A SPECTROSCOPIC STUDY OF THE CHARGE-TRANSFER COMPLEX OF ANTHRACENE AND SYM-TRINITROBENZENE

by

STEPHEN KENT LOWER

B.A., University of California, Berkeley, 1955

a thesis submitted in partial fulfilment of
the requirements for the degree
of
M.Sc.
in the Department
of
CHEMISTRY

We accept this Thesis as conforming to the required standard:

THE UNIVERSITY OF BRITISH COLUMBIA

August, 1960

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Stephen K. Lower

Department of **Chemistry**

The University of British Columbia,
Vancouver 8, Canada.

Date **22 September, 1960**

ABSTRACT

Complexes of aromatic hydrocarbons (donors) with electron acceptors such as 1,3,5-trinitrobenzene (TNB) are stabilized principally by resonance between a dative and a "no-bond" wave function:

$$\Phi_N = a\,\psi_o\,(DA) + b\,\psi_i\,(D^+A^-).$$

By means of second-order perturbation theory it can be shown that, providing certain symmetry requirements are met, the energy W_N corresponding to Φ_N will be less than that of the free separated donor and acceptor. The resulting molecular complexes have a stability of 2-10 kcal, and usually possess a colour which is associated with a transition between the ground state W_N and an excited state W_E. These charge-transfer spectra have previously been studied only in solution, and have been useful sources of thermodynamic data. In order to learn more of the transition itself, it is necessary to study the spectrum of the crystal, where the molecules are held in fixed and (sometimes) known positions.

The procedure by which the polarized crystal spectrum of the anthracene-TNB complex was obtained is briefly described. Comparison of the observed spectrum with the partially-known crystal structure has shown

1) The supposition that the transition dipole moment is perpendicular to the planes of the aromatic rings is supported;

2) Vibrational structure can exist in a charge-transfer band; this is the first reported observation of it;

3) The band is split into two oppositely-polarized components, differing in energy by about 200/cm.

An attempt is made to explain this splitting in terms of Davydov's "weak-coupling" model of a crystal, in which degenerate molecular states are presumed to become crystal states whose degeneracy depends on the symmetry of the associated unit-cell wave functions. Some preliminary steps are described which should eventually lead to the detailed calculation of this effect in the present case.

Abstract Approved:

_____

TABLE OF CONTENTS

INTRODUCTION 1

THEORY OF THE CHARGE-TRANSFER COMPLEX 3

PROPERTIES OF THE ANTHRACENE-TNB COMPLEX IN SOLUTION . 9

THE POLARIZED CRYSTAL SPECTRUM OF ANTHRACENE-TNB . . . 17

General Principles 17

Experimental Procedure 19

Results 22

Discussion 28

BIBLIOGRAPHY 35

APPENDIX I 37

APPENDIX II 39

FIGURES

Fig. 1 Correlation Diagram for the Anthracene-TNB Complex 7

Fig. 2 Probable Orientation in the Complex 7

Fig. 3 Absorption of Anthracene-TNB in Solution . . 13

Fig. 4 Absorption of Anthracene-TNB in Solution . . 13

Fig. 5 Effect of Contact-Charge-Transfer 14

Fig. 6 ΔH plots for Anthracene-TNB in Various Solvents 14

Fig. 7 Optical System for Polarized Crystal S pectra 21

Fig. 8 Anthracene-TNB, $-180^{\circ}C$. 23

Fig. 9 Anthracene-TNB, $23^{\circ}C$. 24

Fig. 10 Anthracene-TNT, $-180^{\circ}C$. 26

Fig. 11 9,10-Dimethylanthracene-TNB, $-180^{\circ}C$. 27

Fig. 12 The Space Group C2/c 30

Fig. 13 Projection of Unit Cell in (001). 31

Fig. 14 Orientation of Transition Dipole Moments . . 32

Fig. 15 Transition Moments along (110); Projection on (100) 33

Fig. 16 Projections of Transition Moments in Unit Cell; Two Possibilities 34

Fig. 17 Graphical Determination of Equilibrium Constant of Anthracene-TNB 38

ACKNOWLEDGEMENT

"Res est arduissima
vincere naturam..."

- my attempt to merely observe it would not have been possible without the valuable guidance of Dr. R.M. Hochstrasser, to whom I wish to express my gratitude and thanks.

I am also indebted to Dr. C. Reid for stimulating my interest in this field, and to the National Research Council for summer financial assistance.

I. INTRODUCTION

Molecular compounds or complexes between aromatic hydrocarbons and 1,3,5-trinitrobenzene have been known for many years (3,34), and along with the more widely known picric acid adducts have played an important part in the purification and characterization of a wide variety of aromatic compounds. It is only in recent years that much interest has been shown in understanding their electronic structure, and although the past decade has seen considerable progress in this direction, there is still much that is not understood about the spectroscopic properties of these complexes.

The study of such donor-acceptor complexes is important not only for its intrinsic interest, but also for its possible application to the general problem of inter- and intramolecular energy transfer, which is becoming of special concern to the biologist. There is increasing evidence that donor-acceptor complexes may play an important role in certain biochemical processes. Two recent examples of speculation along these lines deal with two of the most important energy-transfer steps in the life process, namely DPN-DPNH hydrogen transfer and photosynthesis.

It is known (36) that the transfer of hydrogen from substrate to DPN occurs directly at the 4-position of the nucleotide ring, and Chance (6) has given evidence for the existence of DPNH-enzyme and DPN-substrate complexes. Kosower (19) has found that the course of substitution of the 1-methylpyridinium ion is influenced by the complexing ability of the donor, and he discusses the significance

of this result in the light of Chance's findings.

Platt (35) has suggested a new photosynthetic pathway involving a complex of the type

DONOR--(carotene)--ACCEPTOR

as the "energy sink", the complexing being responsible for placing the energy of the carotene below that of the chlorophyll. He suggests various ways in which this or other similar complexes might act as active intermediates in photosynthesis.

The present investigation is a prelude to what is hoped will be a fairly detailed study of the polarized absorption and emission spectra of several polyacene-TNB* complexes. The immediate need for this study arises from the question of the origin of the emission spectrum of the anthracene-TNB complex. The earlier idea (38) was that the emission is from the triplet level of the hydrocarbon, and is thus really donor phosphorescence, the T→S forbiddeness rule being broken down by the strong field of the TNB. Later work (9a) suggested that the emission consists of a fluorescence component (reverse of C-T absorption) and a superimposed polyacene phosphorescence. The current status of the problem, as summarized by McGlynn (20, 20a) is still one of some uncertainty.

The first part of the present investigation consists of a study of the properties of the anthracene-TNB complex in solution. The major part deals with the absorption spectrum of the anthracene-TNB crystal.

---

*Abbreviations used here are as follows:

TNB = 1,3,5-trinitrobenzene; C-T = charge-transfer; D= donor; A = acceptor; T= triplet; S = singlet.

II. THEORY OF THE CHARGE-TRANSFER COMPLEX

Molecular complex formation has long been thought due to the combination of an electron donor (D) with an acceptor (A). Weitz (42,43) and Weiss (40) suggested an ionic structure D^+A^- and predicted that a low ionization potential for the Lewis base D and a high electron affinity for the Lewis acid A would lead to a stable complex. Brackmann (3) came much closer to the present concept by proposing resonance between a "no-bond" and a bonded structure in which the color of the complex (assuming colorless components) is due to the complex as a whole, and not localized to any one component.

The presently accepted ideas on the nature of the donor-acceptor complex were set forth by Mulliken in a series of papers (22-30) beginning in 1950. His original concern was with complexes of the benzene-iodine type (22), but he later (25) generalized his theory to include all charge-transfer complexes of the weak type. The theory was applied specifically to the TNB-polyacene complexes by McGlynn and Boggus (20). The following theoretical treatment applies specifically to the TNB-anthracene system.

The wave function for a molecular compound DA in its ground state can be written

$$\Phi_N = a\,\Psi_0(DA) + b\,\Psi_1(D^+A^-) + c\,\Psi_2(D^-A^+), \qquad (1)$$

where Ψ_0 is the "no-bond" wave function and includes the various classical intermolecular forces such as dipole-dipole and dipole-induced dipole interaction, hydrogen bonding, etc. The dative-bond wave functions Ψ_1 and Ψ_2 correspond to electron transfer from one member to another, resulting in the establishment of a weak

covalent bond involving the odd electron remaining in D and A. In the present treatment, $\underline{a} \gg \underline{b}$, and $\underline{c}$ can be taken as zero. Corresponding to Φ_N, there is also postulated an excited-state wave function given by

$$\Phi_E = a' \psi_1 + b' \psi_0 \tag{2}$$

where $a' \sim a$, $b' \sim b$.

Starting with the ground-state wave function written as

$$\Phi_N = a \psi_1 + b \psi_2 , \tag{3}$$

we define

$$S_{12} = \int \psi_1^* \psi_2 \, d\tau \quad , \quad H_{12} = \int \psi_1^* \mathcal{H} \psi_2 \, d\tau . \tag{4,5}$$

The energy is given by

$$E = \frac{\int \psi^* \mathcal{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} . \tag{6}$$

Substituting with (3) and simplifying, we find

$$E = \frac{a^2 H_{11} + 2ab H_{12} + b^2 H_{22}}{a^2 S_{11} + 2ab S_{12} + b^2 S_{22}} \tag{7}$$

or $$E(a^2 S_{11} + 2ab S_{12} + b^2 S_{22}) = a^2 H_{11} + 2ab H_{12} + b^2 H_{22} . \tag{7a}$$

We wish to find the coefficients which minimize the energy. Taking first the derivative with respect to $\underline{a}$, and setting it equal to zero, we obtain

$$\frac{\partial E}{\partial a}\left(a^2 S_{11} + 2ab S_{12} + b^2 S_{22}\right) + E(2a S_{11} + 2b S_{22}) = 2a H_{12} + 2b H_{22}, \tag{8}$$

and E is a minimum when

$$E(2a S_{11} + 2b S_{12}) = 2a H_{12} + 2b H_{22} . \tag{9}$$

Similarly, minimizing E with respect to $\underline{b}$, we have

$$E(a S_{12} + b S_{22}) = a H_{12} + b H_{22} . \tag{10}$$

Equations (9) and (10) can be rewritten

$$a(H_{11} - S_{11}E) + b(H_{12} - S_{12}E) = 0 \tag{9a}$$

$$a(H_{21} - S_{21}E) + b(H_{22} - S_{22}E) = 0 \tag{10a}$$

which are satisfied when the coefficients a and b are such that

$$\begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E \\ H_{12} - S_{12}E & H_{22} - S_{22}E \end{vmatrix} = 0 \tag{11}$$

In the complex, the hamiltonian operator $\mathcal{H}^0$ for the separated molecules is perturbed by their interaction, giving rise to a new operator

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}' \tag{12}$$

and we seek the corresponding energies, given by

$$\mathcal{H}\Phi_i = E_i\Phi_i . \tag{13}$$

The secular equation (11) now becomes

$$\begin{vmatrix} H_{11}' - (E - E_1^0) & H_{12}' - ES \\ H_{12}' - ES & E_2^0 - E_1 \end{vmatrix} = 0 \tag{14}$$

where E has been replaced by E_1 in the second diagonal element, and H_{22}' has been dropped (it is small compared to $E_1^0 - E_2^0$). The determinant is evaluated by multiplying the second row by $(H_{12}' - ES)/(E_2^0 - E_1)$ and subtracting it from the first:

$$\begin{vmatrix} H_{11}' - \Delta E - \dfrac{(H_{12}' - ES)^2}{E_2^0 - E_1} & 0 \\ H_{12}' - ES & E_2 - E_1 \end{vmatrix} = 0 \tag{15}$$

$$\left(H_{11}' - \Delta E_1 - \frac{(H_{12}' - ES)^2}{E_2^0 - E_1} \right)(E_2^0 - E_1) = 0$$

and since the energies are non-degenerate,

$$\Delta E_1 = H'_{11} - \frac{(H'_{12} - ES)^2}{E_2^\circ - E_1} . \tag{16}$$

Following the usual convention, we replace E_1 by W_o, the energy of the structure DA, and E_2 by W_1, the energy of D^+A^-. The ground- and excited-state energies are W_n and W_e, respectively. The relations between these quantities are shown in the simplified correlation diagram of Fig. 1.

Equation (16) now becomes

$$\Delta E_1 = E - E_{10}^\circ = W_N - W_o^\circ = W_o' - \frac{(H_{01} - W_o S)^2}{W_1 - W_o} . \tag{17}$$

Similarly, for the excited state deriving from eq. (2), we have

$$W_E = W_1 + \frac{(H_{01} - W_1 S)^2}{W_1 - W_o} . \tag{18}$$

The ratio of the coefficients is easily found. From (14),

$$a[H'_{11} - (E - E_1^\circ)] + b[H'_{12} - ES] = 0 \tag{19}$$

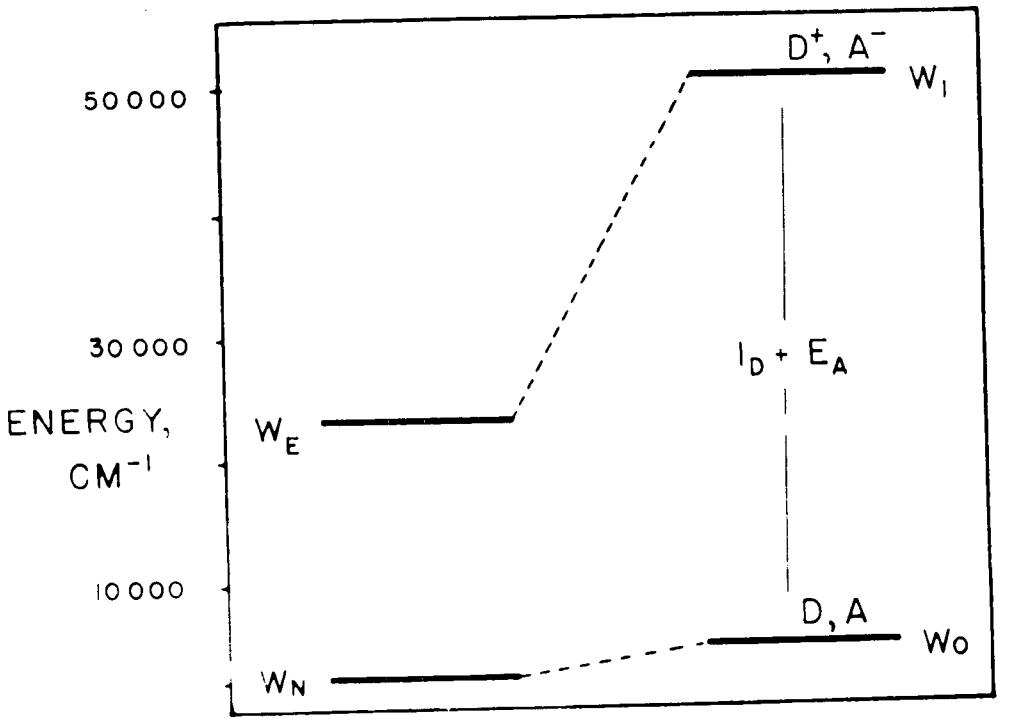
or, again since $E \equiv W_N$ is close to W_o,

$$a(W_1 - W_o) + b(H'_{12} - W_o S) = 0 \tag{20}$$

whence

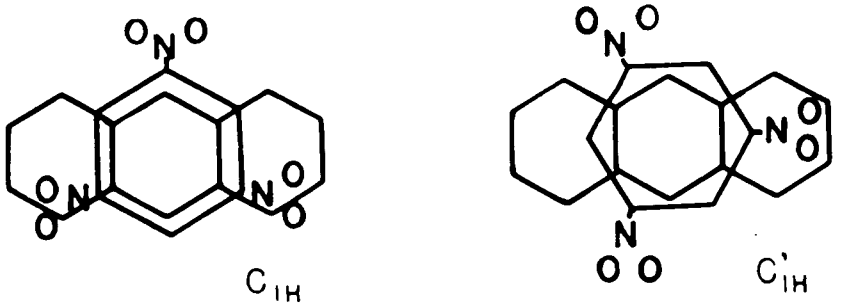
$$a/b = - \frac{H'_{12} - W_o S}{W_1 - W_o} . \tag{21}$$

In the above equations, W_o includes the energies of the separated donor and acceptor molecules as well as all the various attractive and repulsive intermolecular forces. In addition, W_1 also includes an attraction energy of covalent and ionic bonding. The difference between W_1 and W_o is the sum of the donor ionization potential and acceptor electron affinity. The ground-state resonance



CORRELATION DIAGRAM FOR THE ANTHRACENE-TNB COMPLEX

FIG. 1



PROBABLE ORIENTATIONS IN THE COMPLEX

FIG. 2

energy is the difference between W_0 and W_N, and will be large if $(H_{01} - SW_0)^2$ is large and $W_1 - W_0$ is small. In the case of relatively weak complexes of the type under discussion, $W_0 - W_N$ should be 0-10 kcal (20b). It is seen that Φ_N has mostly no-bond character while Φ_ϵ is mostly ionic; the transition connecting the two states thus corresponds to the partial transfer of an electron from the donor (hydrocarbon) to the acceptor (TNB).

If we assume that the resonance energy $(W_E - W_N)$ is the primary stabilizing force in the complex, then H_0 and S must be non-zero, requiring that Φ_0 and Φ_1 be of the same symmetry species (in the point group of the complex). TNB most probably belongs to the point group D_{3h}, and its ground state (considering only the π-electrons) is $....(a_2'')^2(e'')^4(a_2'')^2(e'')^4$, $^1A_1$, while that of the anion TNB^- is probably $...(a_2'')^2(e'')^4(a_2'')^2(e'')^4(e'')^1$, $^2E''$. Using the perimeter method of Mofitt (21), the symmetry species of the ground state of the anthracene cation has been assigned as $^2B_{2g}$ (D_{2h}) (20a). The molecular complex, having only one plane of symmetry, belongs to C_{1h}' or C_{1h} (both usually called C_s; see Fig. 2). Inspection of the appropriate character tables shows that B_{2g} transforms like A'' and $^2E''$ like A'' + A', the latter being the only two representations of C_s. Thus $\Gamma_{\Phi_0}\Gamma_\mu\Gamma_{\Phi_1} = A'A'A' = A'A''A'' = A'$, and the transition is allowed by symmetry.

III. PROPERTIES OF THE ANTHRACENE-TNB COMPLEX IN SOLUTION

Previous studies of molecular complexes have been carried out in solution, and since thermodynamic data so obtained are of importance in understanding charge-transfer bonding, some consideration of the TNB-anthracene complex in solution seems pertinent here. It has been studied by Bier (2a) and Briegleb (5) in carbon tetrachloride and benzene. Their work has been repeated here using these solvents and 1,3-dioxane and ethanol in addition.

The method of Benesi and Hildebrand (2) was used to determine the equilibrium constants. This assumes the relation (for a 1:1 complex)

$$K = \frac{X_C}{(X_D - X_C)(X_A - X_C)} \tag{22}$$

to hold, where X_C is the mole fraction of complex, and X_D and X_A are the initial mole fractions of donor and acceptor, respectively. From the Beer-Lambert law,

$$D = \log (I_o/I) = (C)l\epsilon \tag{23}$$

where D is the optical density, (C) is the concentration of complex, and ϵ the extinction coefficient of the complex at the observed wavelength. This method is generally applicable to a 1:1 complex AB where an absorption band exists which is characteristic of the complex and outside the regions where A and B absorb separately. Substituting concentrations for mole fractions and making $B \gg A$, (22) becomes

$$K = \frac{C}{(B - C)(A)} \tag{24}$$

or

$$C = KAB - KAC \tag{24a}$$

Inserting (23),

$$D/1\epsilon + (D/1\epsilon)KA = KAB \qquad (25)$$

which can be written

$$\frac{1}{A}\,\frac{1}{K\epsilon} + \frac{1}{\epsilon} = \frac{BL}{D}\,. \qquad (25a)$$

If BL/D is now plotted as a function of 1/A, there should result a straight line of slope $1/K\epsilon$ and intercept $1/\epsilon$.

The TNB used was Eastman 639 "white label" and was recrystallized from alcohol and water. Neither a solid melt nor a 0.1M solution in chloroform (1 cm cell) showed any absorption above 4400Å. Because of its higher solubility and lower cost, it was (in most cases) used as "B" in eq. 25a. The reagent grade anthracene was also recrystallized from alcohol. The carbon tetrachloride, benzene, 95% ethanol, and dioxane were all redistilled prior to use. The dioxane was additionally purified by the procedure given in Weissberger.(41). Absorption measurements were made on a Cary model 14 recording spectrophotometer, in 1- or 5-cm cells, with the hydrocarbon component of the complex in the reference beam at the same concentration as in the complex in the sample cell. Runs were made at three or four temperatures, held constant (within 0.5° C. by means of thermostatted cell holders. In most cases five concentrations of TNB were used, as well as a blank containing only hydrocarbon. The scanning was begun at a point well above the tail of the CT absorption, and was continued at 20A/sec through the peak and into the aromatic bands. The absorption readings were made to three significant figures, but only the first two are really dependable. Details of the calculations are presented in tabular form in the appendix, along with the graphicall analysis of a typical run. As well be discussed below, there is some uncertainty in the value of ϵ, and this quantity was taken as constant

for a given complex-solvent combination. The equilibrium constants obtained in this way were used to calculate ΔH values, by means of the familiar relations

$$-\Delta F = RT \ln K \tag{26}$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta F^\circ}{T}\right)\right] = -\frac{\Delta H^\circ}{T^2} \tag{27}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{28}$$

$$\frac{d \ln K_P}{d(1/T)} = -\frac{\Delta H_o}{R} \tag{28a}$$

Before considering the above results, it is perhaps pertinent to note some of the recent discussion (1, 20b) regarding the validity and meaning of data obtained by the Benessi-Hildebrand method. Especially noteworthy is the contribution of Orgel and Mulliken (32) in which they discuss the effects of formation of more than one 1:1 complex with different orientations, and of "contact" CT spectra. They show first that the conventional Benessi-Hildebrand method applied to measurements made at one temperature does not permit one to distinguish between a system in which one well-defined complex exists, and one in which several (differently oriented) complexes are present. The observed properties of complexes are statistical averages over all possible configurations in thermal equilibrium, and especially in relatively loose complexes like these, there is a strong likelyhood that the observed equilibrium constant K' is made up of several terms:

$$K8 = \sum_i K_i$$

One check on this is to plot values of log K' against 1/T. The resulting graph should be a straight line only if one complex is present (or if all the ΔH_i are identical). Another indication of multiple configurational complexes would be temperature dependence of the effective oscillator strength.

The present results do not clearly show such an effect of any magnitude, although the small number of points taken, their scatter due to experimental error, and the relatively narrow temperature range would obscure a small effect. There is some indication (in two independent runs) that the apparent ΔH of anthracene-TNB in carbon tetrachloride is higher at lower temperatures, but further discussion of the matter should await more detailed experimental work.

One of the greatest drawbacks of the B-H method is that values of ϵ so determined for weakly absorbing complexes are subject to considerable uncertainty. In a given system, considerable scatter of results (showing no trends) was noted for observations at different temperatures, and it was decided to take an "average" or "most probable" value of ϵ for a given complex-solvent system. There is really no reason why it should be constant with temperature and certainly not with the solvent, but the present technique does not provide the accuracy required to discuss these effects even qualitatively.

The second point made by Orgel and Mulliken is that intermolecular charge-transfer spectra can occur as the result of specific interactions between donor and acceptor molecules through mere physical proximity, and that such interactions can exist even if the equilibrium constant for complex formation approaches zero.

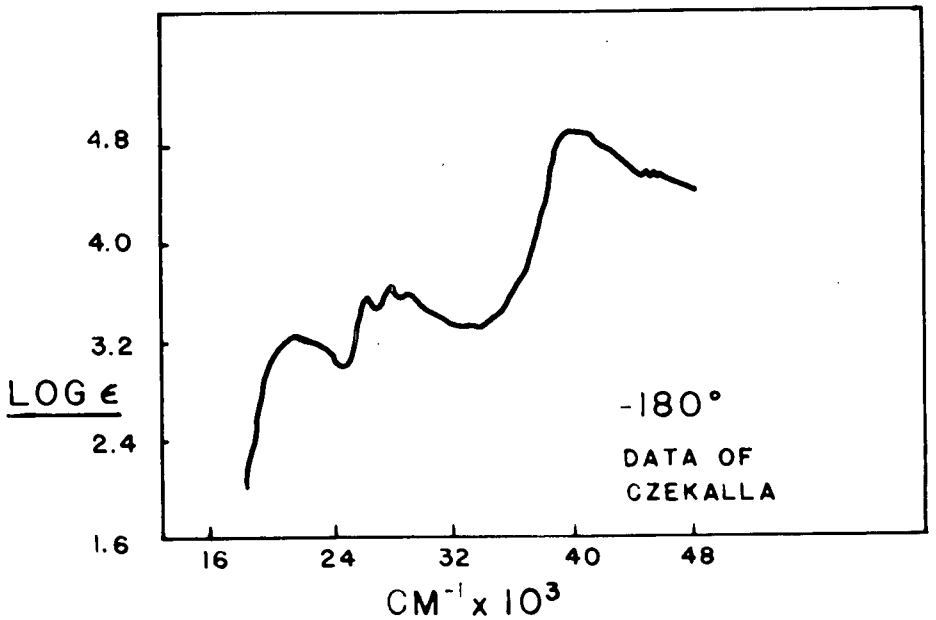


FIG. 3

ABSORPTION OF ANTHRACENE-TNB IN SOLUTION

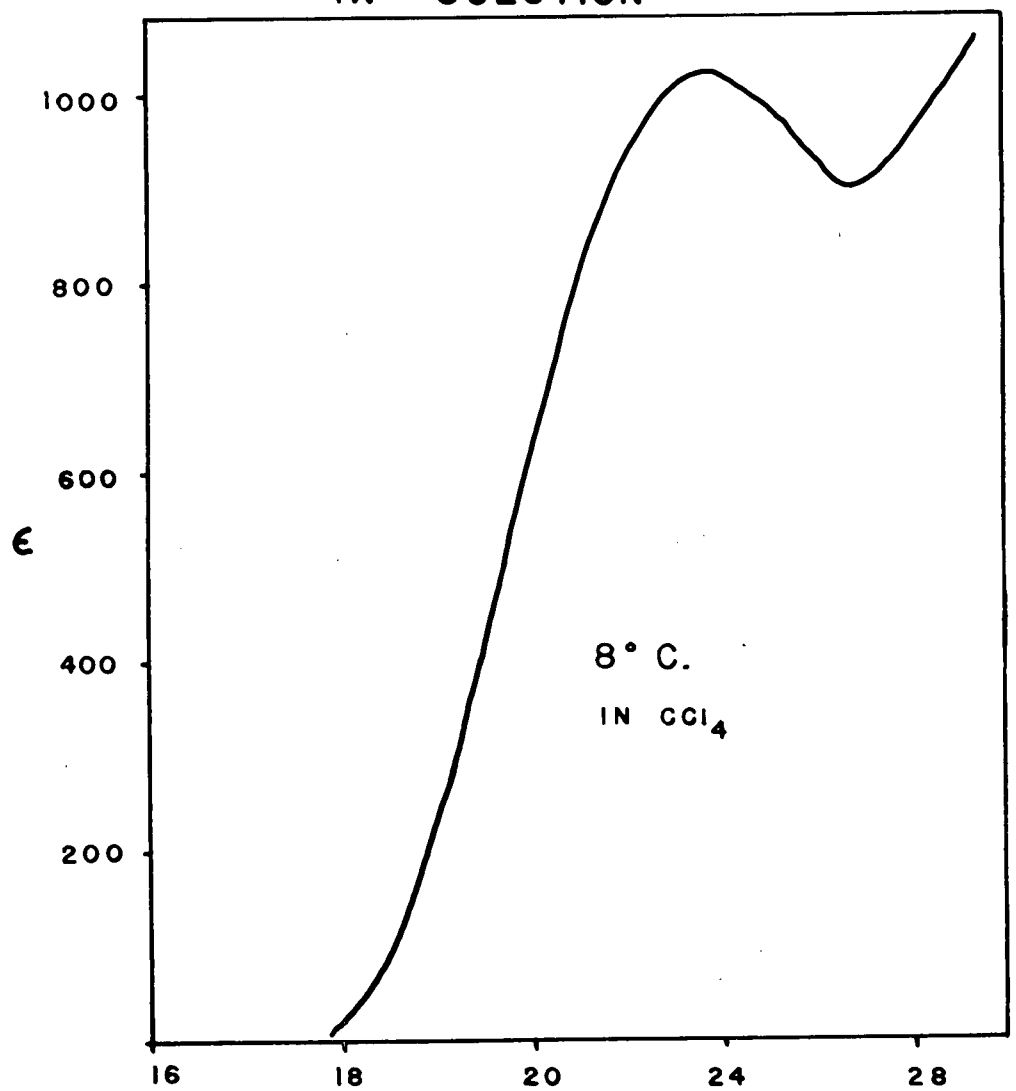
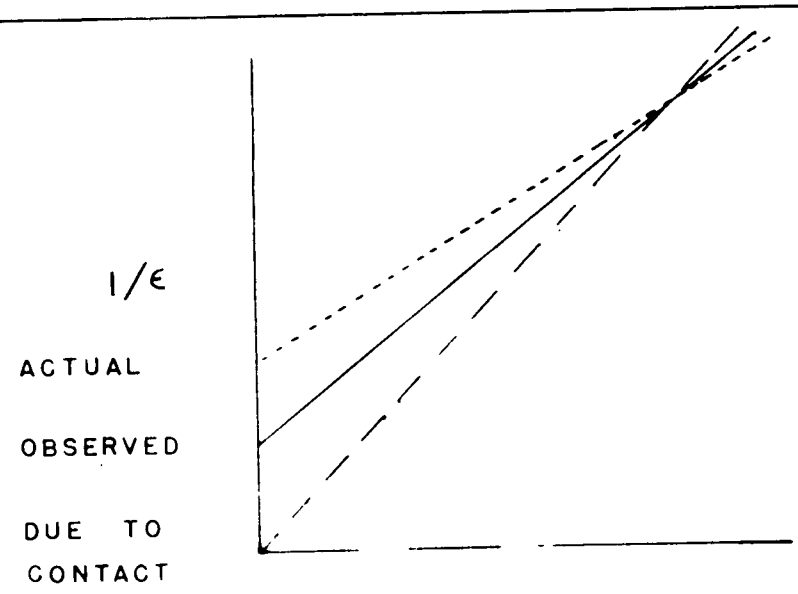
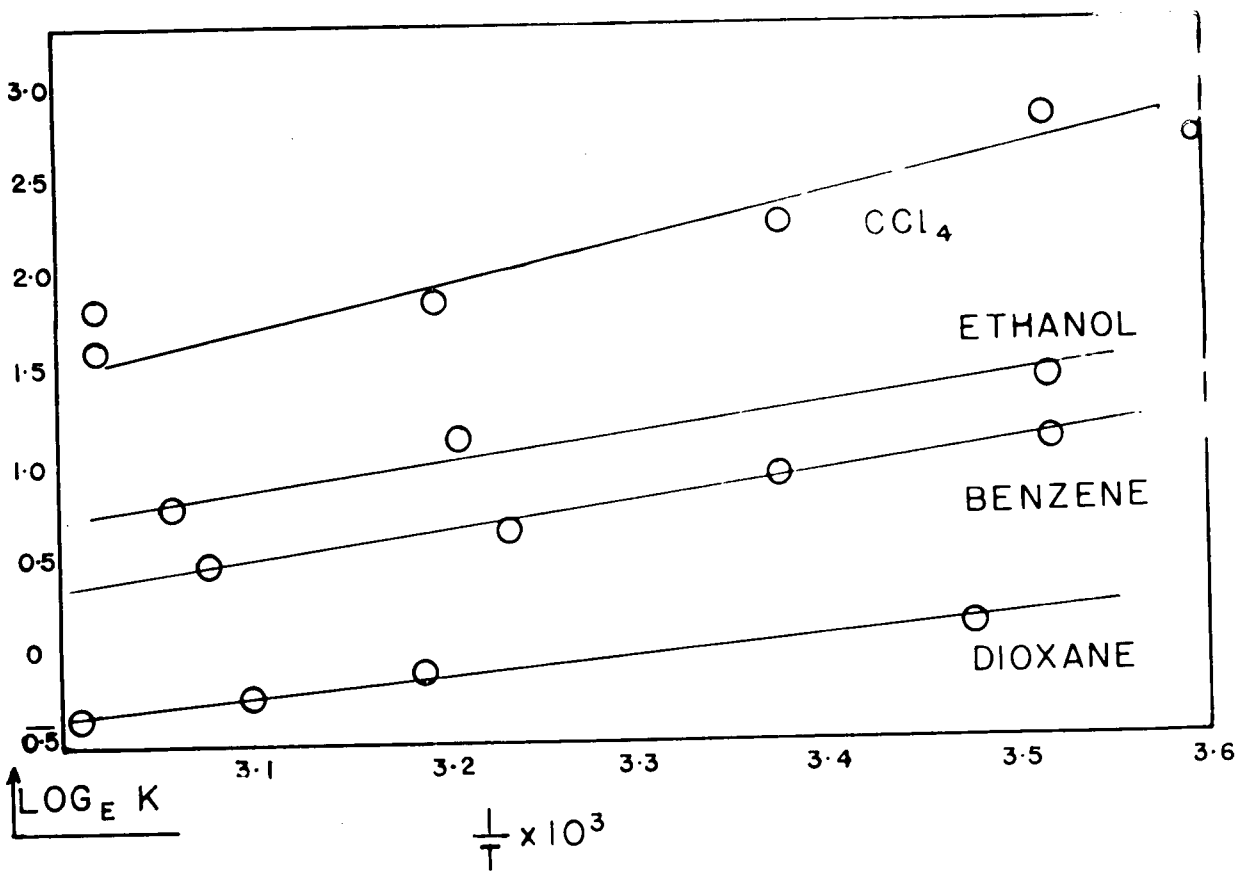


FIG. 4



EFFECT OF CONTACT CHARGE-TRANSFER

FIG. 5



ΔH PLOTS FOR ANTHRACENE - TNB IN VARIOUS SOLVENTS

FIG. 6

Mulliken explains (30) contact charge-transfer spectra on the basis that the acceptor orbital of the anion may exceed the van der Waals size of the neutral acceptor molecule, permitting a donor molecule to interact with it while still outside the van der Waals distance of approach. Orgel and Mulliken discuss the effects of such contact charge-transfer complexing in terms of a simple statistical model. The most significant result is that such behavior would result in a serious overestimation of ϵ ; if the equilibrium constant approaches zero and all absorption is due to contact charge-transfer, the $1/\epsilon$ intercept occurs at zero and the results lose their meaning, as shown in Fig. 5, page 14.

These points are mentioned here to bring out the fact that the interpretation of charge-transfer spectra in solution is even more uncertain than in the case of "conventional" electronic spectra, and it is correspondingly more necessary to be cautious in applying results of such studies to other problems.

A good example of this is the effect of the solvent on the heat of formation, as determined from the equilibrium constant data and the graph of Fig. 6. In carbon tetrachloride, which should presumably show the least interaction with the complex, it is 4.4 kcal. In the other three solvents the value is between 2-3 kcal, and since it is known that TNB forms complexes with benzene (16,17), ethanol (20a), (and no doubt with dioxane), it is obvious that we are not looking at anything as simple as the 1:1 TNB-anthracene complex alone. The same effect was noted in a similar series of experiments with the benzpyrene complex, in which the heat of formation was found to be 6.2 kcal in carbon tetrachloride and 3.3 kcal in benzene. Other

authors have noted similar effects, and Kosower (19) finds a correlation between the heat of formation of the charge-transfer complex and the "Y-value" of the solvent.

IV. THE POLARIZED CRYSTAL SPECTRUM OF TNB-ANTHRACENE

The study of crystal spectra affords one the opportunity of examining molecules which are held in fixed positions, and in favorable cases where the crystal structure is known, the use of polarized light often permits one to find the direction of the transition moment, and to make important decisions regarding the assignment of symmetry species to the electronic states involved. However, the very forces which hold the molecules in position give rise themselves to effects which radically change the appearance of the spectra from the vapor or liquid states. Besides a considerable shift (to the red) and change in intensity, other effects arise, such as mixing of nearby strong and weak transitions, and splitting of a fairly intense transition into two components, differing in intensity and polarization (Davydov splitting).

To understand these phenomena it is necessary to consider the entire crystal as a molecule, and to replace "molecular states" by "crystal states", where the symmetry properties of the unit cell assume primary importance. This view was first applied to ionic crystals by Frenkel (14,15) with much success, and was later applied to molecular crystals by Davydov (12,13; see Craig, 8).

The simplest view of a crystal which Davydov proposes is the "oriented gas model" in which there is no interaction between the molecules. More practical for all but the weakest transitions is the "weak coupling" model in which a small interaction occurs, which however is not strong enough to perturb the electronic structure of the individual molecules. Thus the crystal ground state can be

written as a product of the individual molecular wave functions

$$\Phi_o = \varphi_1 \varphi_2 \varphi_3 \cdots \varphi_N \tag{29}$$

while in the excited state, any <u>one</u> of the molecules can be excited:

$$\begin{aligned} \phi_1 &= \varphi_1^* \varphi_2 \varphi_3 \cdots \varphi_N \\ \phi_2 &= \varphi_1 \varphi_2^* \varphi_3 \cdots \varphi_N \\ \phi_3 &= \varphi_1 \varphi_2 \varphi_3^* \cdots \varphi_N \end{aligned} \tag{30}$$

Interaction of these results in crystal states (unit cell wave functions) composed of linear combinations of the Φ_i :

$$\begin{aligned} \Phi_\alpha &= \tfrac{1}{\sqrt{N}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 \cdots) \\ \Phi_\beta &= \tfrac{1}{\sqrt{N}} (\phi_1 + \phi_2 - \phi_3 - \phi_4 \cdots) \\ \Phi_\gamma &= \tfrac{1}{\sqrt{N}} (\phi_1 - \phi_2 - \phi_3 + \phi_4 \cdots) \\ \Phi_\delta &= \tfrac{1}{\sqrt{N}} (\phi_1 - \phi_2 - \phi_3 - \phi_4 \cdots) \end{aligned} \tag{31}$$

in which the combinations of molecular wave functions must transform like representations of the unit cell symmetry group if the transition is allowed.

Davydov considers the electrostatic interaction energy between two molecules (a) and (b) which arises from the coulombic interaction between the electrons (e) and the nuclei (n), and which can be roughly expressed as

$$V_{1,2} = n_1 e_2 - n_2 e_1 + e_1 e_1 + n_1 n_2 \tag{32}$$

Further elaboration of the theory (8) results in the summation of these terms over all atoms in the molecule, the derivation of a crystal wave function, and finally in an expression for the shift in peak position from the gas to crystal state, and the splitting

between oppositely polarized components of corresponding peaks, which can be written

$$\Delta E^{\alpha,\beta,\gamma} = (\text{constant}) + \sum_p I_{jp} + \sum_q I_{jq} + \sum_r I_{jr} \qquad (33)$$

where the I_{jk} are interaction integrals between the jth and kth molecules, p runs over all molecules translationally equivalent to j, and the q, r, etc. run over all molecules related to j by the other symmetry operations of the unit cell group. The summed interaction integrals are taken in linear combinations corresponding to those of eq. 31 which are allowed.

The integrals I_{jk} are given by (34)

$$I_{jk} = -\frac{e^2}{r^3_{jk}} |M|^2 \; 2\cos\theta_{j1}\cos\theta_{j2} - \cos\theta_{j2}\cos\theta_{k2} - \cos\theta_{j3}\cos\theta_{k3}$$

in which M is the molecular transition moment (in $\mathring{A}^2$) and r_{jk} is the distance between their centers. The angles θ_{k1}, θ_{k2}, θ_{k3}, etc., are angles made by the transition moment with an orthogonal set of axes erected at its center, with θ_{jk} referring to an axis along the line connecting the centers of the two transition moments.

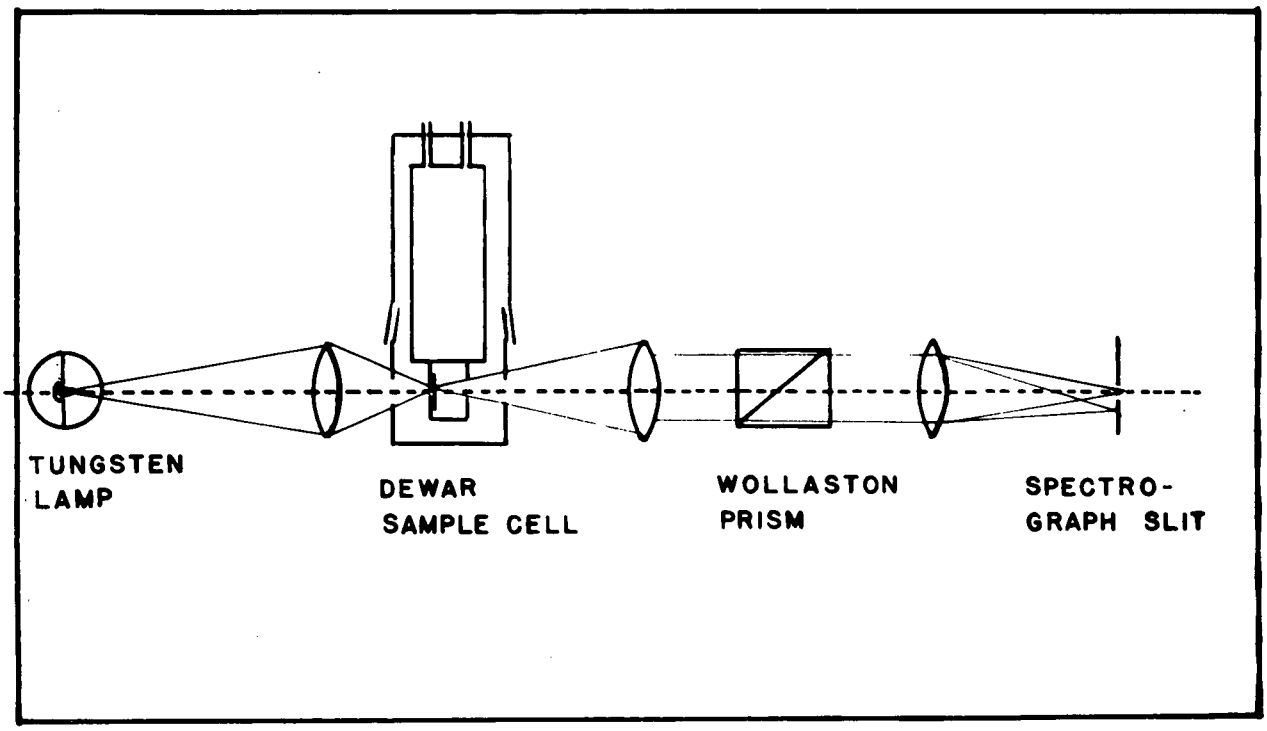
Experimental.

Both the anthracene and TNB were Eastman reagent grade. The former was recrystallized twice from alcohol, and the latter from water. The complex was prepared by combining a hot alcoholic solution of anthracene with a hot concentrated solution of TNB, and allowing the mixture to crystallize in the dark. The orange crystals were removed by filtration and recrystallized from concentrated alcoholic TNB.

The samples were prepared by melting a small quantity of the solid complex between two silica discs (or a silica disc and a microscope cover glass) and allowing the melt to cool under pressure. In order to obtain large uniform areas, the sample was usually partially remelted and cooled several times, the unmelted areas being used to seed the remelted ones. Examination through the polarizing microscope located an area of sufficient size which showed uniformity and complete extinction. The sample disc was then oriented on a brass disc so that the pinhole (# 60 drill) in the latter corresponded with the area to be examined. The brass disc and sample were then placed in a Dewar cell in such a manner that the direction of extinction corresponded to either the horizontal or vertical axis of the optical system.

The spectrograph was a Hilger medium quartz prism instrument, equipped with a Hilger motor-driven scanning attachment containing a 1P28 photomultiplier which was operated at 800 volts from a Cintel stabilized supply. The detector was a Keithly Model 200 B electrometer equipped with a decade shunt. The output of the meter was connected to a standard Leeds & Northrup chart recorder. The phototube currents varied from full-scale meter readings of 2×10^{-8} to 2×10^{-5} amperes. Ranges were changed by altering the shunt resistance.

The optical system is shown diagramatically in Fig. 7. The light source was a six-volt, 18 ampere air-cooled projection lamp, operated from a stabilized ac supply. A converging lens focussed a spot of light onto the pinhole covering the sample. The emerging light was collected and made parallel by a second lens, then passed through a Wollaston prism. The resulting two beams were then



OPTICAL SYSTEM FOR
POLARIZED CRYSTAL SPECTRA

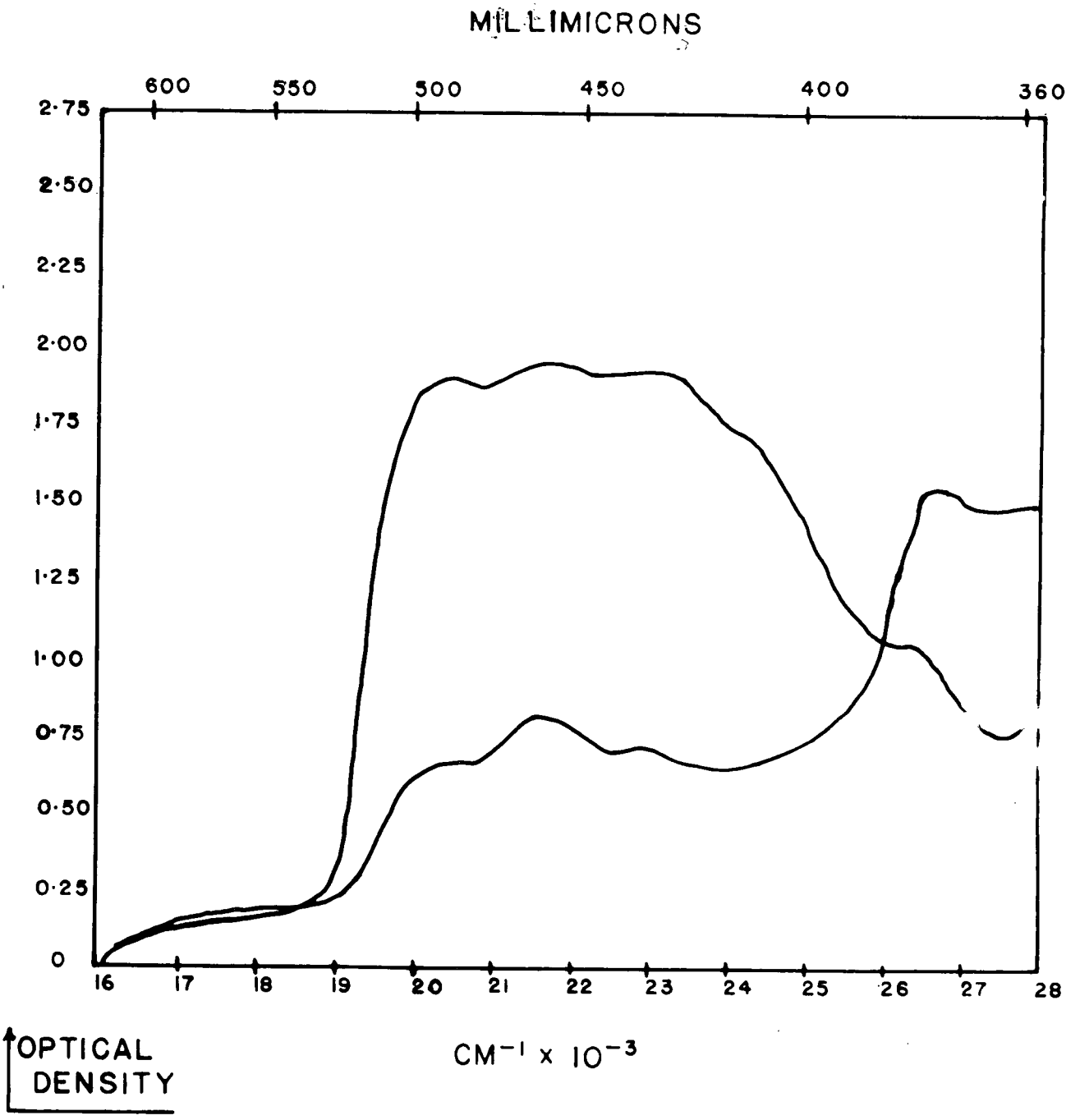
FIG. 7

focussed on the entrance slit of the spectrograph. The polarization to be used was selected by rotating the Wollaston prism so that only the desired beam fell on the slit. Before running a spectrum, the optical system was adjusted so as to give equal intensities in each polarization at a wavelength well separated from the C-T absorption. This adjustment was found to be very critical, and after making it care was taken to avoid disturbing any part of the optical system except the Wollaston prism. After recording the two spectra, the sample was replaced by a simple aperture and the spectrum of the light source and photomultiplier response were determined. Throughout the process, care was taken to avoid diffraction patterns and spurious effects due to chromatic aberrations of the simple lenses used.

In interpreting the results, it was assumed that the transmitted light at a wavelength outside the region of absorption was the same for both sample and reference beams. The readings of sample beam intensity were then corrected to zero optical density at this wavelength, and log I_o/I calculated.

Results.

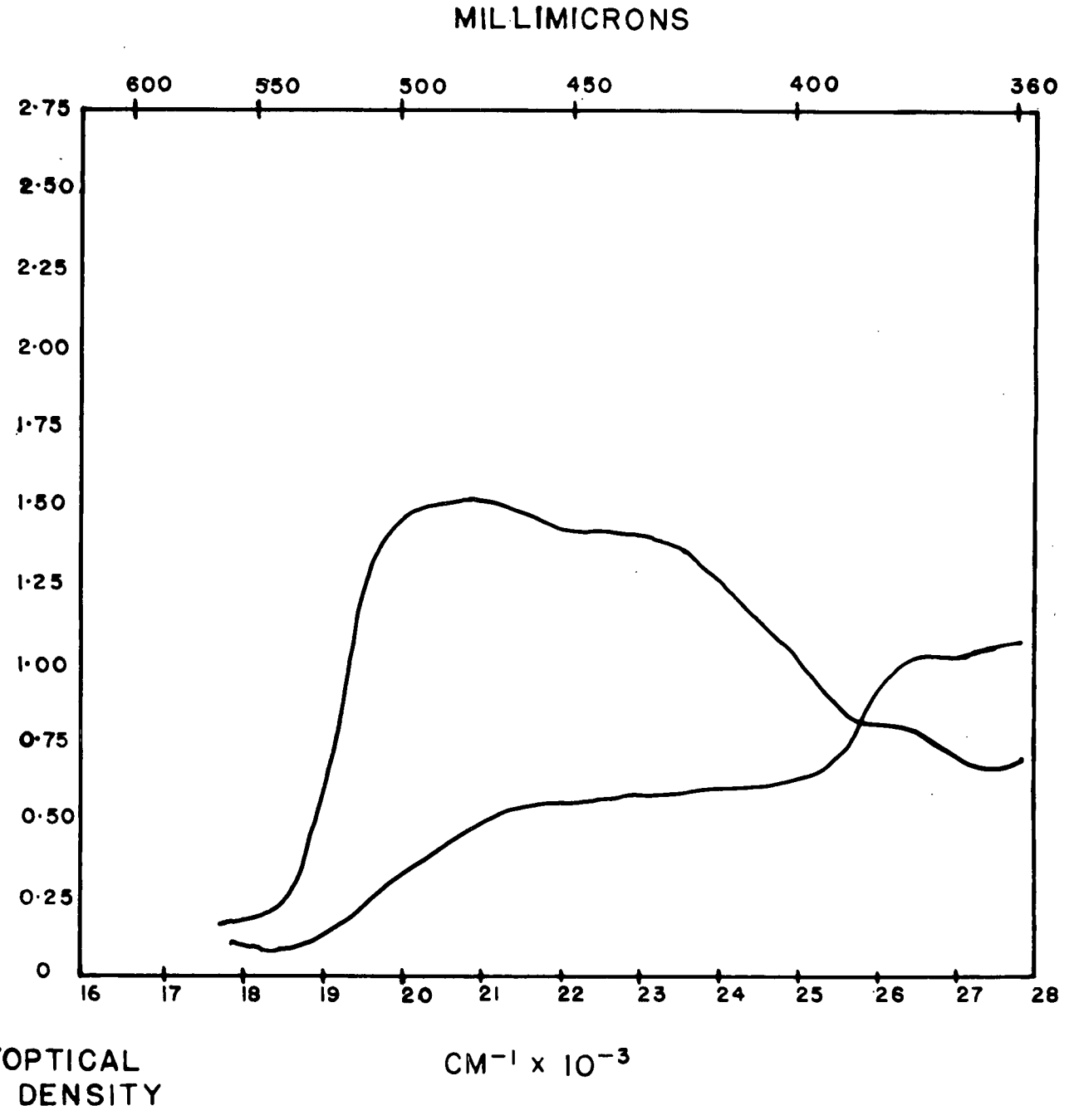
Several spectra were run, and the results are in substantial agreement. As expected (see following section on crystal structure), the absorption is more intense along the long axis. The absorption commences near 19000/cm and rises sharply to form a broad band, the most interesting feature of which is the presence of a 1400/cm vibrational interval, probably corresponding to an anthracene ring breathing vibration. This is the first reported observation of vibrational structure in a charge-transfer band. A second point of



ANTHRACENE- T.N.B.

-180°

FIG. 8



ANTHRACENE - T.N.B.

23° C.

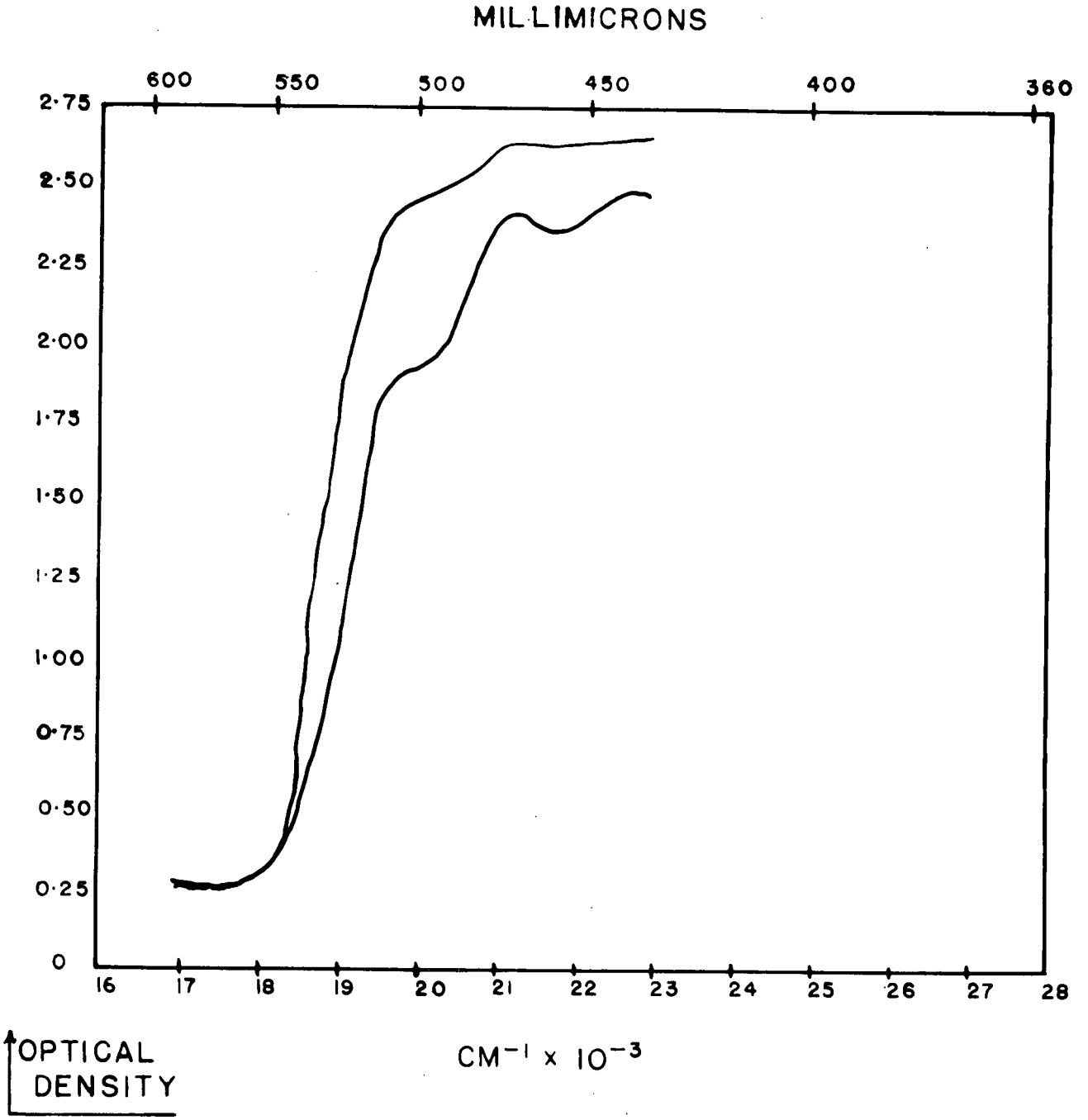
FIG. 9

interest is that the peaks in the short-axis polarized absorption are located 100-200 /cm to the red of the corresponding peaks of the other component. These shifts, though not much greater than the accuracy and reproducibility of the method (100/cm), are always seen. They appear to be quite sensitive to the nature of the crystal; preliminary experiments with a crystal of anthracene containing a small amount of complex show a reversal of the shift.

The spectrum shown in Fig. 8 is most representative. The apparent absorption to the red of 16000/cm is attributed to reflection losses, which are expected to change with wavelength. Thus the apparent optical density should be corrected by extrapolation of the reflection loss. Making such a rough extrapolation out to the center band (21700/cm) and subtracting the reflection from the optical densities of the two peaks at this wavelength, we arrive at a very approximate optical density ratio (not polarization ratio) of 3:1.

Fig. 9 shows the spectrum of the same sample at room temperature. The expected broadening obliterates the detail of the peaks, although some structure remains in the strongly-absorbed polarization. The optical density ratio is approximately the same.

Preliminary studies have been made on the 9,10-dimethylanthracene-TNB complex, and of anthracene-TNT (2,4,6-trinitrotoluene), and their spectra are shown in Figs. 10-11. The apparently small optical density ratio is probably a consequence of the rather thick crystals used, and further work on these complexes is necessary. It is very difficult to obtain good single crystals of either of them.



ANTHRACENE - T.N.T.

-180°

FIG. 10

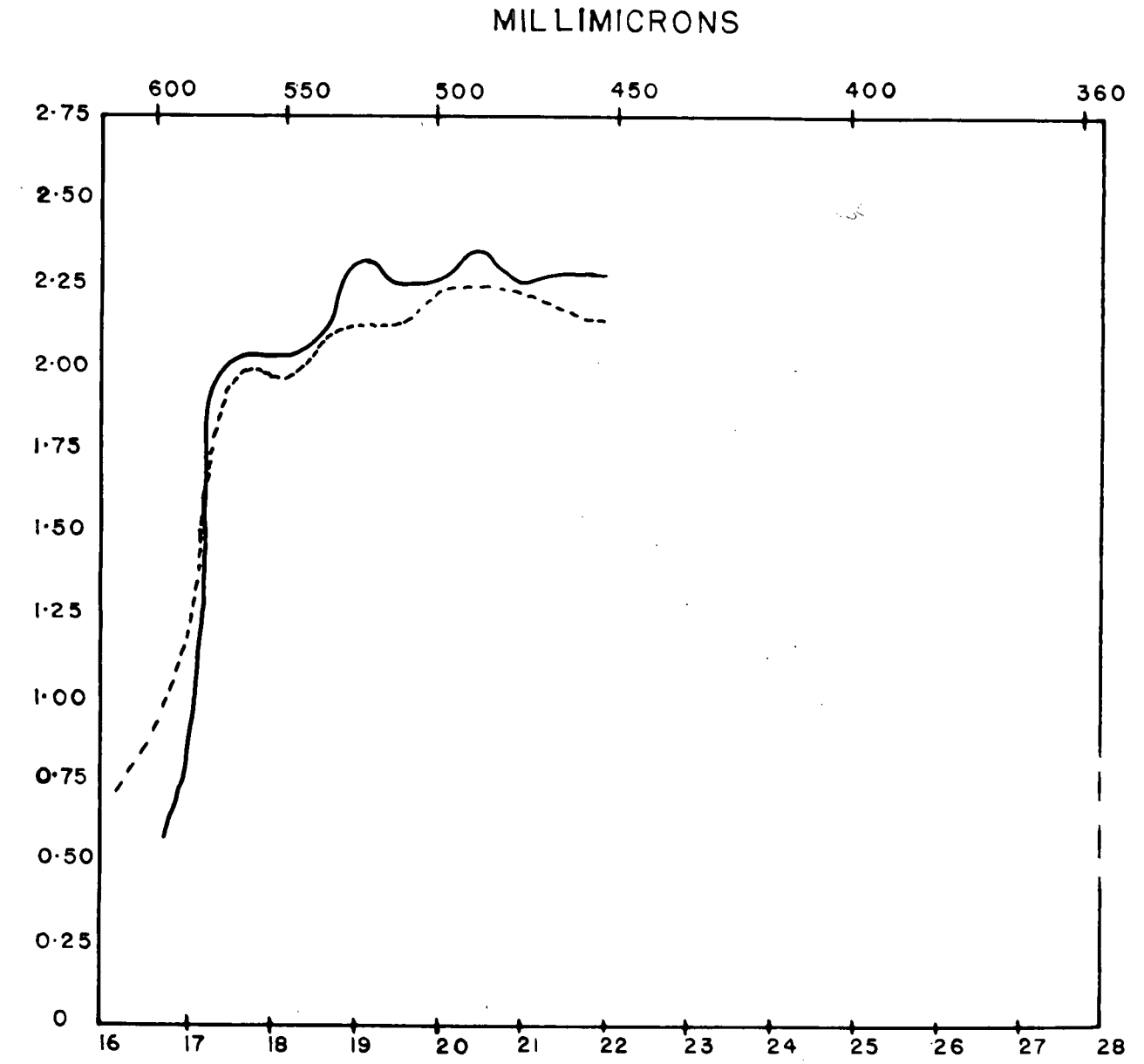


FIG. 11

9, 10-DIMETHYLANTHRACENE - T.N.B.

-180°

FIG. 11

Discussion.

The orange acicular prisms of anthracene-TNB complex (as obtained by crystallization from solvents) show a strong dichroism when examined in polarized light, the orange color being most intense when the light is polarized along the long axis of the crystal. Similar examination of a thin section of the needle (looking down the long axis) fails to reveal any dichroism. Since the C-T transition presumably occurs with a moment perpendicular to the planes of the anthracene and TNB molecules, these results suggest that the crystal is made up of such units stacked up along the long (c) axis. The relative intensities of absorption in the two polarizations also indicate such a structure.

Detailed interpretation of the energy splittings cannot yet be given, as the crystal structure of the complex is not completely known, and certain questions regarding Davydov splitting calculations and the effect of permanent dipoles (as in TNB) on the splittings are currently being studied and discussed. The calculations summarized below are to be regarded purely as preliminary steps toward the explanation of the observed effects.

The crystal structure of the complex has been partially determined by Wallwork (39), who states that the crystals are monoclinic, $= 133\frac{1}{2}^{\circ}$, and belong to the space group C2/c (C_{2h}^{6}), with eight molecules (i.e., four complexes) per unit cell. The molecules are stacked alternately in a staggared manner in columns parallel to the c-axis, but tilted by about 6° from the position in which they would be perpendicular to that axis. The unit cell dimensions are a_o = 11.69 A, b_o = 16.36 A, and c_o = 13.23 A. The special positions are assigned as follows:

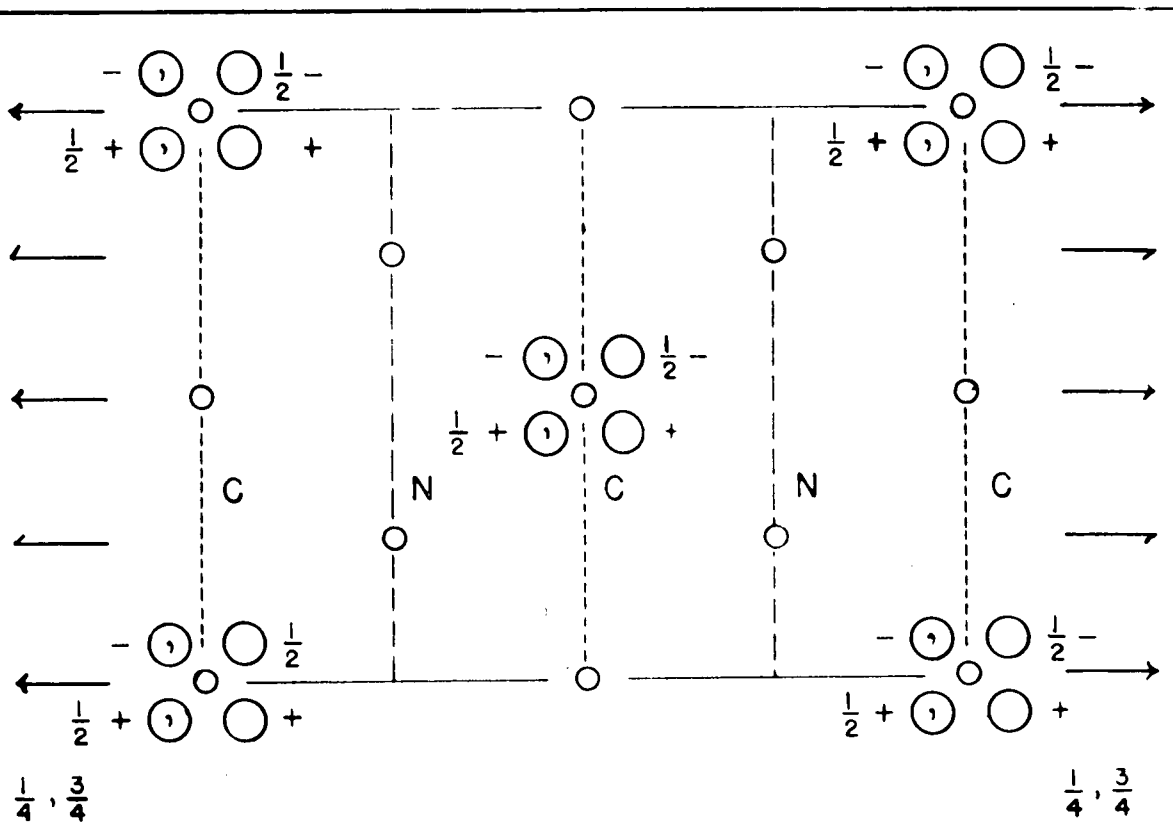
Anthracene: 0,0,0; 0,0,½; ½,½,0; ½,½,½.

TNB: 0,y,¼; 0,y,¾; ½, ½+y,¼; ½,½+y,¾.

Fig. 12 shows the general point positions and symmetry operations of the space group c2/c, and Figs. 13 and 15 show projections of the unit cells (as deduced from Wallwork's data) in the ab and bc planes, respectively.

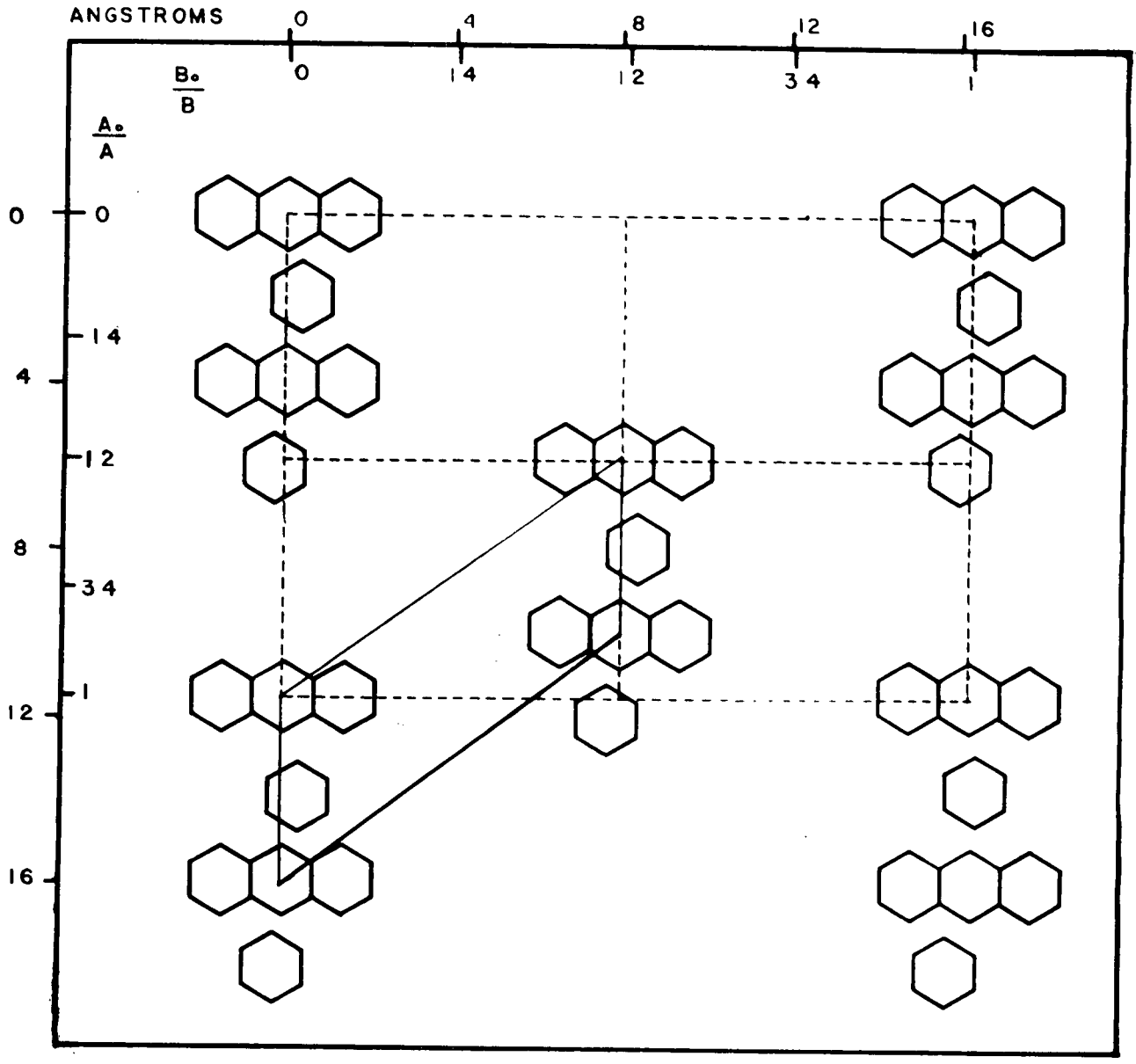
Without knowing the value of "y", the exact locations of the TNB molecules cannot be known; in the present calculations it has been assumed to be 0.17 A, which would be the distance required to tilt the line connecting the centers of the anthracene and TNB molecules by 6°. It is further assumed that the molecules are inclined along the b axis, and that the transition moments are perpendicular to the planes of the aromatic rings.

There is some question as to just what constitutes a complex "molecule" in this crystal, and it is defined for the purposes of the present discussion as the pair of centers between which the charge-transfer process is taking place. If we assume that this process will occur between parallel molecules in preference to those inclined 12° with respect to each other, then a knowledge of the relative directions of inclination of the TNB and anthracene would fix the location of the complex "molecules" in the crystal. Thus in Fig. 16 (pg 33), the transition moments are drawn in two different ways, using the same locations of the individual molecules. The calculations summarized in Appendix II. are based on the relationships of Figs. 16a, 14 and 15, and on a transition moment length of 0.88A as estimated from the absorption spectrum of Fig. 4 and the



THE SPACE GROUP $C2c - C_{2H}^{6}$

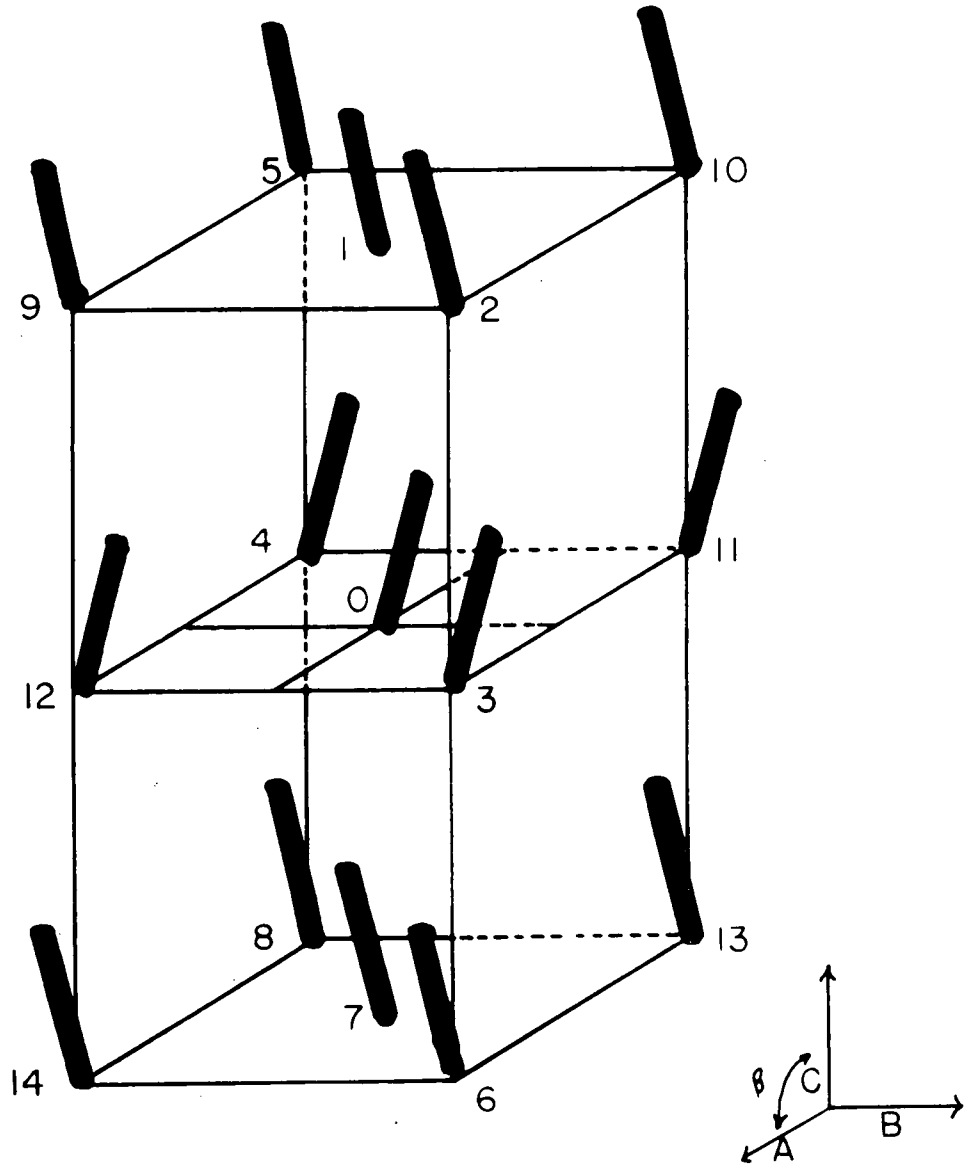
FIG. 12



PROJECTION IN (001)

(UNIT CELL SHADED)

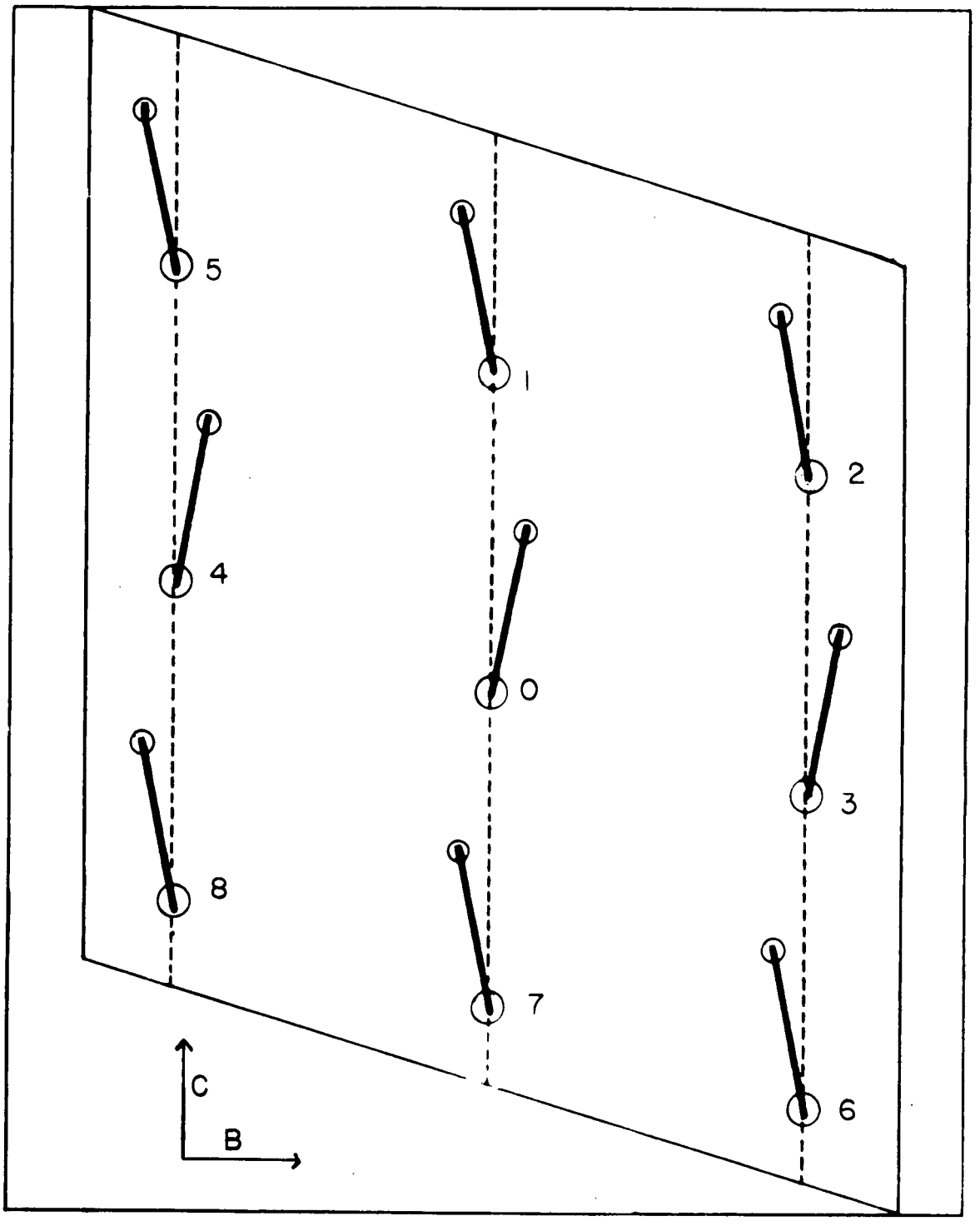
FIG. 13



ORIENTATION OF TRANSITION DIPOLE MOMENTS

(NOT TO EXACT SCALE; INCLINATION OF MOMENTS EXAGGERATED)

FIG. 14



TRANSITION MOMENTS ALONG (110);

PROJECTION ON (100)

LARGE CIRCLES REPRESENT ANTHRACENE LOCATIONS

UNIT CELL SCALE

FIG. 15

equilibrium constant data. The values of the interaction integrals between molecule "0" (Fig. 14) and the other fourteen adjacent molecules are calculated and given in Appendix II. The integrals between molecules related to each other by the same space group operations are summed in the table below:

molecule "0" transformed into no.:	operation	$\sum I_{jk}$, cm^{-1}
3,4; 11,12.	translation	+ 760
1,7.	c screw axis	- 2440
2,6,8,5; 10, 13, 14, 9.	a+c /2 glide	+ 1230

Further interpretation of the splitting awaits the completion of work now in progress. It should be mentioned that there is reason to feel that the relations shown in Fig. 16b may be more likely, and it is hoped to confirm this shortly.

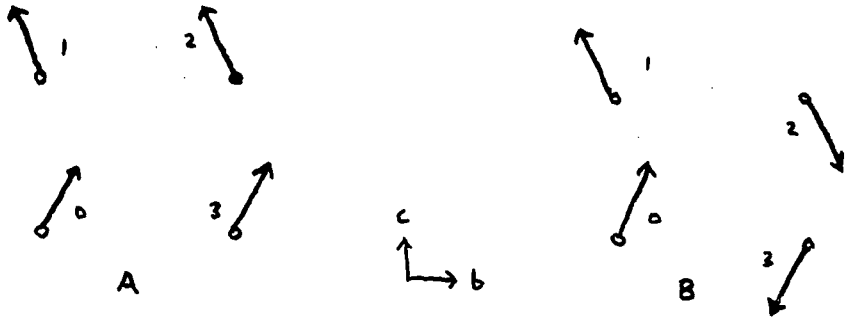


Fig. 16. PROJECTION OF TRANSITION MOMENTS IN A UNIT CELL ON (100). Two possibilities are shown; part A is identical with Fig. 15. TNB molecules are at heads of arrows.

BIBLIOGRAPHY

1. ANDREWS, L.J.: Chem. Revs. 54. 713 (1954).

2. BENESI, H.A., and J.H. HILDEBRAND: J. Am. Chem. Soc. 71, 2703 (1949).

3. BRACKMAN, W.: Rec. trav. chim. 68, 147 (1949).

4. BRIEGLEB, G.: Zwischenmolekulare Krafte: G. Braun, Karlesruhe, 1949.

5. BRIEGLEB, G., and T. SCHACHOWSKOY: Z. Physik. Ch. B19, 255 (1949).

6. CHANCE, B.: Mechanism of Enzyme Action: Johns Hopkins Press, Baltimore, Md., 1954. Ppg 433-452.

7. COULSON, C.A.: Valence: Oxford, 1952. Ppg 58-67.

8. CRAIG, D:P.: J. Chem. Soc. 1955, 539.

9. CZEKALLA, J.: Die Naturwissenschaften 20, 467 (1956).

10. CZEKALLA, J.: Z. Elektrochemie 61, 537 (1957).

11. CZEKALLA, J.: Z. Elektrochemie 63, 1157 (1959).

12. DAVYDOV, A.S.: Zhurn. Eksp. Teor. Fyz. 18, 210 (1948).

13. DAVYDOV, A.S.: Theory of Molecular Excitons, trans. M. Kasha: McGraw-Hill, N.Y. (in press).

14. FRENKEL, J.: Phys. Rev. 37, 17 (1931).

15. FRENKEL, J.: Fyz. Zhurnal Sovjet. 9, 958 (1936).

16. HAMMICK, D., G. HILLS and J. HOWARD: J. Chem. Soc. 1932, 1530.

17. HEPP, P. Annalen 215, 344 (1882).

18. KETELAAR, J.A.A., et al.: Rec. trav. chim. 71, 1104 (1952).

19. KOSOWER, E.M.: J. Am. Chem. Soc. 80, 3467 (1958).

20. McGLYNN, S.P., and J.D. BOGGUS: J. Am. Chem. Soc. 80, 5096 (1958).

20a. McGLYNN, S.P.: Chem. Revs. 58, 1113 (1958).

20b. McGLYNN, S.P., J.D. BOGGUS, and E. ELDER: J. Chem. Phys. 32, 357 (1960).

21. MOFITT, W. J. Chem. Phys. 22, 320 (1954).

22. MULLIKEN, R.S.: J. Am. Chem. Soc. 72, 600 (1950).

23. MULLIKEN, R.S.: J. Am. Chem. Soc. 72, 4493 (1950).

24. MULLIKEN, R.S.: J. Chem. Phys. 19, 514 (1951).

25. MULLIKEN, R.S.: J. Am. Chem. Soc. 74, 811 (1952).

26. MULLIKEN, R.S.: J. Phys. Chem. 56, 801 (1952).

27. MULLIKEN, R.S. Symposium on Molecular Physics. Nikko, Japan, 1953.

28. MULLIKEN, R.S.: J. chim. phys. 51, 341 (1954).

29. MULLIKEN, R.S.: J. Chem. Phys. 23, 397 (1955).

30. MULLIKEN, R.S.: Rec. trav. chim. 75, 845 (1956).

31. NAKAMOTO, K.: J. Am. Chem. Soc. 74, 390 (1952).

32. ORGEL, L.E., and R.S. MULLIKEN: J. Am. Chem. Soc. 79, 4839 (1957).

34. PFEIFFER, P.: Organische Molekulverbindungen, 2nd. ed. F. Enke, Stuttgart, 1927.

35. PLATT, J.R.: Science 129, 372 (1959).

36. PULLMAN, M., A. SAN PIETRO, and S.P. COLOWICK: J. Biol. Chem. 206, 129 (1954).

37. REID, C.: Excited States in Chemistry and Biology: Butterworth's, London, 1957. Ppg 113-118.

38. REID, C.: J. Chem. Phys. 20, 1212 (1952).

39. WALLWORK, F.: Acta Cryst. 7, 648 (1954).

40. WEISS, J.: J. Chem. Soc. 1942, 245.

41. WEISSBERGER, ed.: Technique of Organic Chemistry, Vol. IV: Organic Solvents: Interscience, New York, 1955. Pg. 371.

42. WEITZ-HALLE, E.: Z. Elektrochem. 34, 538 (1928).

43. WEITZ-HALLE, E.: Angew. Chem. 66, 658 (1954).

44. WOODWARD, R.B.: J. Am. Chem. Soc. 64, 3058 (1942).

APPENDIX I.

DETERMINATION OF THE EQUILIBRIUM CONSTANT OF THE TNB-ANTHRACENE COMPLEX BY THE METHOD OF BENESI AND HILDEBRAND.

Solvent: carbon tetrachloride, Cells, 1 cm.

Stock solutions: Anthracene ("B"), 0.0337 M; TNB ("A"), 0.0119 M; concentration of TNB in each sample was 0.953 mM.

			296°K		278°K		331°K	
ml "A"	A	1/A	D	B/D	D	B/D	D	B/D
10	.0135	74.0	.168	5.67	.266	3.58	.---	[illegible]
12	.0162	62.7	.193	4.94	.309	3.08	.460	10.35
14	.0189	52.9	.211	4.51	.348	2.74	.533	8.94
16	.0216	46.3	.241	3.96	.392	2.43	.599	7.95
18	.0243	41.1	.270	3.53	.420	2.27	.664	.7.18
20	.0270	37.0	.294	3.24	.453	2.10	.733	6.50
22	.0297	33.7	.320	2.98	.484	1.97	.800	5.95

These results are plotted in Fig. 15 on the following page. The average intercept is taken as $1/\ = (0.70 \pm .05) \times 10^{-3}$, or $= 1430 \pm 100$. The equilibrium constants are calculated below.

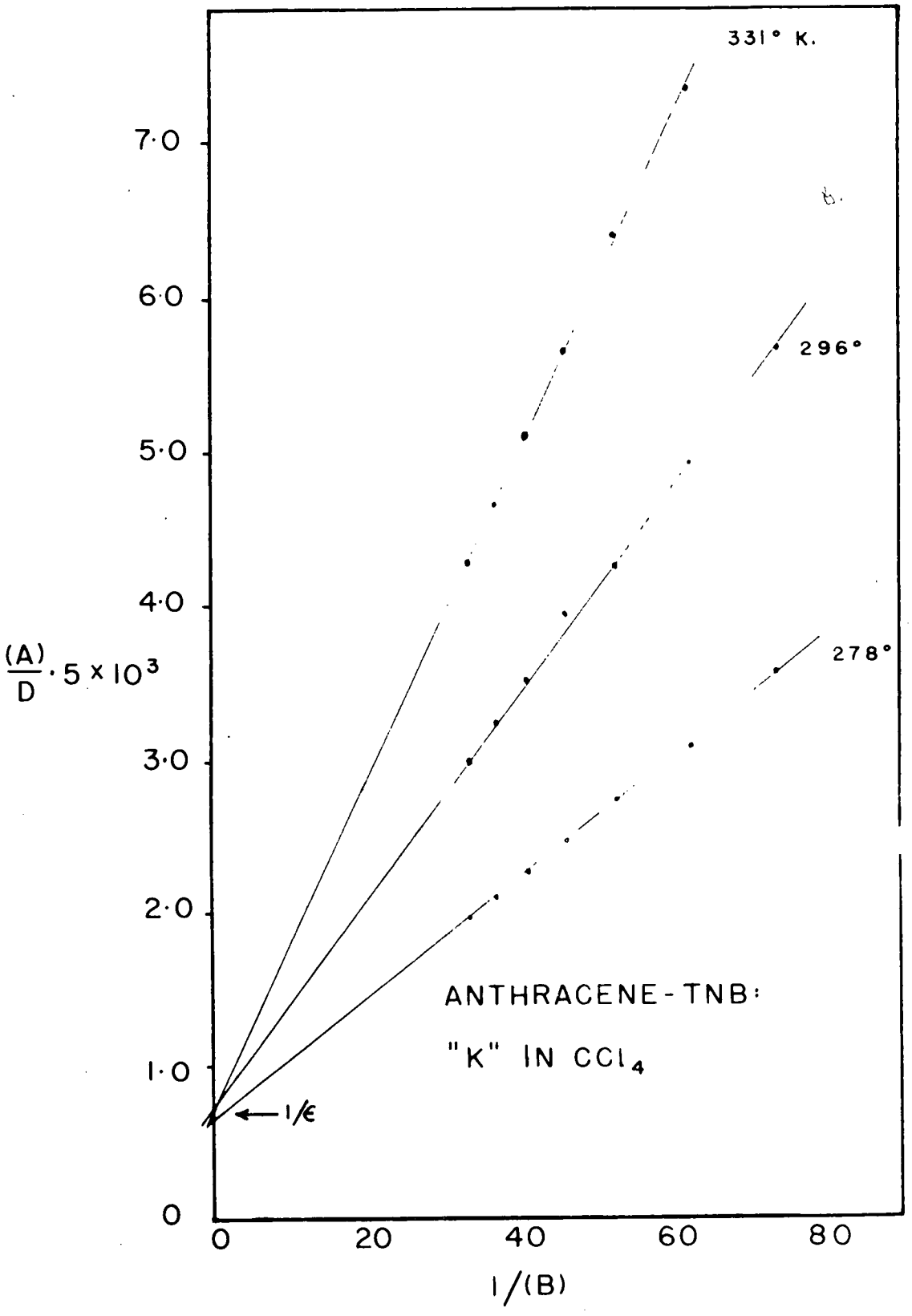
278°K: slope = $1/K = .0485 \times 10^{-3}$; $K = .70/.0485 = \underline{14.5}$.

296°K: $K = .70/.0775 = \underline{9.0}$.

331°K: $K = .70/.119 = \underline{5.9}$.

The values for H of TNB-anthracene in various solvents are calculated to be the following (see Fig. 6):

Benzene	2.7	kcal
Ethanol	2.5	
Carbon Tetrachloride	4.4	
Dioxane	2.3	


331° K.
296°
278°
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
(A)/D · 5 x 10³
0
20
40
60
80
1/(B)
1/ε
ANTHRACENE-TNB:
"K" IN CCl4

APPENDIX II.

NOTES ON THE CALCULATION OF THE ENERGY SPLITTING

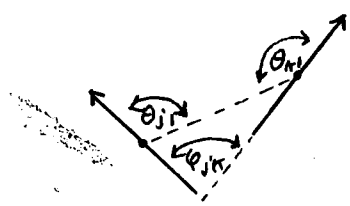
The direction cosine between two lines j and k in terms of the orthogonal coordinates (1,2,3) is given by

$$\cos \varphi_{jk} = \cos \theta_{j1}\cos\theta_{k1} + \cos \theta_{j2}\cos \theta_{k2} + \cos \theta_{j3}\cos \theta_{k3} .$$

By the use of this relation we can simplify Eq. 34:

$$I_{jk} = \frac{e^2}{r^3_{jk}} |M|^2 \quad 3 \cos \theta_{j1} \cos \theta_{k1} - \cos \varphi_{jk}. \qquad (34a)$$

Thus we must calculate the angle between the two transition moments, and the angles between each moment and the line connecting their centers. This problem is in general quite laborious, but is considerably simplified when we assume (as we do here) that all the transition moments lie in the same plane or in parallel planes.



The calculation of I_{jk} for the various interactions (j = 0, k = 1-14; see table 14 for numbering of adjacent moments) is summarized in the following table. The transition dipole moment is estimated at 0.88A.

k *	cosθjk	cos θkj	3ab	3ab-cos	r x10	I_{jk}
3, 11	-.232	+.232	-.161	-1.16	1090	+ 190
4, 12	+.232	-.232	-.161	-1.16	1090	+ 190
1, 7	+.999	+.999	+.987	+1.98	289	-1220
2, 10	-.009	-.009	-.006	-0.98	810	+ 216
6, 13	+.540	+.540	-.572	-1.55	3370	+ 82
8, 14	+.280	-.280	-.384	-1.36	985	+ 246
5, 9	-.472	-.472	-.395	-1.37	3500	+ 70

* value of k in I_{jk}, with j = 0.