larger than the outer occupied MO's in the normal state of I_2. The iodine is in close association with a donor molecule in a complex and upon absorption of visible light is excited ($\sigma_u \leftarrow \pi_g$). Its suddenly swollen size increases the repulsion energy between it and the donor (analogously, as if the two had collided). This repulsion energy is added to the usual energy of the excited iodine molecule yielding the blue shift that is to lower wavelength. A contribution to the blue shift is also made by the - ΔW_f (change in internal energy on formation of a complex). However its effect would be canceled or more than canceled by the - ΔW_f that would be expected for a complex formation of the donor with the $^3\Pi_{ou}^{+}$ excited iodine molecule if it were not for the repulsion effect just discussed.

The difference visible absorption spectra of the triphenylene/iodine solutions exhibit two partially overlapped bands with approximate maxima at 540 and 490 mμ . (See figure 16.) The MCD difference spectra reveal the two oppositely-signed B-terms. The 470 band is due to the $^1\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ transition. Its slight but definite intensification could be explained in terms of increased mixing of the $^1\Pi_{1u}$ state with either the CT state or with the $^1\Sigma_u^+$ state of iodine as a result of the shift in position of the $^1\Pi_{1u}$ level to the higher energies. The 530 mμ band is due to the following transition $^3\Pi_{ou}^+ \leftarrow {}^1\Sigma_g^+$ and its intensification is due to increased mixing of the $^3\Pi_{ou}^+$ state with a CT state or with $^1\Sigma_u^+$ of iodine as above. There is also a slight increase in intensity of the 665 mμ band which in the absorption spectrum is a barely perceptible shoulder. The increase in intensity is due to increased mixing between the following states: $^3\Pi_{1u}$, the CT state and $^1\Sigma_u^+$.

Summarizing the effects upon the visible region spectrum the following statements may be made. Originally the visible absorption spectrum of iodine exhibits one broad absorption band and a small shoulder at 665 mμ , according to Ham with an $\epsilon_{max} = 25$ in n-heptane.[77] In

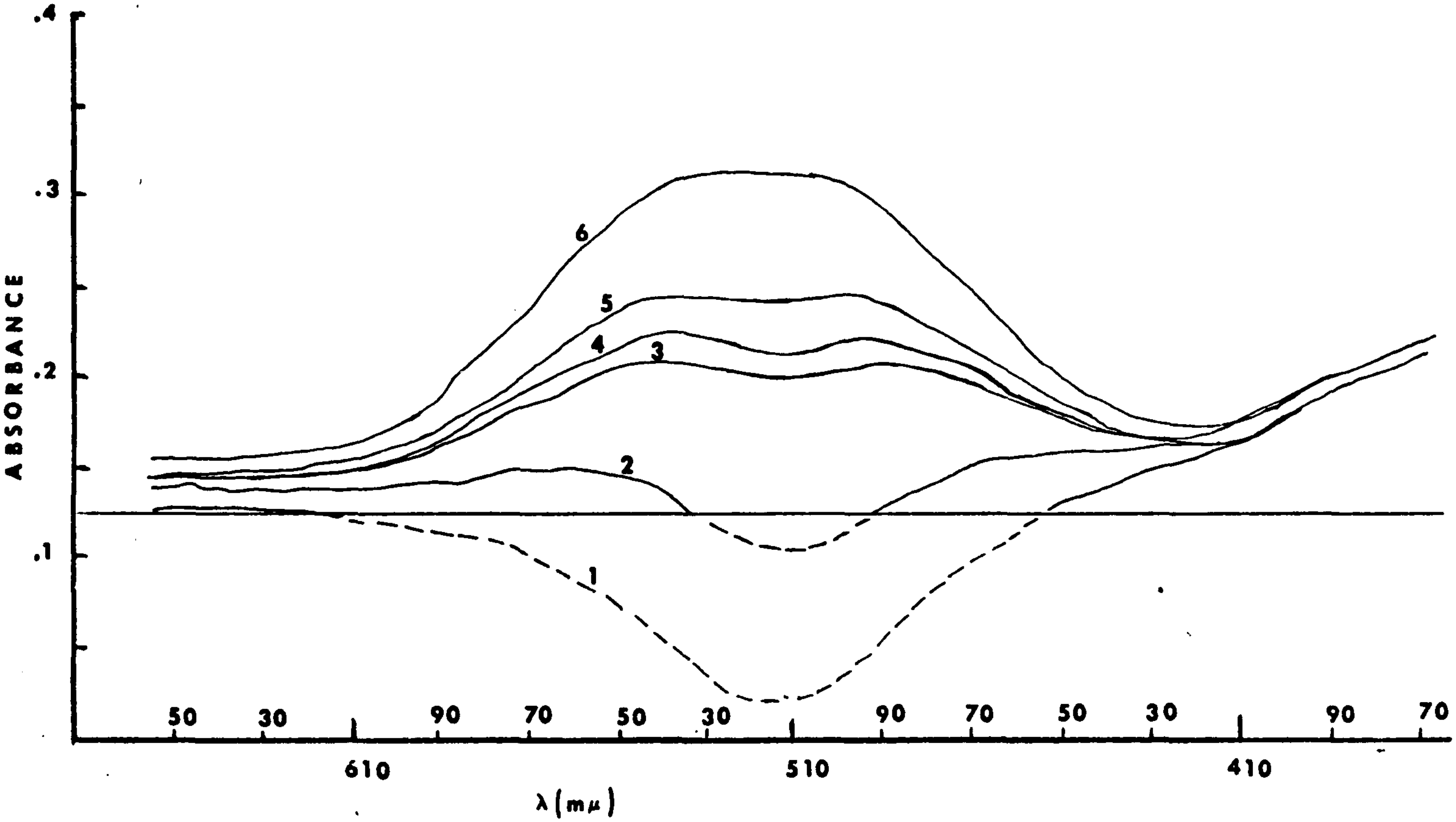


Fig. 16. Visible absorption difference spectrum of triphenylene (TØ) plus iodine (I_2). 1.7×10^{-2}M/TØ plus 1.36×10^{-2} versus in reference cell: (1) 1.36×10^{-2}M/I_2, (2) 1.25×10^{-2}M/I_2, (3) 1.15×10^{-2}M/I_2, (4) 1.13×10^{-2}, (5) 1.10×10^{-2}, (6) 1.03×10^{-2}. Solvent: $CHCl_3$; cell path length: 1 mm.

this study the band was not even perceptible in the visible spectrum. However, the MCD uncovers the 665 mμ band as a very large broad band which intensifies upon complexation. Furthermore upon complexation with triphenylene the difference visible absorption spectrum exhibits two partially overlapped bands which in the MCD difference spectrum are completely resolved into two oppositely-signed B-terms.

The partially overlapped CT band which is clearly seen in the difference MCD spectrum is an A-term. This suggests that the geometry of the complex is such as to preserve the overall original symmetry of the triphenylene. Before complexation triphenylene is of D_{3h} symmetry and iodine of $D_{\infty h}$. The MCD results indicate the formation of the axial model complex with C_{3v} symmetry. (See figure 17.)

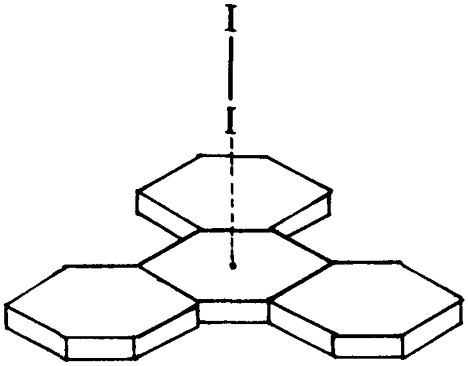
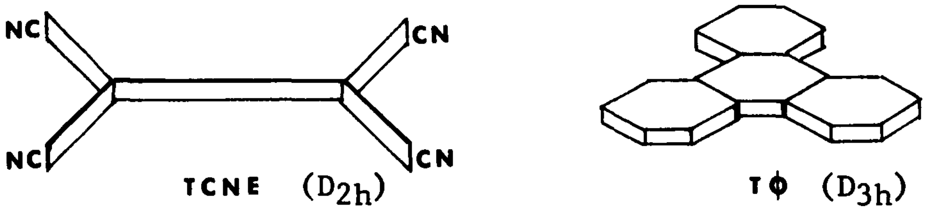


Fig. 17. The structure of the triphenylene·iodine complex.

Another factor which strengthens the suggestion for the axial model is the dramatically large enhancement of the A-term at 265 mμ (the ^1B_b band which is longitudinally polarized.) For example, a solution of 4.10 x10^{-5} M/triphenylene plus 8.00 x10^{-5} M/iodine shows a 5.5-fold increase in intensity from .004° to .022° (ellipticity in 10 kG magnetic field). From the visible spectrum data the equilibrium constant for the formation of this complex was determined - 13.7 l-mole^{-1}. Therefore the ΔG^o at 25°C was calculated as -1.54 kcal-mole^{-1}. The magnitude of K (or ΔG^o is usually used to indicate the "stability of a complex". However ΔH^o, enthalpy of formation, is more closely allied to the stabilization by the charge transfer forces. ΔS^o on the other hand must always be negative. At the same time ΔH^o becomes more negative. It has been determined empirically that $-\Delta S^o$ is a linear function of $-\Delta H^o$ for most complexes.[6] They have opposing effects on ΔG^o because the charge transfer resonance interaction makes ΔH^o more negative and the decrease in entropy does not permit ΔG^o to become negative as quickly as ΔH^o. But at room temperature is a relatively good indication of complex stability since at these conditions ΔH^o and K vary in the same way. Thus for triphenylene·iodine the equilibrium constant of 13.7 is indicative of a "moderately stable" complex.

In order to obtain additional information concerning the relationship between the geometrical configuration of triphenylene complexes and types of MCD CT bands, another acceptor was selected. Tetracyanoethylene (TCNE) was chosen in place of iodine since in its complex with triphenylene (TΦ) a three-fold axis of symmetry would be impossible regardless of the resulting geometrical configuration. (For structures see figure 18 and for MCD spectra figures 19-21.)



TCNE (D_{2h}) TΦ (D_{3h})

Fig. 18. The structures of tetracyanoethylene (TCNE) and triphenylene (TΦ).

Tetracyanoethylene is a planar molecule which exhibits a weak and complicated MCD spectrum in the 250 to 275 mμ region. It presented no solubility problems in chloroform and upon complexation yields two MCD CT bands at 440 and 567 mμ. Clearly the MCD bands are B-terms rather than the A-term obtained for the triphenylene·iodine

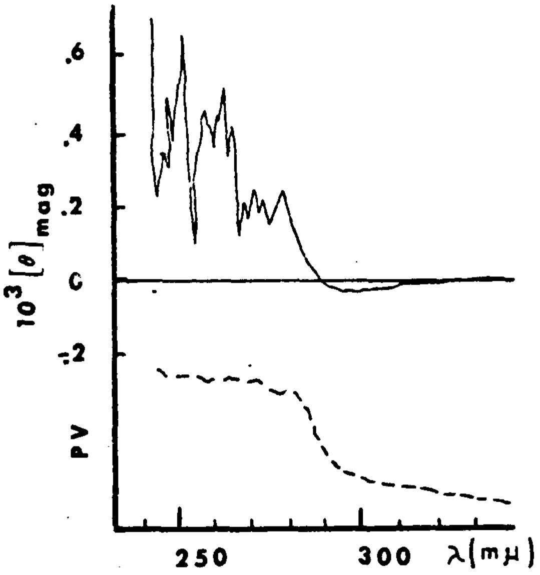


Fig. 19. MCD spectrum (——) of tetracyanoethylene. PV (---) corresponds to the absorption spectrum. Solvent, PV, and $[\theta]_{mag}$ as in fig. 14.

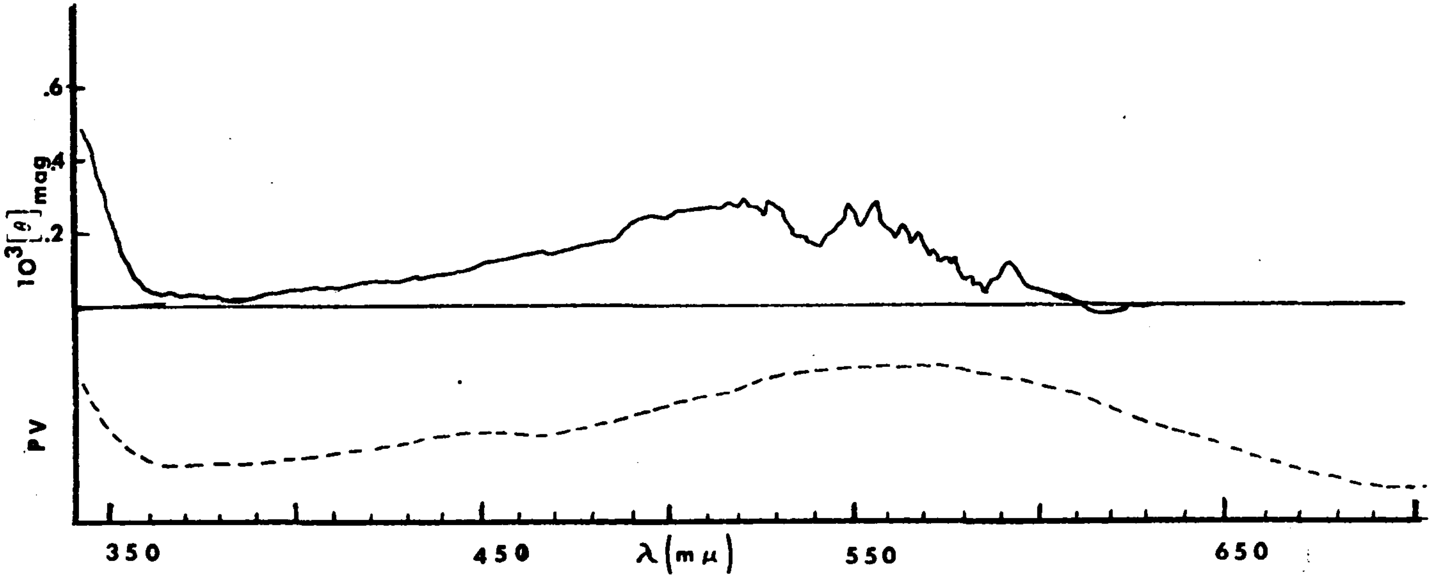


Fig. 20. MCD spectrum (——) of triphenylene plus tetracyanoethylene. PV (---) corresponds to the absorption spectrum. Solvent, PV, and $[\theta]_{mag}$ as in fig. 14. Wavelength expansion: 200 mu/cm.

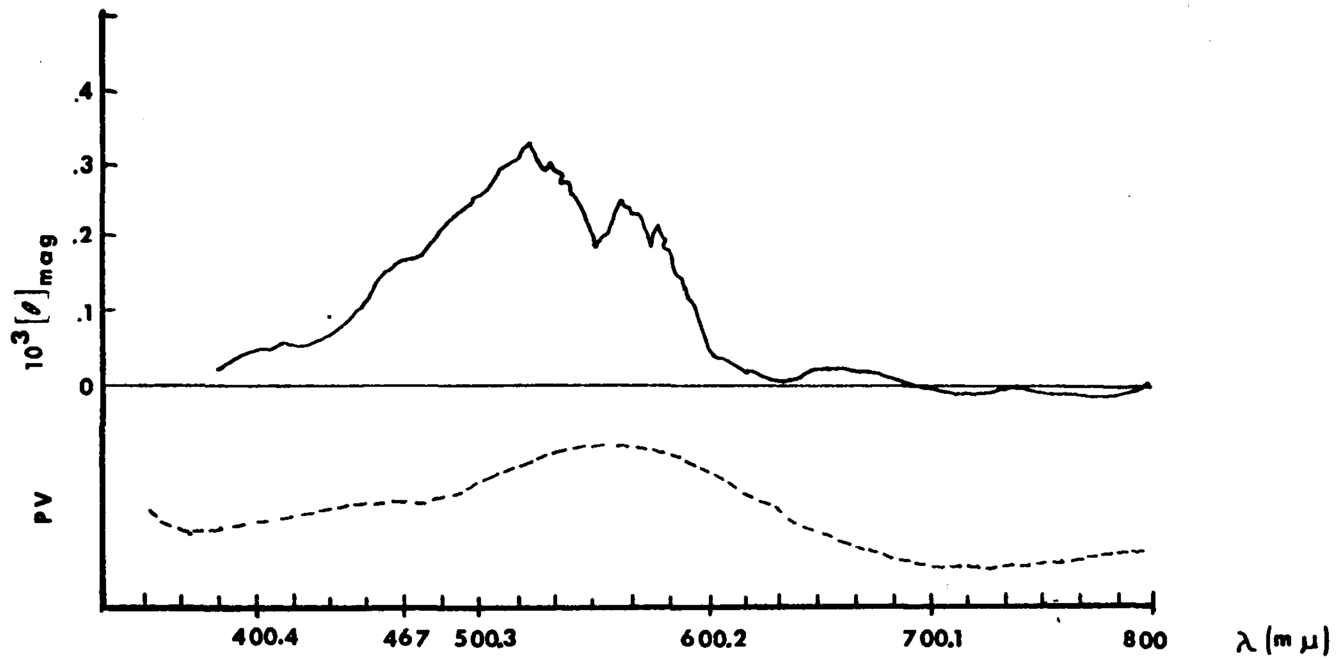


Fig. 21. MCD spectrum (——) of triphenylene plus tetracyanoethylene. PV (---) corresponds to the absorption spectrum. Solvent, PV, and $[\theta]_{mag}$ as in fig. 14. Wavelength expansion: 33.3 mu/cm.

complex. The absorption maxima are identical to those found by M. S. Dewar for triphenylene·tetracyanoethylene in chloroform.[83] The appearance of more than one CT band could be the result of electron donation from more than one energy level of tripheneylene or acceptance at more than one energy level in TCNE. Be that as it may, the MCD bands were the anticipated B-terms indicative of a complex with less than a three-fold axis of symmetry.

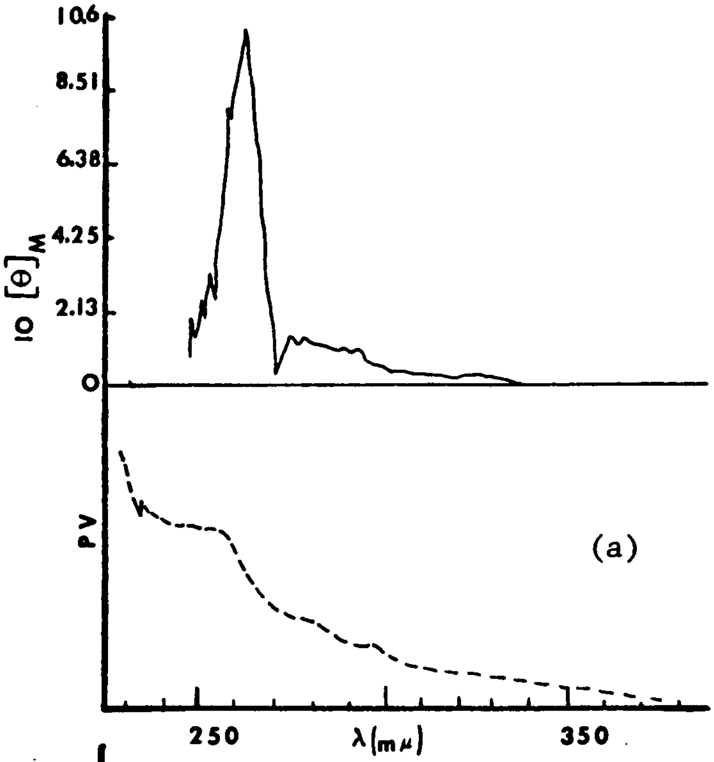
An attempt was made to utilize mellitic trianhydride, MTA, as an acceptor, which analogously to triphenylene possesses a three-fold axis of symmetry. Therefore, upon complexation one might expect to generate a geometrical configuration with a three-fold axis of symmetry. Unfortunately it presented solubility problems of great magnitude. (See the experimental section.) An attempt was made to determine the MCD spectrum in acetic anhydride since the complex was slightly soluble. However, precipitation of the complex occurred during the measurement which led to a great deal of light scattering and resulted in masking of the MCD spectra. Although there is a hint of a broad band at 580 mμ the results were inconclusive.

Phenanthrene

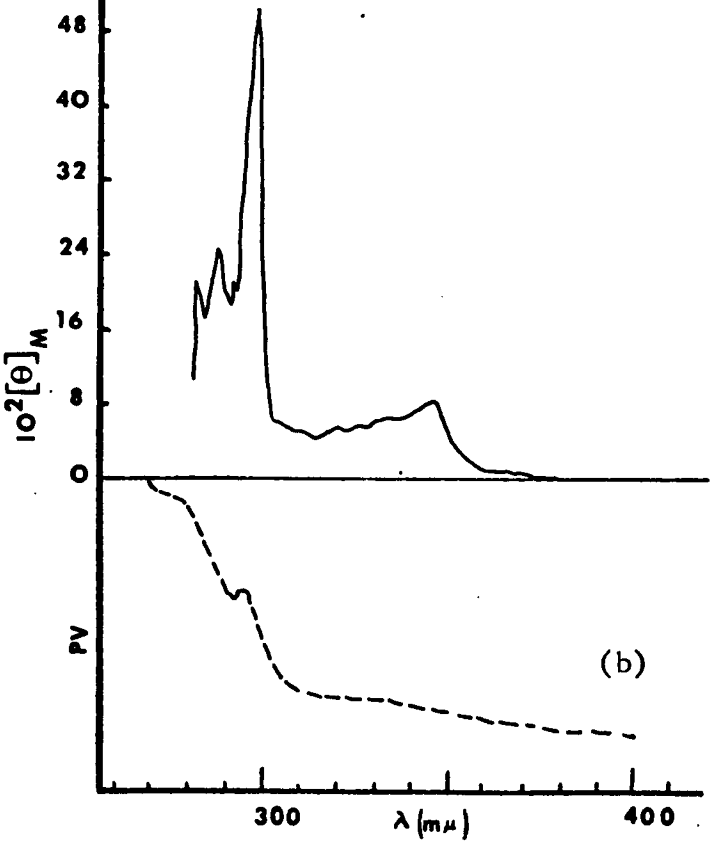
The MCD spectrum of phenanthrene is a series of B-terms, some overlapped, consisting of the following: the band of 260 mμ due to ^1B_b state, the one at 300 mμ due to ^1L_a and the band at 347 mμ due to ^1L_b. (See figures 22 and 23.) Upon complexation with iodine there is the expected overall enhancement of all the bands and the appearance of a new partially overlapped CT band due to the complex at 390 mμ . Upon plotting the MCD difference spectrum one obtains a small (+) B-term for this CT band, and two oppositely signed B-terms in the visible region. (See figures 24 and 25.) The visible absorption difference spectrum again shows two partially overlapped bands with maxima at about 480 and 540 mμ. Since these maxima are at about the same wavelength as in the case of triphenylene-iodine, additional support is furnished for the argument that these are the two originally hidden bands due to iodine which upon complexation are enhanced. (See the discussion of iodine and triphenylene.) Furthermore the band at approximately 665 mμ again is more pronounced.

Only B-terms and obviously no A-terms would be

Fig. 22. MCD spectra (——) of phenanthrene. PV (---) corresponds to the absorption spectra: (a) ϵ_{260} = 6.3 x 10^4, (b) ϵ_{295} = 1.6 x 10^4 . Solvent, PV, and $[\Theta]_M$ as in fig. 11.


10.6
8.51
6.38
4.25
2.13
0
10 [θ]M
PV
250
λ(mμ)
350

(a)


48
40
32
24
16
8
0
10²[θ]M
PV
300
λ(mμ)
400

(b)

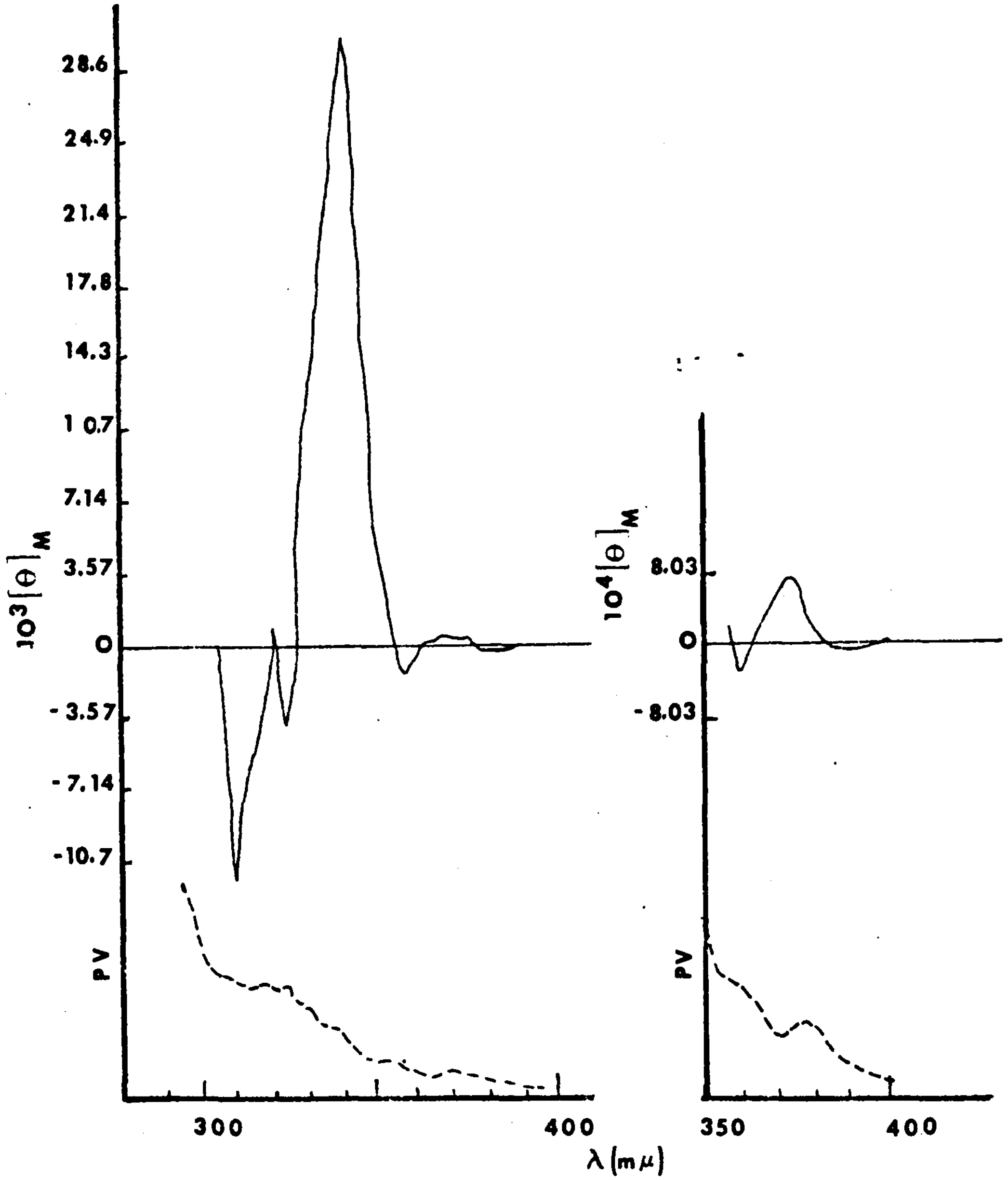


Fig. 23. MCD spectrum (——) of phenanthrene. PV (---) corresponds to the absorption spectrum (ϵ_{330} = 250, ϵ_{375} = 50). Solvent, PV and $[\theta]_M$ as in fig. 11.

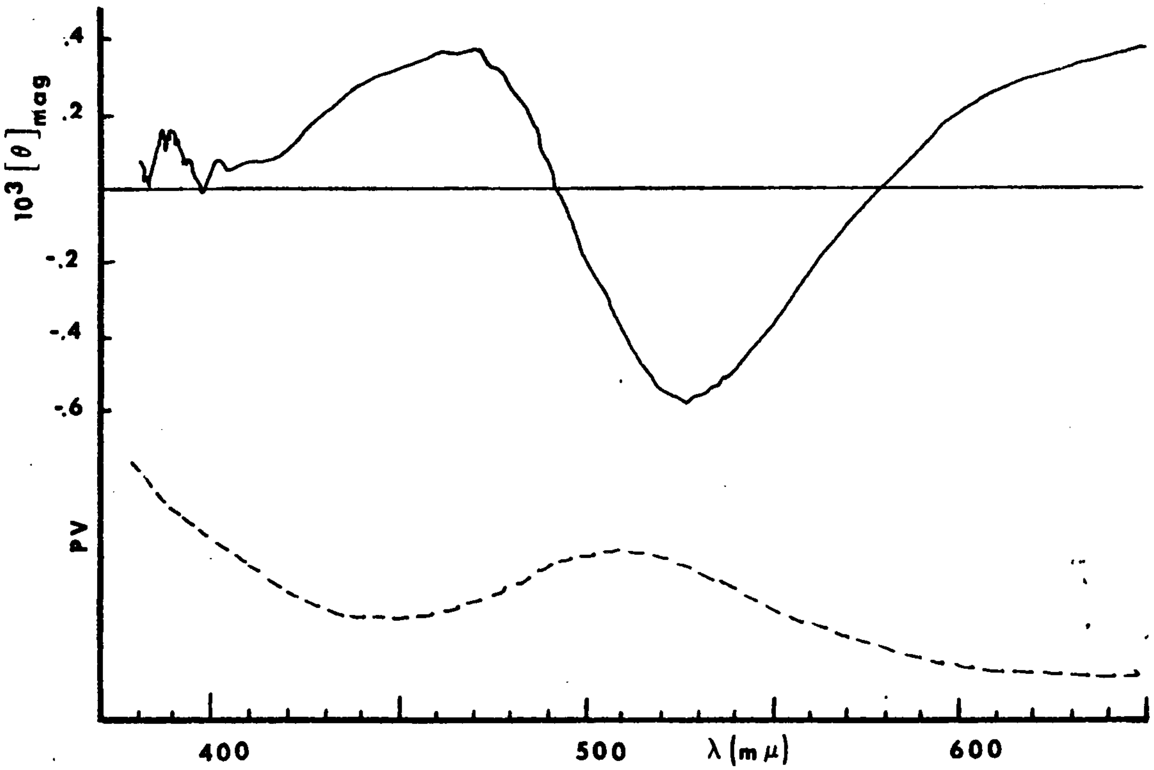


Fig. 24. MCD Spectrum (——) of phenanthrene plus iodine. PV (---) corresponds to the absorption spectrum. Solvent, PV, and $[\theta]_{mag}$ as in fig. 14. Phenanthrene = 3.80×10^{-1} M, $I_2 = 3.10 \times 10^{-2}$M.

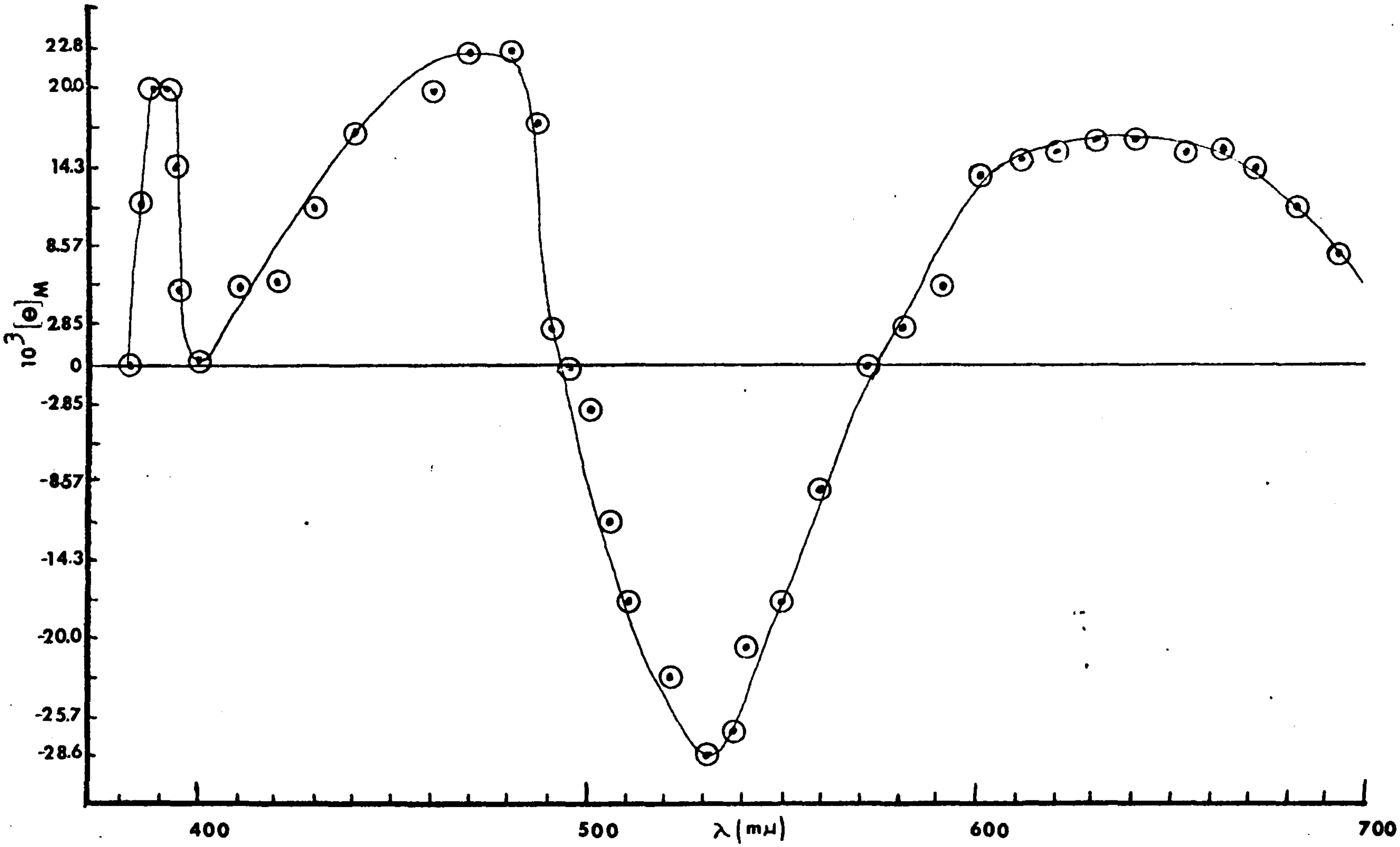
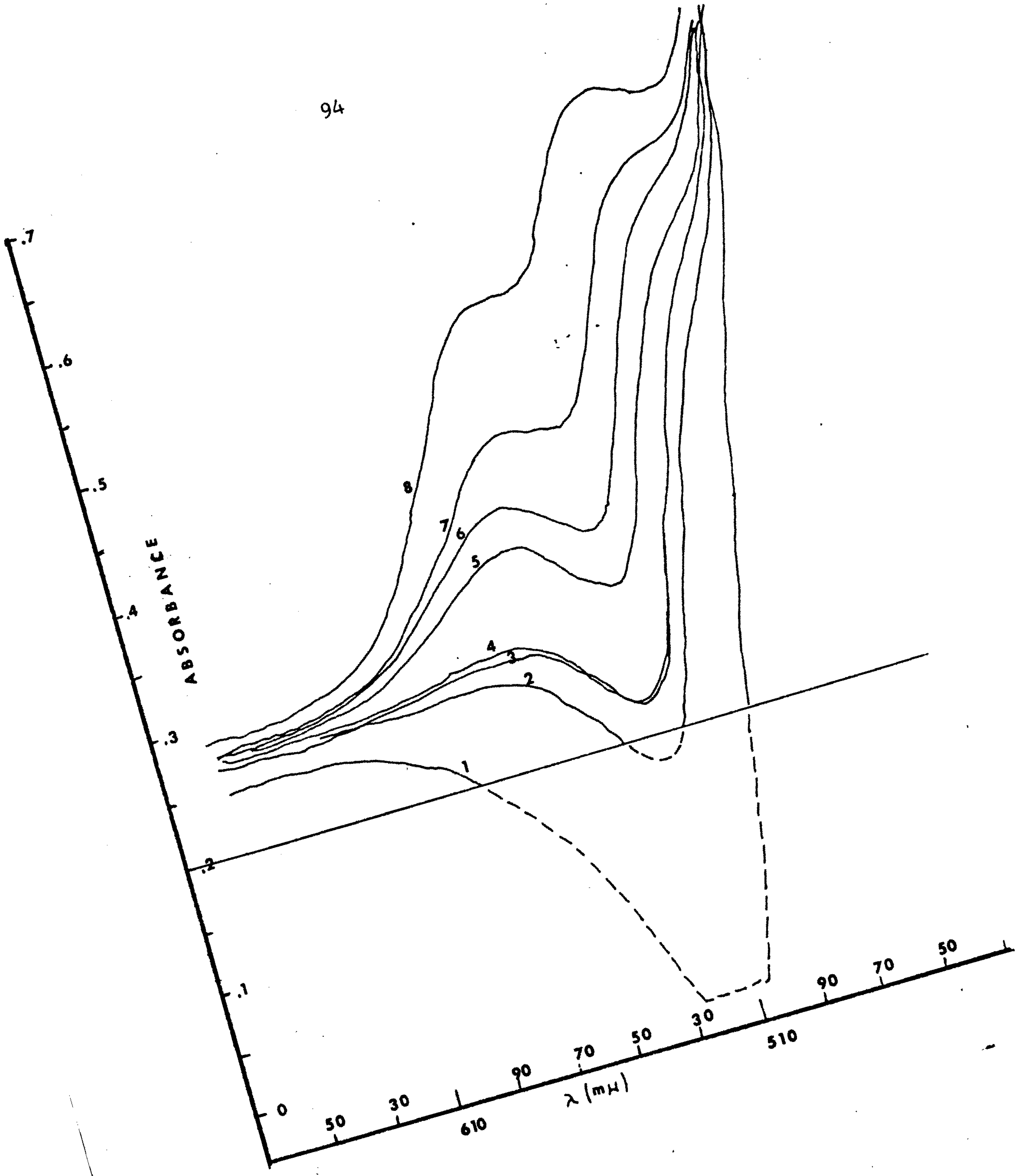


Fig. 25. MCD difference spectrum of phenanthrene plus iodine. Solvent and $[\Theta]_M$ as in fig. 11.

Fig. 26. Visible absorption difference spectrum of phenanthrene plus iodine. 3.00 x 10^{-1}M/phenanthrene plus 2.40 x 10^{-2}M/I_2 versus in reference cell: (1) 2.30 x 10^{-2}M/I_2, (2) 2.20 x 10^{-2}M/I_2, (3) 2.00 x 10^{-2}M/I_2, (4) 1.99 x 10^{-2}M/I_2, (5) 1.97 x 10^{-2}M/I_2, (5) 1.97 x 10^{-2}M/I_2, (6) 1.96 x 10^{-2}M/I_2, (7) 1.95 x 10^{-2}M/I_2, (8) 1.90 x 10^{-2}M/I_2. Solvent: $CHCl_3$; cell path length: 1 mm.


ABSORBANCE
.7
.6
.5
.4
.3
.2
.1
0
λ (mμ)
50
30
610
90
70
50
30
510
90
70
50
1
2
3
4
5
6
7
8

anticipated for phenanthrene due to its C_{2v} symmetry. The MCD CT band should then obviously be a B-term, as was the case. Although no definite statement can be made about the exact site of complexation, in view of the previously discussed cases it seems likely that the iodine is axially located on either the central ring or the terminal ring. (See figure 27.) Conceivably one might also have a mixture of both structures.

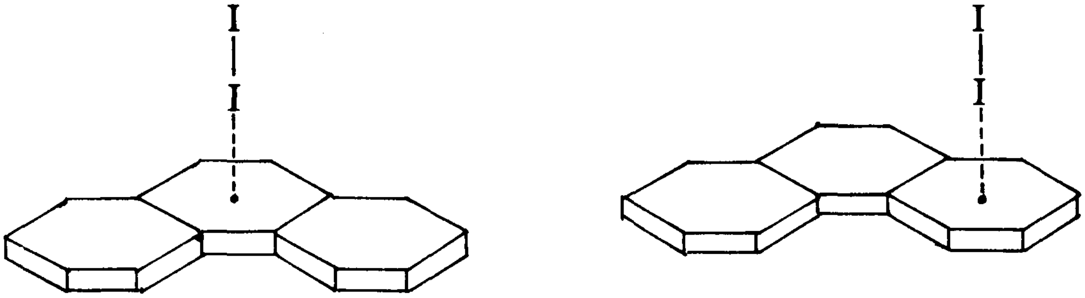


Fig. 27. Structures of the phenanthrene·iodine complex.

Another interesting aspect of the phenanthrene study is the band at approximately 375 mμ, which is very weak in the absorption spectrum and has been missed by a number of investigators.[68, 69] Consequently its appearance upon complexation has led to its assignment as the CT band. However in this study the MCD uncovered a band at 375 mμ for the phenanthrene in the absence of iodine. Schooley, and others, in reporting the MCD spectrum of phenanthrene indicated no MCD band but they did show an absorption maximum at 375 mμ.[80] Larkindale and Simkin also did not observe an MCD band at 375 mμ.[84] In this study the 375 mμ band was a clear B-term. (See figure 23.) Furthermore upon complexation a new MCD band is obtained at 390 mμ.

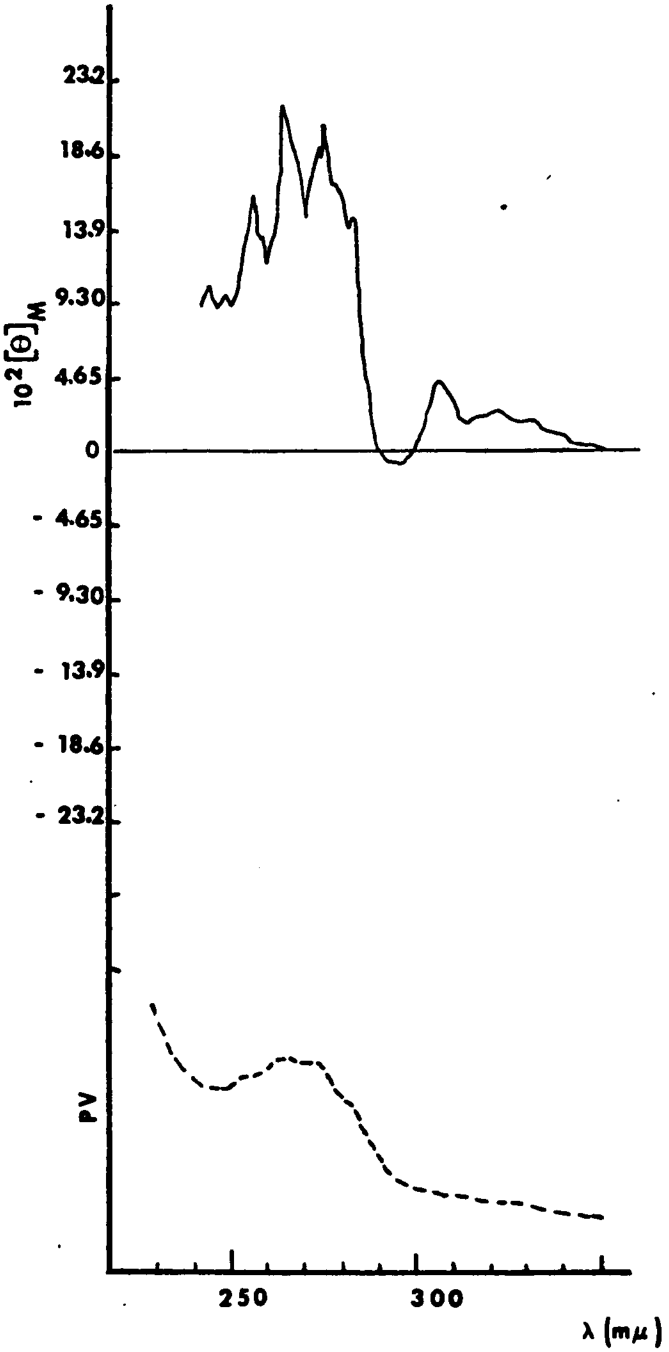
As was pointed out in the experimental section the equilibrium constant was determined to be 0.79 l-mole^{-1} in chloroform. A controversy exists in the literature concerning the validity of the methods used in determining K. For example Person[68] found a value of 0.45 l-mole^{-1} in carbon tetrachloride in contrast to Basu[69] who found a value of 1.06 l-mole^{-1}.

An attempt was also made to utilize mellitic trianhydride as an acceptor but the problems described previously in the experimental section made it impossible to obtain informative MCD spectra.

Naphthalene

The MCD spectrum of naphthalene consists of a band at 308 mμ attributable to the ^1L_b state and a complicated set of bands from 258 mμ to 285 mμ attributable to the ^1L_a state. The MCD spectrum is in good agreement with that of Schooley and others.[80] Upon addition of iodine there

Fig. 28. MCD spectrum (——) of naphthalene. PV (---) corresponds to the absorption spectrum (ϵ_{270} = 4900, ϵ_{300} = 240). Solvent, PV, and $[\theta]_M$ as in fig. 11.


23.2
18.6
13.9
9.30
4.65
0
- 4.65
- 9.30
- 13.9
- 18.6
- 23.2
$10^2[\theta]_M$
PV
250
300
λ (mμ)

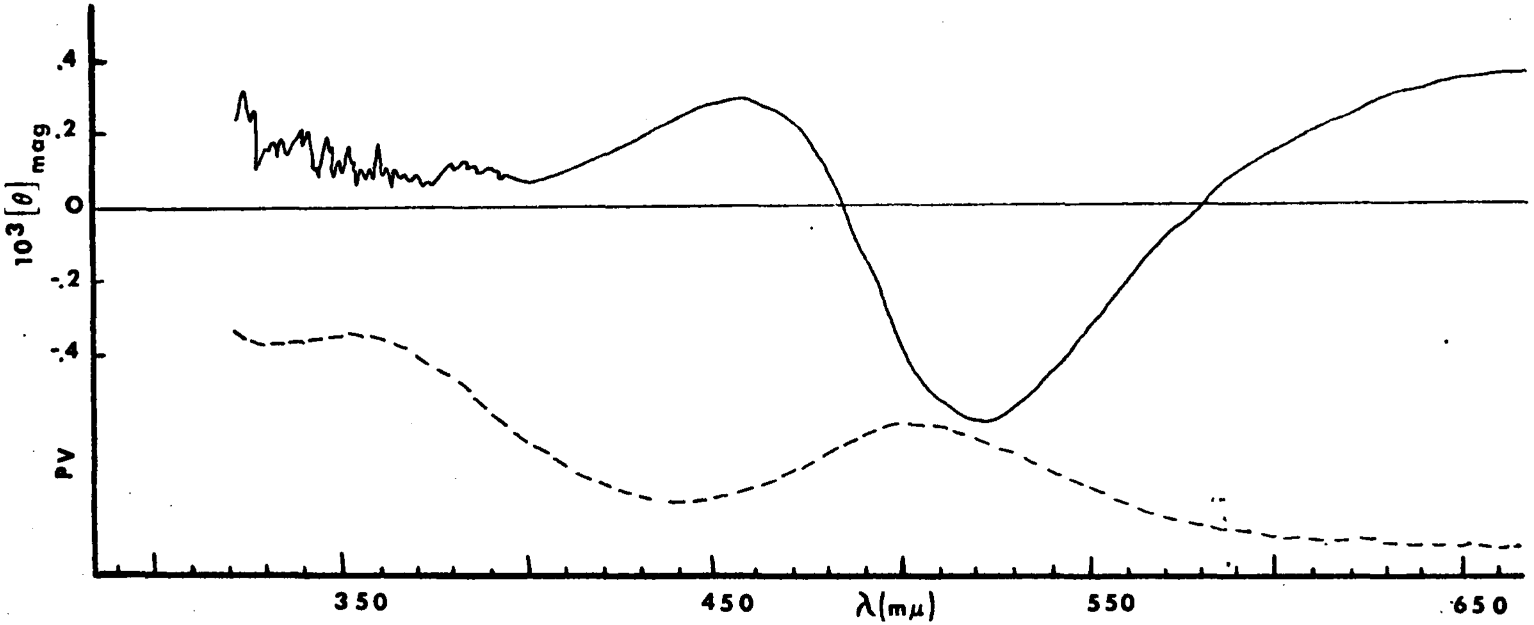


Fig. 29. MCD spectrum of naphthalene plus iodine. PV (---) corresponds to the absorption spectrum. Solvent, PV and $[\theta]_{mag}$ as in fig. 14. Naphthalene = 7.00×10^{-1}M, $I_2 = 6.00 \times 10^{-2}$M.

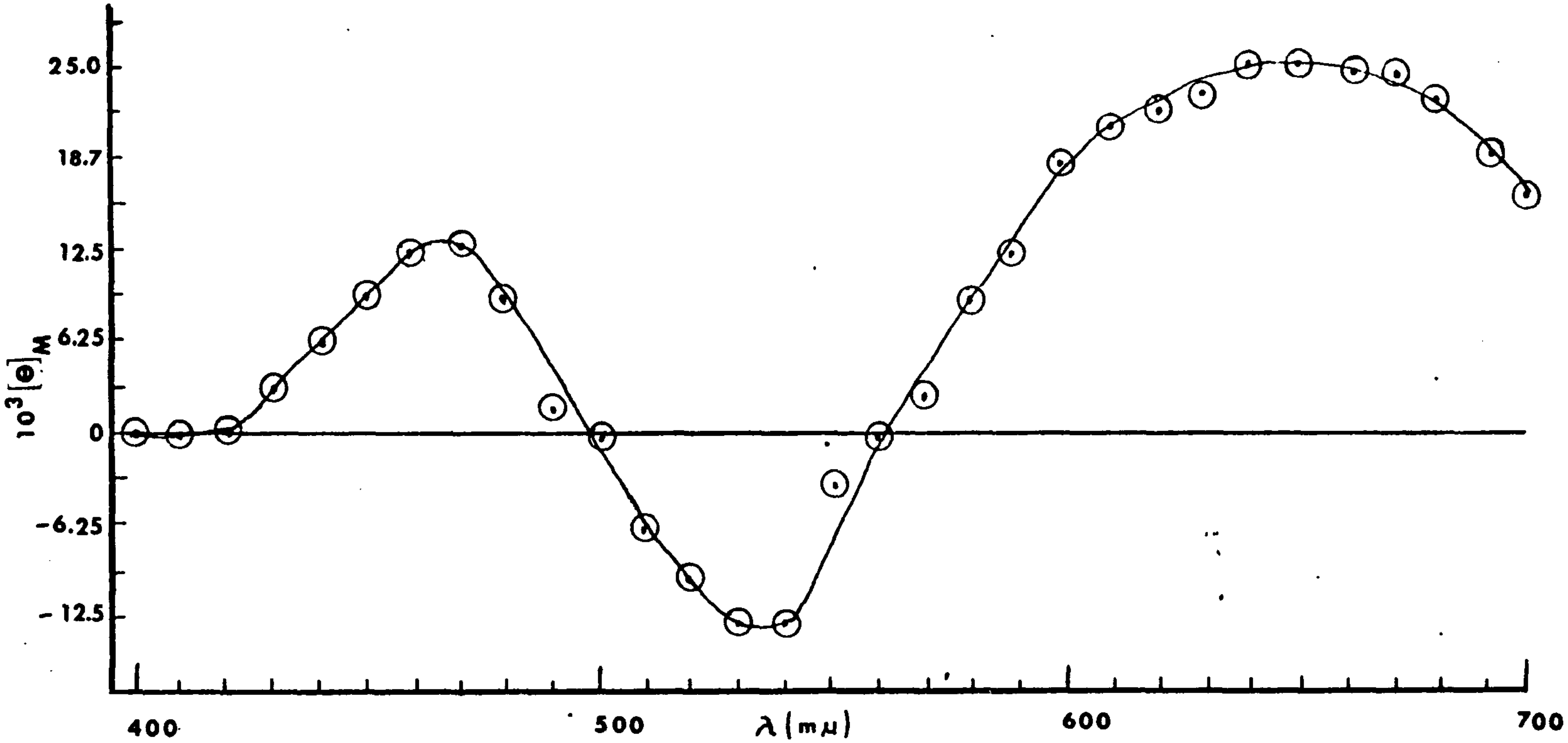


Fig. 30. MCD difference spectrum of naphthalene plus iodine. Solvent and $[\theta]_M$ as in fig. 11.

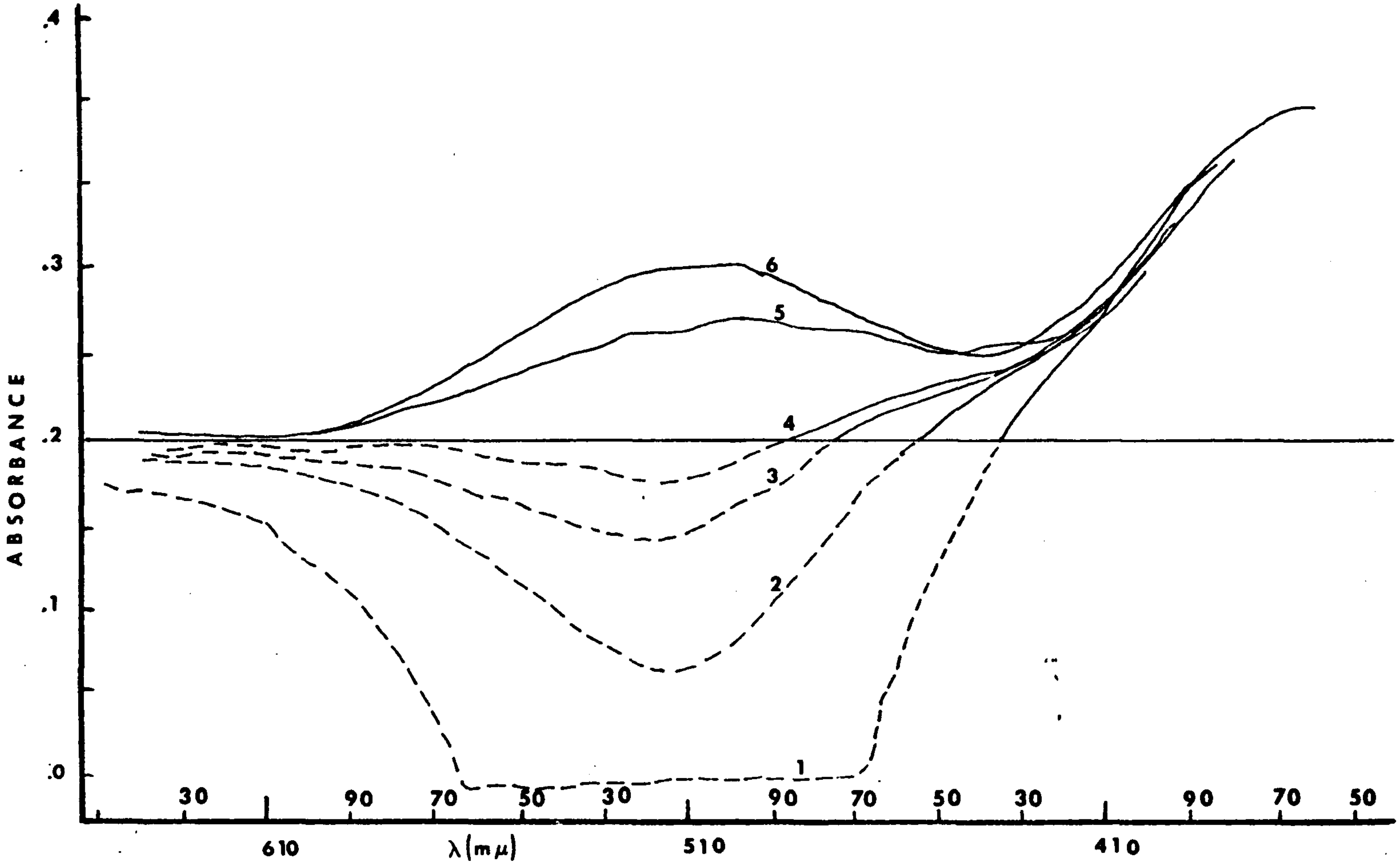


Fig. 31. Visible absorption difference spectrum of naphthalene (N) plus iodine. 8.7 x 10^{-2}M/N plus 1.37 x 10^{-2}M/I_2 versus in reference cell: (1) 1.40 x 10^{-2}M/I_2, (2) 1.37 x 10^{-2}M/I_2, (3) 1.35 x 10^{-2}M/I_2, (4) 1.31 x 10^{-2}M/I_2, (5) 1.28 x 10^{-2}M/I_2, (6) 1.20 x 10^{-2}M/I_2. Solvent: $CHCl_3$; cell path length: 1 mm.

appears a new CT band at 350 mμ and an expected overall increase in intensity of the other bands. The CT band is complex and very weak. Since naphthalene is of D_{2h} symmetry it is expected that the resulting iodine complex could not have any symmetry greater than D_{2h}. Thus the MCD band at 350 mμ is, as anticipated, a B-term. In the visible region there are two oppositely signed B-terms appearing at (+) 470 mμ and (-) 530 mμ. In addition there appears a band at (+) 650 mμ . There is also the expected blue shift in the visible spectrum to approximately 500 mμ . (See previous explanation). It might be expected from the cases discussed previously that iodine will orient itself with its linear axis perpendicular to the plane of the naphthalene rings. (See figures 28 - 31 for spectra and figure 32 for structure.)

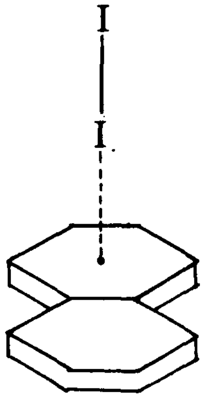


Fig. 32. The structure of the naphthalene·iodine complex.

Of course the MCD spectrum does not allow a simple assignment of structure to the complex due to the low symmetry of naphthalene itself.

Utilization of mellitic anhydride as acceptor proved unsuccessful because of all the experimental difficulties described earlier.

Anthracene

The MCD spectrum of anthracene exhibits a series of B-terms (some partially overlapped). The band at 256 mμ is an obvious B-term corresponding to the ^1B_b state. The complex band at approximately 355 mμ corresponds to the ^1L_b state and the band at 374 mμ corresponds to the ^1L_a state. (See figures 33 and 34.) This is in good agreement with the MCD spectrum obtained by Schooley and others.[80] It must be pointed out that there has been considerable controversy concerning the exact location of the ^1L_b band which is submerged in the ultraviolet region. However, recently (1973) Mason and Peacock have located exactly the ^1L_b state at the lower wavelength (355 mμ) by utilizing measurements of linear dichroism, MCD and meso-phase-induced circular dichroism.[85] This is in contrast to an earlier (1971) study by Larkindale and Simkin who had located the ^1L_b state in the MCD spectrum at 400 mμ even though no corresponding absorption band was found.[84] It

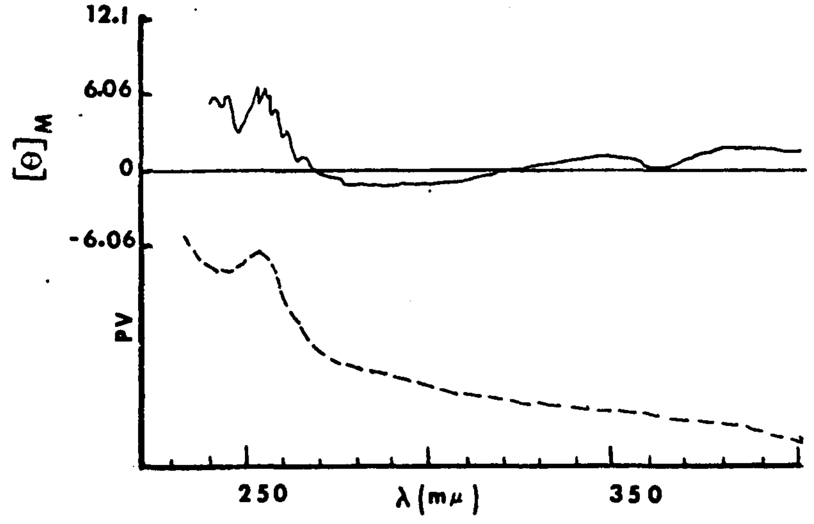


Fig. 33. MCD spectrum (——) of anthracene. PV (---) corresponds to the absorption spectrum. ($\epsilon_{250} = 2 \times 10^5$). Solvent, PV, and $[\theta]_M$ as in fig. 11.

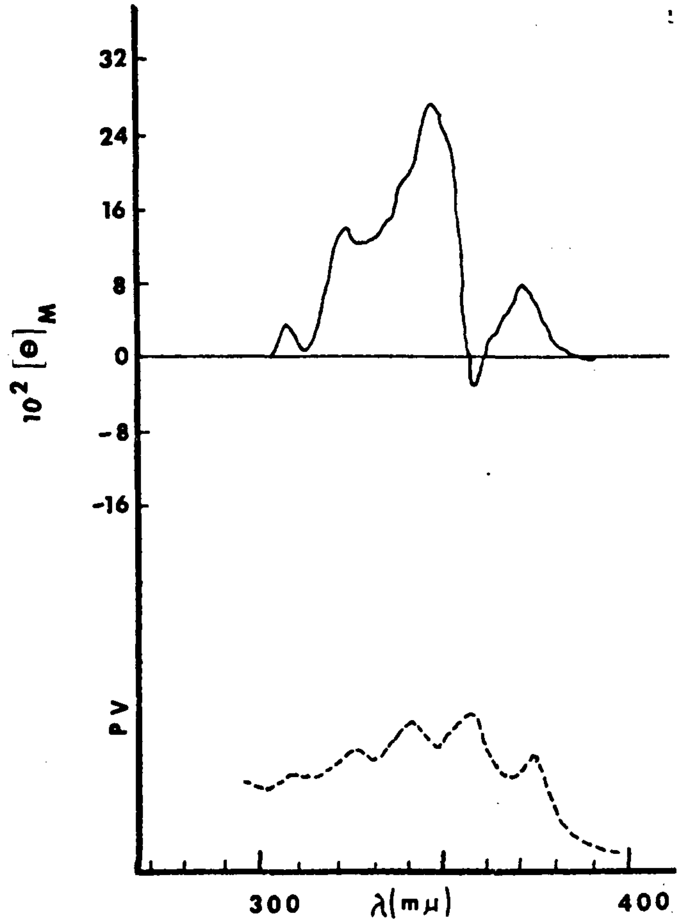


Fig. 34. MCD spectrum (——) of anthracene. PV (---) corresponds to the absorption spectrum (ϵ_{310} = 1000; ϵ_{325} = 2500; ϵ_{340} = 5020; ϵ_{355} = 7940; ϵ_{375} = 3980). Solvent, PV and $[\theta]_M$ as in fig. 11.

must be pointed out that neither in the present investigation nor in the work of Schooley and others absorption or MCD bands in this region were detected.

In this study upon complexation with iodine the MCD spectrum exhibits a partially overlapped new CT band at 420 mμ. The MCD difference spectrum reveals this as a B-term. (See figures 35 and 36.) It has been noted from the absorption spectrum of 9, 10-substituted anthracenes that no changes occur in the ^1B_b band but there is enhancement of the ^1L_a and ^1L_b bands.[86] After complexation all the MCD bands increase generally in intensity with the exception of the band at 256 mμ. Since this band does not show any appreciable change in intensity an analogy with respect to spectral changes on 9, 10-substitution could be made. Thus one might take this as an indication that the iodine positions itself preferrentially on the central ring in the anthracene·iodine complex.

The CT band of the complex is a B-term which is consistent with the expected symmetry. Anthracene with D_{2h} symmetry will not result in a complex of greater symmetry and a B-term should be observed. Axial orientation seems most likely as before and most probably on the central ring. (See figure 37.)

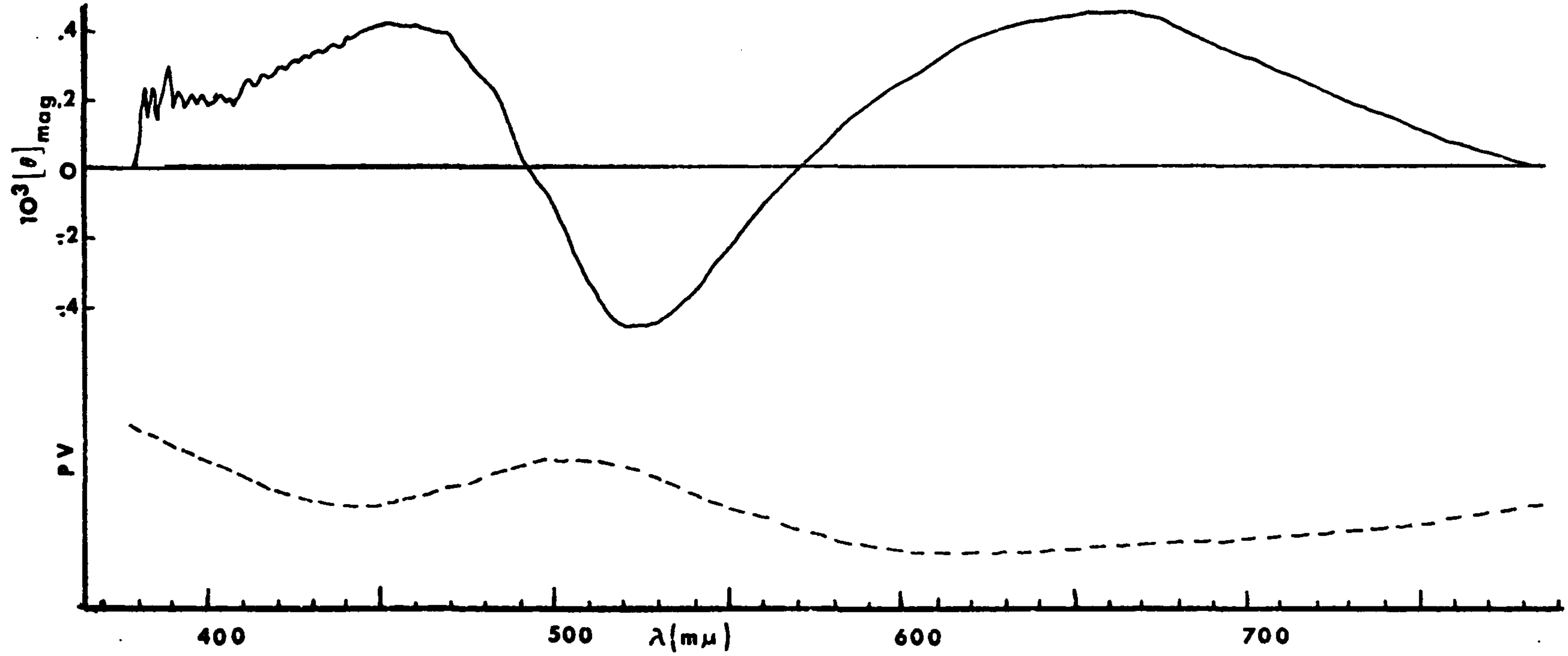


Fig. 35. MCD spectrum (——) of anthracene plus iodine. PV (---) corresponds to the absorption spectrum. Solvent, PV and $[\theta]_{mag}$ as in fig. 14. Anthracene = 2.50×10^{-2}M, $I_2 = 2.00 \times 10^{-2}$M.

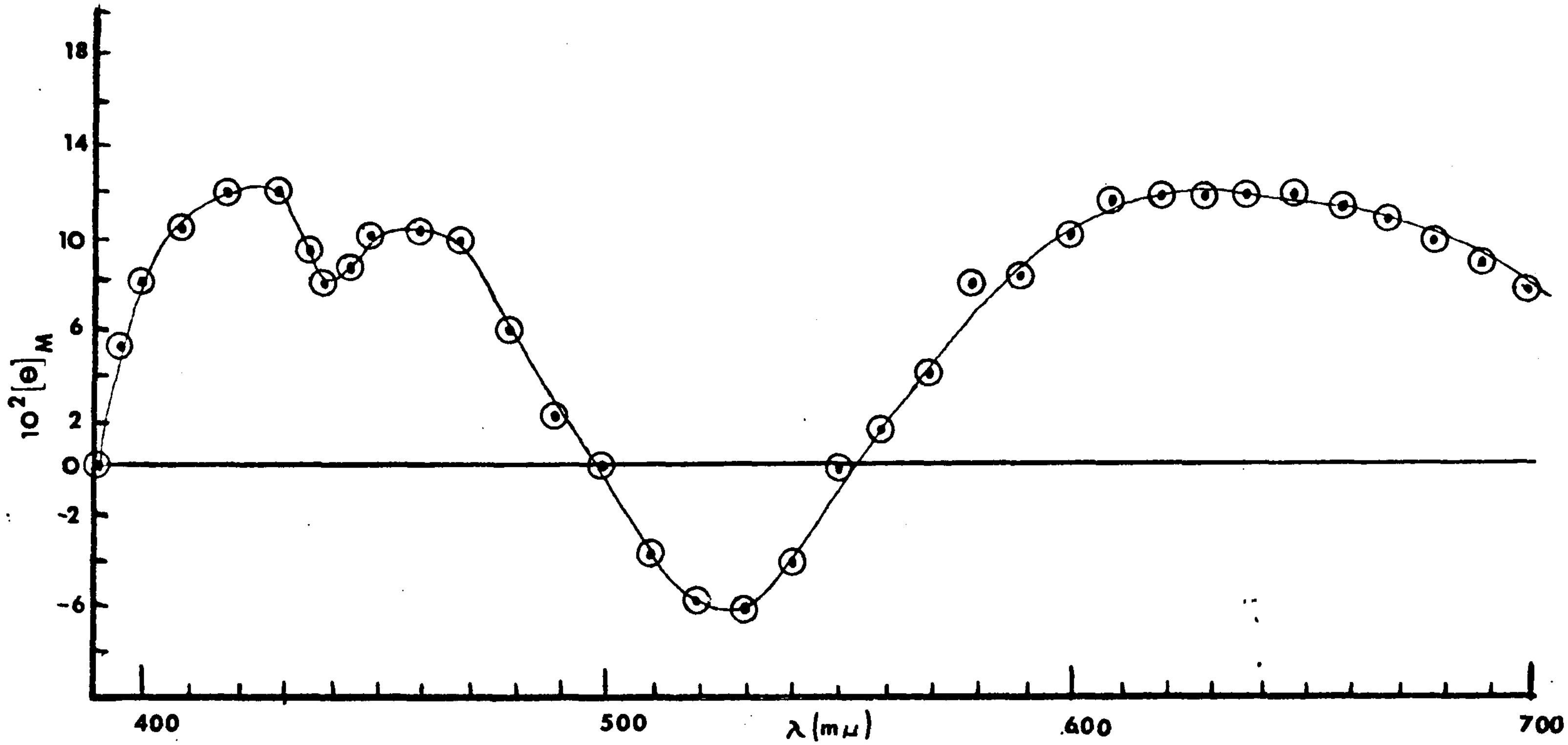


Fig. 36. MCD difference spectrum of anthracene plus iodine. Solvent and $[\theta]_M$ as in fig. 11.

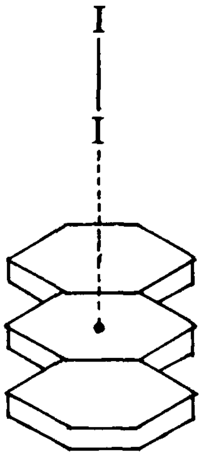
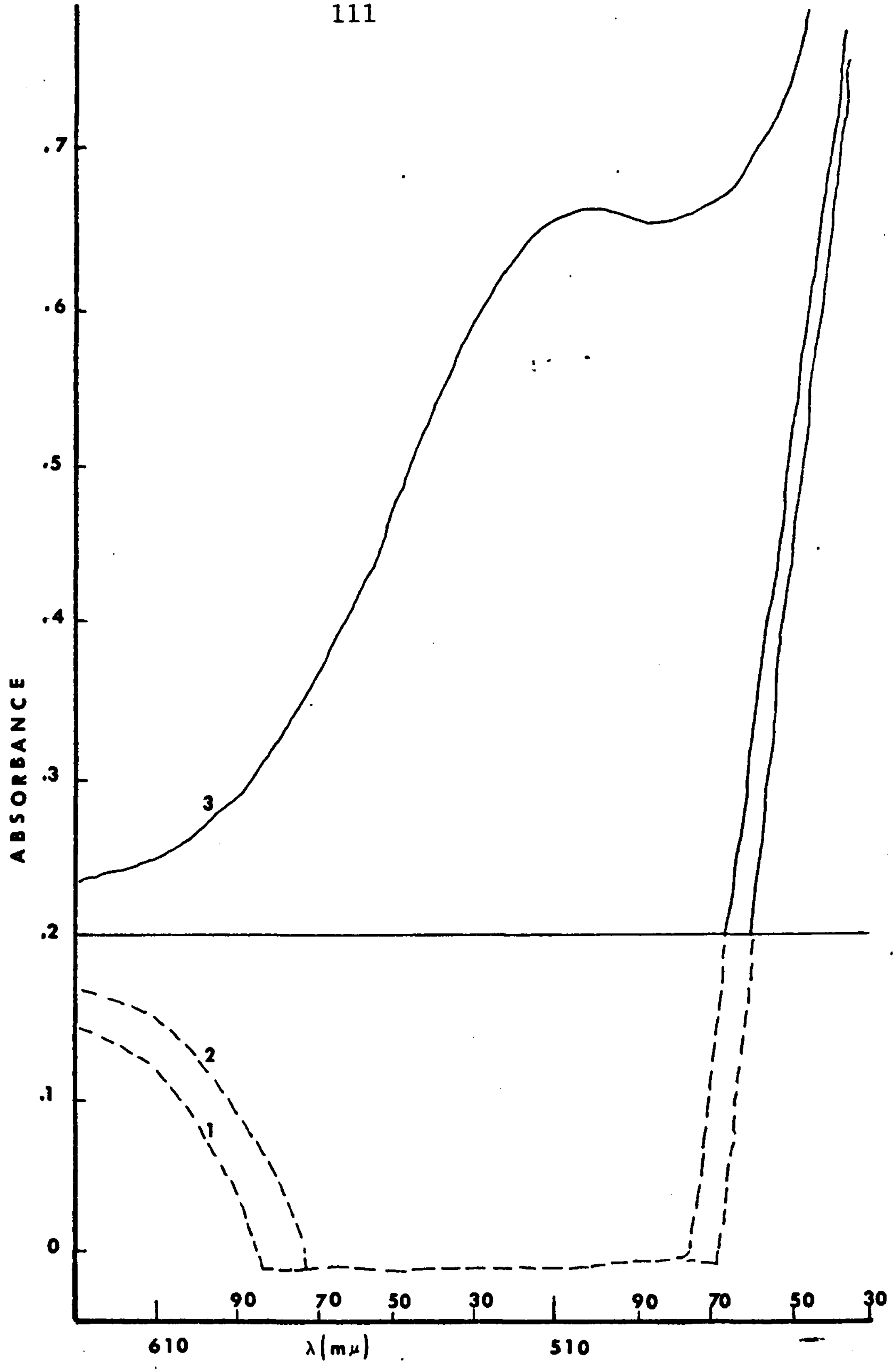


Fig. 37. The structure of anthracene·iodine complex.

The MCD spectrum of the visible region exhibits two oppositely signed bands, but the one at 470 mμ is not as completely resolved since the CT band at 420 mμ overlaps slightly. There is also an intense 650 mμ band (see previous discussions).

The experimental determination of the equilibrium constant yielded a value of 9.7 l-mole^{-1}. The difference visible absorption spectrum did not yield two closely spaced bands, as in the previous cases, but a single maximum at 500 mμ . (See figure 38.) This is due to the overlap of the CT band at 420 mμ . It is obvious that the 500 mμ maximum is due to the blue-shifted iodine band. A survey of the literature indicates some difficulty in the measurement of the equilibrium constant for this complex. For example, Person and Peters[68] found in carbon tetrachloride

Fig. 38. Visible absorption difference spectrum of anthracene (A) plus iodine. 1.25×10^{-2}M/A plus 1.00×10^{-2}M/I_2 versus in reference cell: (1) 1.00×10^{-2} M/I_2, (2) 4.50×10^{-3}M/I_2, (3) 9.00×10^{-3}M/I_2. Solvent: $CHCl_3$; cell path length: 1 mm.


ABSORBANCE
.7
.6
.5
.4
.3
.2
.1
0
3
2
1
90
70
50
30
90
70
50
30
610
λ(mμ)
510

a value of 3.7 $l\text{-mole}^{-1}$ and in CH_2Cl_2 a value of 2.4 $l\text{-mole}^{-1}$. They averaged the results to obtain a value of 3.0 $l\text{-mole}^{-1}$, which seems questionable since the equilibrium constant varies with solvent.[68] In contrast, Basu obtained a value of 50 $l\text{-mole}^{-1}$ in carbon tetrachloride.[69] They did agree on the location of the CT band at 430 mμ .

Studies with mellitic trianhydride as acceptor were attempted. Upon complexation, intense deep blue crystals formed which were slightly soluble in chloroform. A weak broadening was observed in the 600 mμ region. This would correspond to the 587 mμ band reported for this complex in the absorption spectrum.[87] Other solvents were tried but difficulties were experienced as indicated in the experimental section. An interesting but puzzling phenomenon was observed upon utilizing a solvent combination of tetrahydrofuran/benzene. The originally intense color faded more slowly and a series of MCD spectra were determined; there was a noticeable shift of a band originally occurring at 700 mμ to 480 mμ . A reaction was most likely taking place.

Benzene

In the case of benzene it is best to discuss the experimental results by first reviewing the literature data on absorption and MCD spectra.

The absorption spectrum of benzene consists of three bands corresponding to the following electronic transitions:

		Platt's Notation	Group Theory Notation	
(1)	230 mμ to 270 mμ	$^1L_b \leftarrow {}^1A$	$^1B_{2u} \leftarrow {}^1A_{1g}$	"benzenoid" fine structure band
(2)	203 mμ	$^1L_a \leftarrow {}^1A$	$^1B_{1u} \leftarrow {}^1A_{1g}$	
(3)	180 mμ	$^1B \leftarrow {}^1A$	$^1E_{1u} \leftarrow {}^1A_{1g}$	

The (3) transition is symmetry allowed and appears in the far UV with high intensity. Transitions (2) and (1) are symmetry forbidden but "vibronically-allowed".[86] In benzene there are four fundamental e_{2g} vibrational states with frequencies of 608, 1178, 1596 and 3056 cm^{-1} (ground electronic state). With the exception of the 1178 cm^{-1} mode, which involves mainly in-plane C-H bending, they all can be detected in the ultraviolet spectrum. For the first transition (1) the symmetry-forbiddenness is removed by the normal coordinates of e_{2g} symmetry, which mix the $^1B_{2u}$ state with the higher $^1E_{1u}$ state.

Recently (1972) Eyring, and others have investigated the vibrational fine structure in the MCD spectrum of the (1) transition of the benzene.[88] They have shown good agreement between experimental and calculated intensities for the positive MCD bands indicating that these are mainly induced by the e_{2g} 1596 cm^{-1} mode. Poor agreement was obtained between calculated and experimental results for the negative MCD bands. This may be the result of neglecting contributions from the 3056 cm^{-1} mode, from hot bands, and from transitions of normal modes other than the A_{1g} 992 cm^{-1} mode. The striking fact in the MCD spectrum is that for the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition the contribution from different vibronic coupled modes have opposite signs in MCD (positive and negative bands). Furthermore, although the 608 cm^{-1} mode is dominantly represented in the ultraviolet spectrum, but in MCD the 1596 cm^{-1} mode plays the most important role.

Recently (1973) the MCD spectrum of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition in the vapor phase has been investigated by Douglas and others.[89] Utilizing a super-conducting magnet they obtained a highly resolved spectrum which is not exhibited in solution. Many bands due to transitions between single vibronic levels display A-terms. In the 203 mμ region progressions of opposite sign with B-term dispersion have been observed.

In other recent investigation Eyring and Caldwell have made some correlations concerning o, p, and m-directing groups substituted on benzene and the sign of MCD curves.[90] Generally they found that o, p-directing substituents yield MCD curves of opposite sign relative to m-directing substituents. Whenever the $^1B_{1u}$ and $^1B_{2u}$ are close in energy, the MCD spectra are opposite in sign with comparable area. When the two states are far apart either relative sign is possible, i.e. higher states are mixed which allow either relative sign of MCD. Another aspect to consider is the result on the strength of the MCD due to the difference in vibronic and electronic effects. Since the electronic portion of the system is responsible partially for the strength of the MCD, the MCD's of D_{2h} and C_{2v} symmetry benzene derivatives will be larger since electronic effects are more important than vibronic.[91] On the other hand benzene compounds with D_{6h} and D_{3h} symmetry will exhibit MCD's that are less intense. For example, as will be shown later the MCD spectrum of mesitylene (D_{3h}) is weak. The most complicated case occurs when vibronic effects are large, since the sign changes in the middle of the $^1B_{2u}$ band in the same way as for the D_{6h} symmetry compounds. On the other hand, symmetrical substitution of reasonably heavy groups such as iodine will tend to give MCD spectra without sign changes within the $^1B_{1u}$ band $^1B_{2u}$ bands. However it must be pointed out that for substituted benzene of D_{6h} symmetry derivatives little experimental evidence exists for sign changes within the $^1B_{1u}$ and $^1B_{2u}$ bands, and thus benzene itself remains unique in this respect. Eyring and Caldwell utilized variation calculations which included electron donor and acceptor wavefunctions based on occupied and unoccupied substituent orbitals to explain the observed oppositely signed MCD bands of o, p, and m-directing groups.

In the present study, the MCD spectrum of benzene in chloroform and carbon tetrachloride was obtained and the ^1L_b and ($^1B_{2u}$) band (250 mμ midpoint) was observed. Its size is smaller than that of other investigators.[79, 88] However they utilized a magnetic field of forty-five kilogauss in contrast to ten kilogauss in this work. Nevertheless the complicated MCD band of the ^1L_b state is clearly evident. Upon complexation with iodine the new CT band at 290 mμ was observed. It is still a weak band with the same characteristic complicated pattern of benzene. One may draw an anology from the above discussion that the heavy iodine is in close symmetrical association with benzene. This suggests the retention of the six-fold symmetry axis in the complex. The only model which would conform to this is the axial structure for the benzene· iodine complex. (See figure 39 for structure and 40-42 for MCD spectra.)

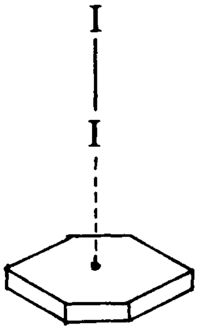


Fig. 39. The structure of the benzene·iodine complex.

In the total MCD spectrum there are clearly evident the blue-shifted visible region bands of increased intensity, especially when iodine is dissolved in benzene. (See figure 42.) The visible absorption shows one broad maximum at 500 mμ which is in agreement with Mulliken's results.[92] However the MCD spectrum again reveals the two completely resolved bands at (+) 460 mμ and (-) 520 mμ. Furthermore there is the distinct band at approximately (+) 640 mμ . The MCD spectra of the 180 m (^1B or $^1E_{1u}$) and the 203 mμ (^1L_a or $^1B_{1u}$) were not observed due to the limitations of

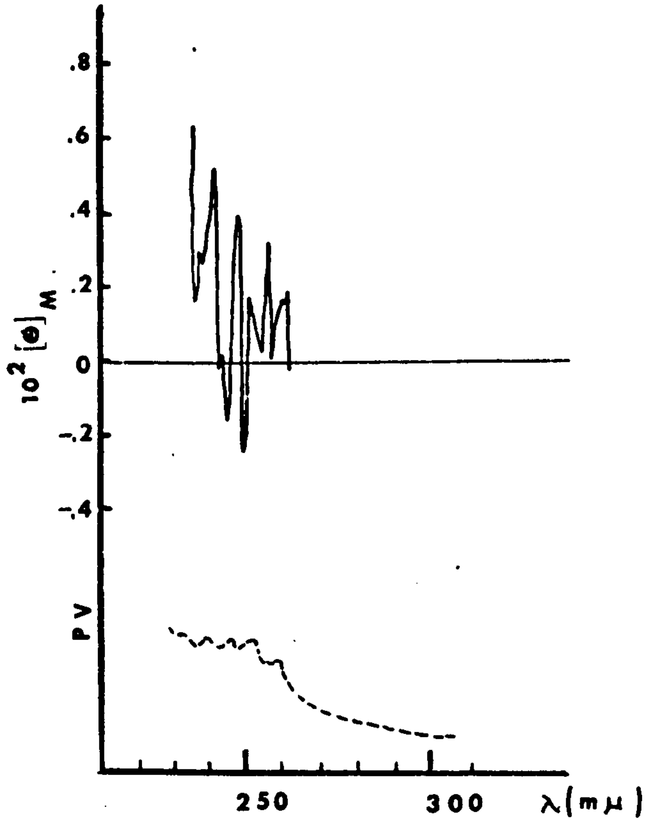


Fig. 40. MCD spectrum (——) of benzene. PV (---) corresponds to the absorption spectrum ($\epsilon_{250} = 220$). Solvent, PV and $[\theta]_M$ as in fig. 11.

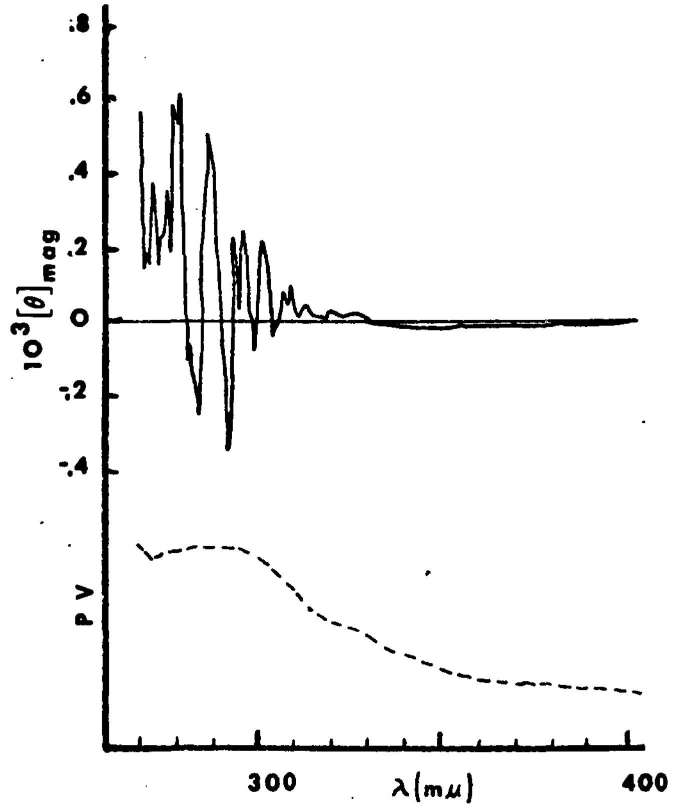


Fig. 41. MCD spectrum (——) of benzene plus iodine. PV (---) corresponds to the absorption spectrum. Solvent, PV and $[\theta]_{mag}$ as in fig. 14. Benzene = 2.4 x 10^{-1}M, I_2 = 6 x 10^{-3}M.

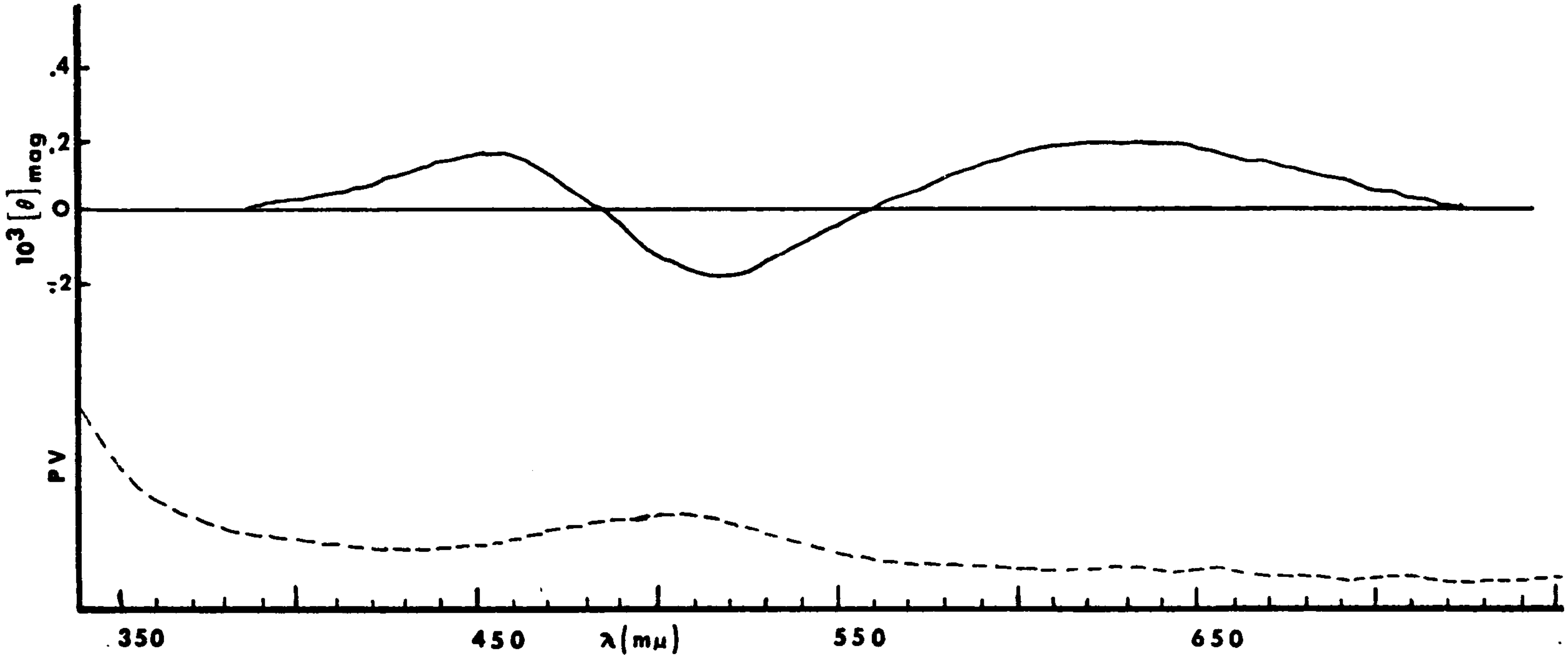


Fig. 42. MCD spectrum (——) of iodine in benzene. (Neat). PV (---) corresponds to the absorption spectrum. PV and $[\theta]_{mag}$ as in fig. 14.

the Durrum-Jasco instrument.

The equilibrium constant for the benzene·iodine complex has been determined by a number of investigators in a variety of solvents. The values of the equilibrium constant range from 0.15 to 1.59 1-mole^{-1} for the next complex and in solutions of carbontetrachloride, n-hexane, cyclohexane, and n-heptane.[93 - 96]

An MCD spectrum of iodobenzene was obtained for comparison. It exhibits a small (+) B-term at 260 mμ with no complicated structure. This is in agreement with the results of Foss and McCarville, who investigated it as part of a series in an attempt to correlate MCD signs with o, p-substitution and m-substitution in monosubstituted benzenes. They found that o, p-directing substituents yield a (+) MCD band for the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition, that is the ^1L_b state. Foss and McCarville have not reported the MCD spectrum for the 226 mμ band of iodobenzene. However, in this study the 226 mμ band was detected as a (+) MCD term. The ^1L_b MCD band was utilized here in an analogy. The nonsymmetrical compound iodobenzene exhibits a simple B-term with no fine benzenoid structure, and in addition nitrobenzene shows a simple negative B-term at 260 mμ. This is in contrast to the MCD spectrum of the complex.

Thus retention of symmetry seemingly implies retention of overall fine benzenoid structure in the MCD. Consequently the suggestion of the axial model is strenghtened. This is in agreement with the conclusions of Fredin and Nelander, which were discussed earlier.[14]

Mesitylene (1,3,5-trimethylbenzene)

The MCD spectrum of mesitylene (D_{3h}) exhibits the expected weak (see benzene discussion) band in the 240 to 270 mμ range. This corresponds to the $^1B_{2u}$ band. (See figure 43.) Upon complexation with iodine the following results are observed. There is the expected blue shift of the visible iodine band with a maximum at 490 mμ , concurring with Mulliken's result.[92] In the MCD spectrum (especially evident when iodine is dissolved in mesitylene) the two B-terms of opposite sign are prominent at (+) 450 mμ and (-) 510 mμ . Furthermore the (+) 630 mμ band is clearly evident. (See figure 44-46.)

A new CT band is observed at 330 mμ. The ultraviolet absorption shows this as one broad band with a maximum at 330 mμ. However the MCD spectrum exhibits two closely spaced bands (containing some fine structure) of opposite sign, with the inflection point corresponding

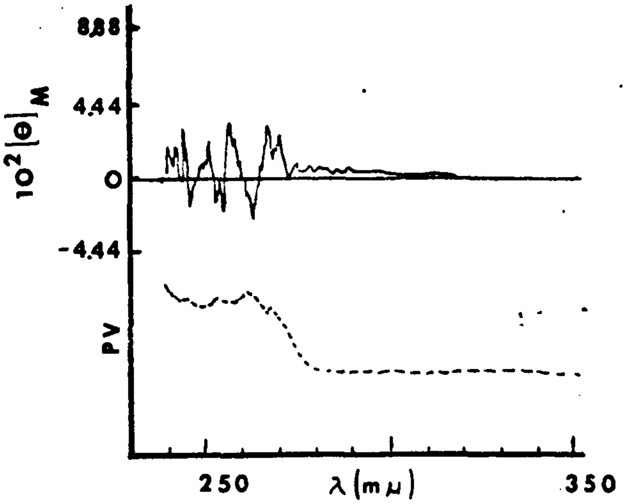


Fig. 43. MCD spectrum of mesitylene. PV (---) corresponds to the absorption spectrum. Solvent, PV, and $[\theta]_M$ as in fig. 11. (ϵ_{260} = 360).

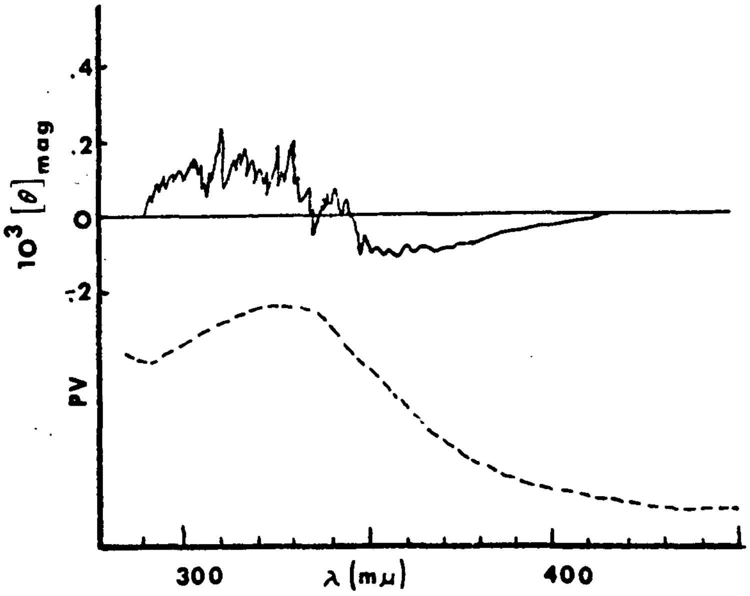


Fig. 44. MCD spectrum of mesitylene plus iodine. PV (---) corresponds to the absorption spectrum. Solvent, PV, and $[\theta]_{mag}$ as in fig. 14. Mes = 3.6×10^{-2}M, I_2 = 2.2×10^{-2}M.

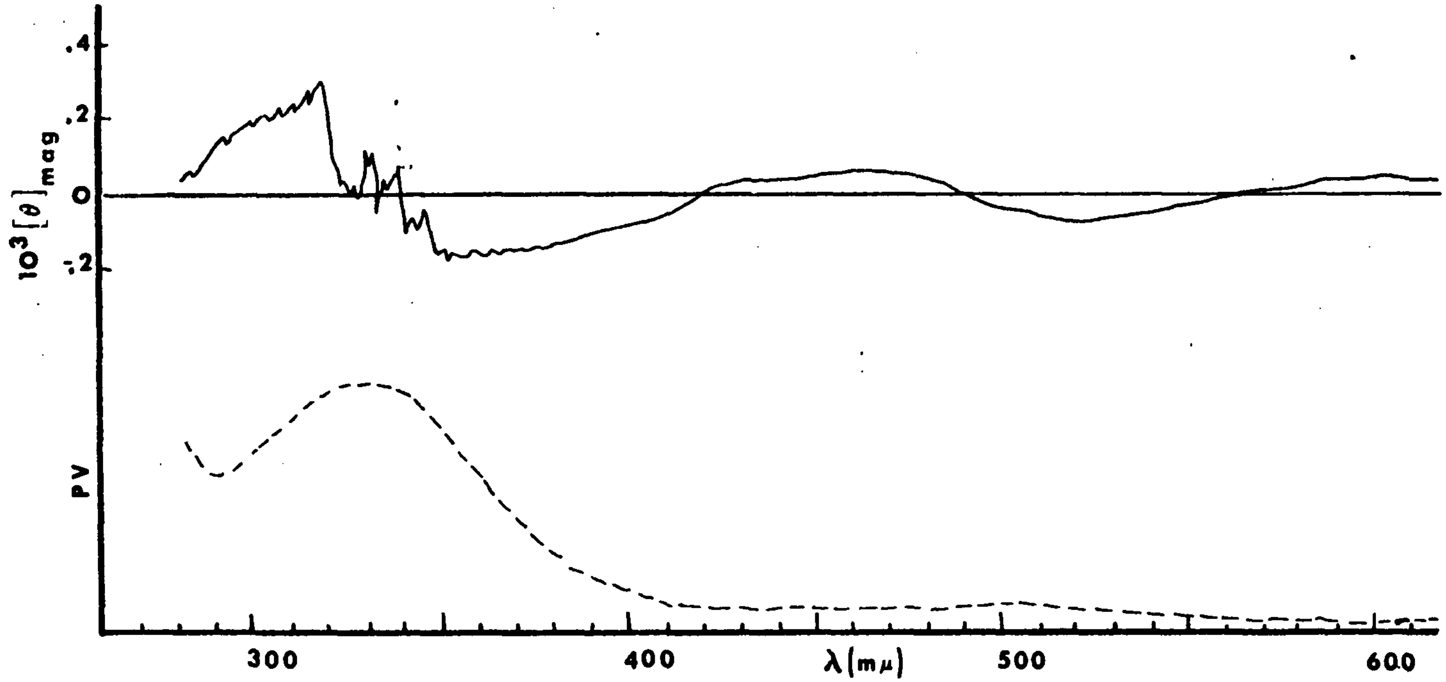


Fig. 45. MCD spectrum of iodine in mesitylene. (Neat). PV (---) corresponds to the absorption spectrum. PV and $[\theta]_{mag}$ as in fig. 14.

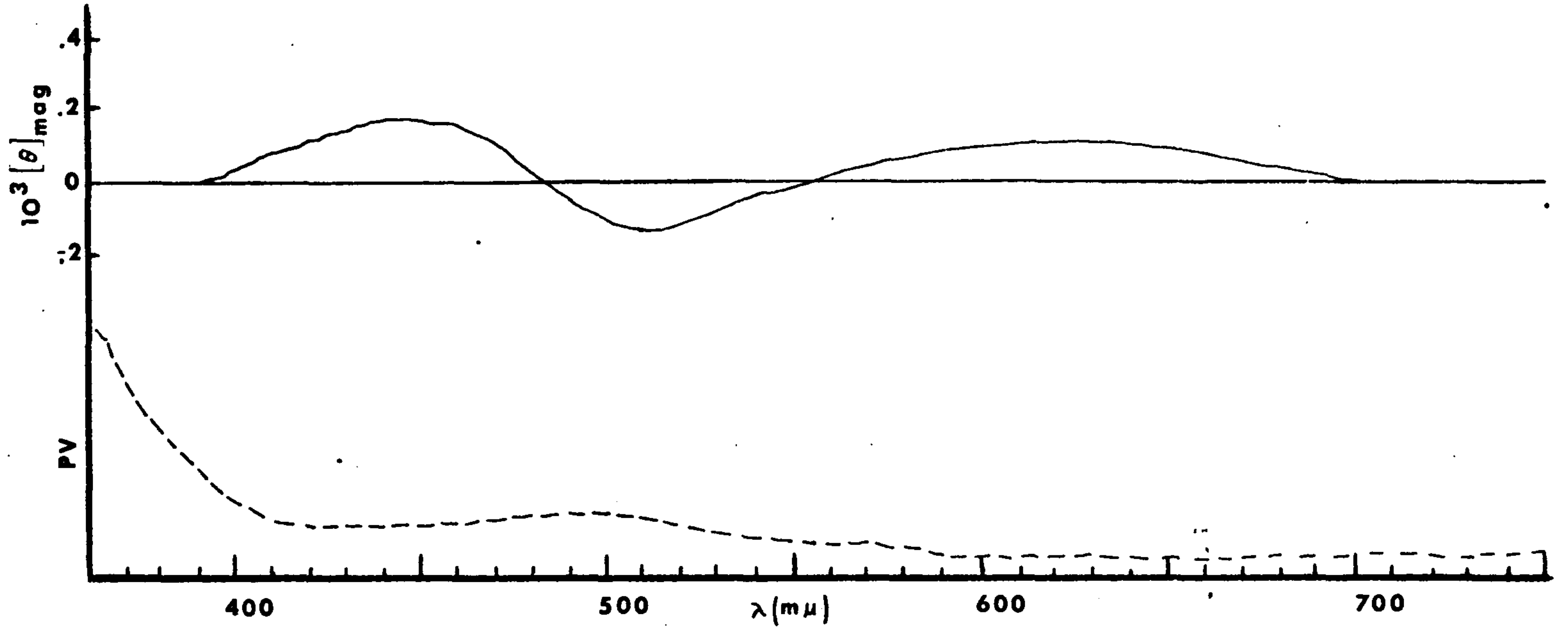


Fig. 46. MCD spectrum of iodine in mesitylene. (Neat). PV (---) corresponds to the absorption spectrum. PV and $[\theta]_{mag}$ as in fig. 14.

approximately to the maximum in the ultraviolet absorption spectrum. (See figure 44.) It is probable that this is a broad A-term superimposed on which are a set of overlapping vibronic terms as occurs in the benzene aromatics. The A-term strongly suggests a mesitylene·iodine complex of C_{3v} symmetry. (See figure 47.)

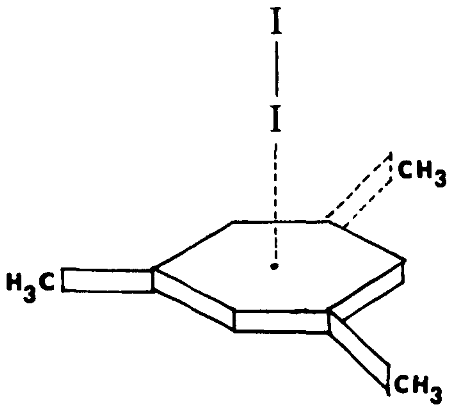


Fig. 47. The structure of the mesitylene·iodine complex.

The equilibrium constant for the mesitylene·iodine complex in carbon tetrachloride has been determined by Murrell[98] to be 0.82 l-mole^{-1} and the CT band located at 332 mμ, which is in good agreement with results reported in this study.

VI. CONCLUSIONS

The MCD results in the preceding study yielded not only additional evidence for the axially-oriented iodine in complexes with aromatic hydrocarbons, but also contributed to the greater elucidation of the absorption spectrum of iodine.

The originally hidden band in the absorption spectrum of iodine due to the $^1\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ transition was revealed clearly as a positive B-term at 470 mμ in the MCD spectrum. The other negatively signed B-term at 530 mμ is due to the $^3\Pi_{ou}^+ \leftarrow {}^1\Sigma_g^+$ transition. Another dramatic result is the discovery of the broad and large positive B-term at about 665 mμ which is extremely difficult to find in the absorption spectrum. Ham found this band as a barely perceptible shoulder and attributed its origin to the transition, $^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$. Furthermore a small positive B-term was found at 280 mμ which has been ascribed to the $I_2 \cdot I_2$ dimer complex.

The effects upon the visible spectrum of iodine when it complexes with the aromatic donors, corroborate the above conclusions. The bands in the 470 mμ and

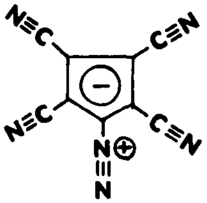
530 mμ regions are observed upon complexation not only in the MCD difference spectra but also in the difference absorption spectra. Furthermore, regardless of the type of donor, for example, triphenylene or phenanthrene, these maxima occur at the same approximate wavelengths. This suggests that in the complex due to increased mixing between the newly formed CT states and the iodine $^3\pi^+_{ou}$ and $^1\pi_{1u}$ states (possibly these could also mix with the now more accessible $^1\Sigma^+_u$ state), an increase in intensity of these bands occur and they become apparent in the visible difference spectrum. A recent (1972) investigation of iodine·nitrile complexes from visible difference spectra by Maguire and others showed maxima at about 460 mμ and 540 mμ independent of the type of nitrile used (that is, aceto-, propio-, butyro-, valero-, and pivalonitriles).[99] No explanation of this behavior was offered since they were mainly concerned with the variation of the equilibrium constant in different solvents. They utilized a modified Scott equation to find the equilibrium constant from visible difference spectra. Their overall conclusion was that the value of the equilibrium constant is a function of solvent type rather than any specific solvent parameter. However, the appearance of the two maxima in their

investigations that lends credence to the structures of iodine complexes proposed in this study.

A technique was developed in this study for the experimental determination of the equilibrium constant which involved utilization of the absorption band of iodine in the visible region. This method served well for the purpose of obtaining MCD difference spectra when in certain cases the MCD CT bands were partially overlapped.

In the MCD spectrum the triphenylene·iodine complex yielded the expected A-term, the mesitylene·iodine complex a broad A-term, the benzene·iodine complex a set of overlapping A-terms, while the others B-terms. This is the first instance where MCD CT bands for molecular iodine·aromatic hydrocarbon complexes have been reported. In addition, two MCD CT bands were detected specifically for the triphenylene·tetrocyanoethylene complex. Consequently evidence was obtained for the structure of aromatic hydrocarbon·iodine complexes where the iodine axis lies perpendicular to the plane of the aromatic hydrocarbons, and in addition the iodine seems to be always centrally located with respect to the aromatic ring. Furthermore, the existence was confirmed of the complexes between iodine and the solvents p-dioxane and ethanol by detection of B-terms in the MCD spectrum.

At this point a word of caution should be stated concerning the interpretation of MCD spectra. It is conceivable that one could obtain a broad sinusoidal curve which immediately suggests an A-term. For example, Tajiri and Hatano recently (1972) reported a broad A-term for the tropylium cation (D_{7h}).[45] However, such a sinusoidal curve could also be interpreted as two closely spaced B-terms of opposite sign. For example Uchimura and Tajiri later (1973) reported what at first appeared to be a broad A-term for diazotetracyanocyclopentadiene (DTCC),



which obviously due to its C_{2v} symmetry cannot yield an A-term.[44] Thus the MCD spectrum was then interpreted as two adjacent B-terms which opposite sign. Indeed in the present study this was the case for the visible region MCD band (approximately of 190 mμ width) of iodine, which had another band hidden in the absorption spectrum. However, the MCD spectrum exhibited two closely-spaced separate B-terms of opposite sign.

APPENDIX

Classification of UV Bands in Terms of Polarization In Electronic States (Platt's Notation)[100 - 102]

Triphenylene

States:	^1L_a	^1L_b	^3L_a*	^1B_b
λ(mμ):	290	340 (onset)	420	265
Polarization:**	tr.	lg.	tr.	lg.

*Phosphorescent triplet state.

**tr. (transverse) - is equivalent to polarization along the short (transverse) axis or perpendicular to the long axis.

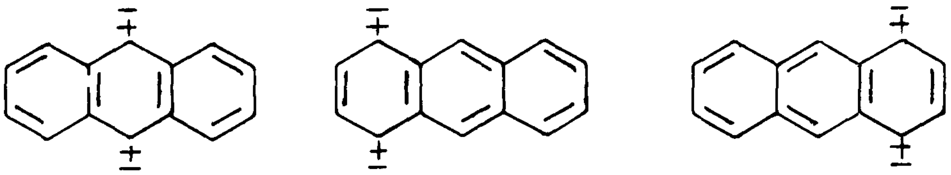
lg. (longitudinal) - is equivalent to polarization along the long axis or parallel to long axis.

Anthracene

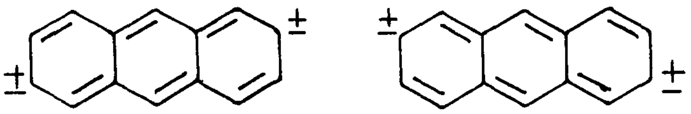
States:	^1L_a	$^1L_b^*$	$^3L_b^*$	$^3L_a^*$	^1B_b	$^1C_b^*$	^1B_a
$\lambda(m\mu)$:	374	355	312	680	255	220	187
Polarization:**	tr.	lg.	lg.	tr.	lg.		tr.

*^1L_b - hidden; ^3L_b and ^3L_a - phosphorescent triplet states; ^1C_b - forbidden.

**tr. (transverse) - is equivalent to polarization perpendicular to the long axis of the molecule. It is for example associated with excitation to a state to which polarized forms such as the following contribute:



lg. (longitudinal)- is equivalent to polarization parallel to the long axis of the molecule. It is associated with excitation to a state to which polarized forms such as the following contribute:



Naphthalene

States:	^1L_a	^1L_b	$^3L_b^*$	$^3L_a^*$	^1B_b	^1C_b	^1B_a
λ(mμ):	286 (onset)	308	276	467	217	186	167
Polarization:**	tr.	lg.	lg.	tr.	lg.	lg.	tr.

*Phosphorescent triplet states.

**Polarization is the same as for anthracene.

Phenanthrene

States:	^1L_a	^1L_b	$^3L_a^*$	^1B_b	^1C_b	^1B_a	^1C_a
λ(mμ):	284	345	460	254	212	186	176
Polarization:**	lg.	tr.		lg.	tr.	tr.	lg.

*Phosphorescent triplet state.

**tr. (transverse) - is perpendicular to the symmetry axis.

lg. (longitudinal) - is parallel to the symmetry axis.

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