A factors can be rationalized in terms of a loose complex in which enhanced entropy of activation arises from low frequency stretching and bending modes involving the I atom.

Heat of Formation and Bond Strength

The observed value of E_1, given by (5), may be used to derive the bond dissociation energy, $D(i\text{-}C_3H_7\text{-}H)$, if E_2 is known. Flowers and Benson[6b] have reported a value of $E_2 - E_3 = 0.8 \pm 1.0$ kcal. for the Me radical, Hartley and Benson[10] give $E_2 - E_3 = 0.9$ kcal. for the C_2H_5 radical, and O'Neal and Benson[6a,27] give $E_2 - E_3 = 1.5$ kcal. for the CH_3CO radical. In the absence of any experimental finding on the isopropyl radical, we may assume it to be between those for Et and CH_3CO, with a chosen value, $E_2 - E_3 = 1.1$ kcal. If $E_3 \simeq 0.2$ kcal.,[10] then $E_2 = 1.3$ kcal./mole and we may further deduce $\Delta H_{1,2}°$ (600°K.) $= E_1 - E_2 = 23.7$ kcal./mole, at the middle of the temperature range of the present work. From the thermodynamic data given in Table II, $\Delta C_{p1,2} = 2.1$ cal./mole °K.,[28] which leads to $\Delta H_{1,2}°$ (25°) $= 23.1$ kcal./mole. Since the bond dissociation energy, $D°(H\text{-}I)_{25°} = 71.4$ kcal./mole,[29] is known very accurately, we can use the relation

$$D°(i\text{-}C_3H_7\text{-}H) - D°(H\text{-}I) = \Delta H°_{1,2} \ (25°)$$

(27) H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **37**, 540 (1962).

(28) $C_p°$ for the i-C_3H_7 radical is assumed the same as for C_3H_8, and $C_p°$ (HI) is taken as the mean of the values at 25°, 7.0 cal./mole °K., and at 600°K., 7.25 cal./mole °K.

(29) National Bureau of Standards Circular No. 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

to find

$$D°(i\text{-}C_3H_7\text{-}H) = 94.5 \text{ kcal./mole}$$

The heat of formation, $\Delta H_f°$ (25°), for the i-C_3H_7 radical may also be computed from thermodynamic quantities given in Table II from the relation

$$\Delta H_f°(i\text{-}C_3H_7) = \Delta H_f°(C_3H_8) - \Delta H_f°(H) + D(i\text{-}C_3H_7\text{-}H)$$

and the value obtained is $\Delta H_f°(i\text{-}C_3H_7) = 17.6$ kcal./mole with an uncertainty of ± 1 kcal./mole.

Electron impact measurements[30] have led to $D(i\text{-}C_3H_7\text{-}H) = 94' \pm 2$ kcal./mole. From competitive bromination of pairs of alkanes, Fettis, *et al.*,[31] derived the bond dissociation energy, $D(i\text{-}C_3H_7\text{-}H) = 93.1$ kcal./mole. In arriving at this value they used the results of Kistiakowsky and van Artsdalen[32] on the bromination of CH_3Br and Polanyi's relation $E = \alpha \Delta H + C$. Though the agreement of our data with these values is good, it is difficult to reconcile with the high precision claimed by Fettis, *et al.* It is our own feeling that the scatter in their reported rate constants and the uncertainties associated with both the bromination work and the Polanyi relation introduces an uncertainty of the order of ± 2 kcal. in their value.

(30) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

(31) G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3037 (1961).

(32) G. B. Kistiakowsky and E. R. van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944).

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Polarization of Charge-Transfer Bands[1]

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The polarization of the charge-transfer (c.t.) band of π-molecular complexes of tetrachlorophthalic anhydride (TCPA) and aromatic hydrocarbons has been determined by a photoselection method correlating the polarized c.t. absorption with polarized triplet emission of the donor. It is found that the c.t. band is polarized predominantly along the intermolecular axis and perpendicular to the plane of the ring, indicating that a well-defined structure exists even in the excited state, and that the change in the permanent dipole moment, on excitation, is mainly responsible for the intensity of the c.t. band in these complexes. The same technique has been utilized to show that the phosphorescence of quinoline is out-of-plane polarized, hence confirming Dörr and Gropper's assignment of the phosphorescent state of quinoline as a (π, π^*) triplet. This kind of experiment should be utilizable for structure determination of c.t. complexes in solution.

Introduction

Mulliken[2] has shown that the electric dipole transition moment, $\mathbf{\mu}$, of the charge-transfer transition frequently appearing in molecular complexes with an excited state predominantly described through

$$\psi_e = a^*\psi_{b_1}(D^+A^-) - b_1^*\psi_0(D,A) + \Sigma d_i\,^*\psi_{d_1}(D^*,A) \quad (a^* \gg b^*, d_i\,^*) \quad (1a)$$

and a ground state described through

$$\psi_g = a\psi_0(D,A) + \Sigma b_i\psi_{b_1}(D^+A^-) \quad (a \gg b_i) \quad (1b)$$

is given (in a.u.) by

$$\mathbf{\mu} = \int \psi_g \mathbf{r}\psi_e d\tau = \int (a\psi_0 + b_1\psi_{b_1} + \sum_{i \neq 1} b_i\psi_{b_1})\mathbf{r}(a^*\psi_{b_1} - b_1^*\psi_0 + \Sigma d_i\,^*\psi_{d_1})d\tau$$

$$\approx a^*b_1\int(\psi_{b_1}\mathbf{r}\psi_{b_1} - \psi_0\mathbf{r}\psi_0)d\tau + (aa^* - b_1b_1^*)\int\psi_0\mathbf{r}\psi_{b_1}d\tau + \Sigma ad_i\,^*\int\psi_0\mathbf{r}\psi_{d_i}\,d\tau + \sum_{i \neq 1}a^*b_i\int\psi_{b_1}\mathbf{r}\psi_{b_1}d\tau \quad (2)$$

In the above relations the contributions from (D^-A^+) have been neglected.[2] The first term in eq. 2 represents the change in permanent dipole moment of the complex on excitation, and was calculated by Mulliken[2] to be of the same order as the transition moments obtained from observed c.t. bands in π-molecular complexes. This moment has a predicted direction along the line joining the centroids of the donating and accepting or-

bitals. For π-molecular complexes having a sandwich structure, the charge centroids of D^+ and A^- are expected to generate a moment with a predominant component perpendicular to the plane of the sandwich and hence predominantly perpendicular to both the donor and acceptor molecular planes. This term is predicted to be the leading term[2] and therefore to give rise to predominantly out-of-plane polarization for the c.t. transitions. The direction of the moment given by the second term in eq. 2 will depend upon the symmetry properties of the orbitals. If the structure of the complex contains an axis of symmetry through the acceptor and donor species and provided that ψ_0 and ψ_{b_1} in eq. 1a and 1b belong to the same spin-orbital representation in the symmetry group of the complex, then this term clearly should be also directed along the intermolecular axis. In the case that ψ_0 and ψ_{b_1} do not belong to the same representation, b_1 will be zero, so that the contribution from the first term in eq. 2 will be negligible, leading to a transition moment not restricted to the intermolecular axis. The third and fourth terms in eq. 2 represent the borrowing of intensity by the c.t. band from the donor bands and must be directed in-plane in the case of π-complexes. The importance of this term has not been established, though Murrel[3] pointed out its possible large contribution in the case of contact charge transfer. The mixing of a (π,π^*) state with the c.t. state may also occur if the complex has low symmetry, or through vibronic interaction. An example of this latter possibility was shown by Albrecht[4] for the case of the intramolecular c.t. band in tetramethyl-p-phenylene-diamine.

This paper describes an attempt toward experimental determination of the polarization of the c.t. band in sandwich-type complexes. It is clear that such an experiment could determine the important sources of intensity in these transitions. There have been two such attempts before. In 1952, Nakamoto[5] studied the dichroism of quinhydrone and related complexes, and concluded that the perpendicular component (to the plane) has greater intensity than the in-plane component. Recently, Lower, Hochstrasser, and Reid,[6] in a study of the crystal (absorption) spectra of the anthracene–TNB complex, found that the c.t. band is again polarized predominantly out-of-plane. There are, however, serious difficulties in analyzing the polarization of single crystal spectra.[7] In addition to these difficulties, complexes frequently form only microcrystals. Some complexes do not exist in the solid state; of those that do, the crystal structures of a relatively small number have been analyzed fully, specially for cases with unsymmetrical acceptors. There are several examples where the molecules are tilted at odd angles, with each donor interacting non-uniformly with more than one acceptor, resulting in crystal absorption spectra differing markedly from those in solution.[5] These factors make it desirable to carry out an experiment determining the polarization of the c.t. band in rigid solution. McGlynn,[8a] Briegleb

and co-workers,[8b] and Reid[9] have shown that on excitation of the complex into the c.t. band, the donor molecule phosphorescence appears. An experiment can be designed to determine the polarization of the charge-transfer band inasmuch as the polarization of the phosphorescence of free polyacene donors such as naphthalene, phenanthrene, and chrysene has already been shown to be predominantly perpendicular to the plane of the ring.[10,11] The basic step is to photoselect an oriented phosphorescent state by excitation with polarized light into the charge-transfer band. The donor molecules are prevented from changing their orientation between excitation and emission by the rigid matrix. If the direction of the T $\rightarrow$ S transition moment in the complexed hydrocarbon is the same as that in the free hydrocarbon, then the degree of polarization,[12] in the present case of electric dipole emission from the donor triplet state, should ideally be $+0.50$ if the c.t. band is polarized perpendicular to the plane and -0.33 if it is in-plane polarized. A necessary condition is that the spin–orbit coupling scheme either does not alter in going from the free to the complexed hydrocarbon, or that coupling with (π,π^*) states does not become important in the complex. Because of the distance between the donor and acceptor, this condition is very probably fulfilled. Measuring the polarization of the fluorescence excited with polarized light will not be applicable in the present case, since the charge-transfer fluorescence cannot be obtained by excitation into either the donor or the acceptor bands.[8a,b]

Experimental

The emission polarization was determined by a photoselection method[13] with the axis of observation at 90° to the exciting electric vector, as described previously.[14] Using a narrow exciting beam (band width ~60 Å.) from a Bausch and Lomb 500-mm. grating monochromator and a GE AH6 mercury lamp, we scanned the c.t. band region from 410 to 365 mμ for three polycyclic hydrocarbon–tetrachlorophthalic anhydride (TCPA) complexes. The thin samples (1–2 mm. thick) contained in square quartz dewars were prepared by mixing the hydrocarbons with TCPA in EPA solvent, carefully purified to remove depolarizing impurities, and slowly cooled to 77°K. The choice of solvent was dictated by the solubilities of the complexes at 77°K. Solutions in hydrocarbon glasses under these conditions did not exhibit sufficient emission intensity to carry out polarization measurements with the detector at hand (vide infra). Rigid EPA is an excellent solvent for polarization measurements provided the alcohol is completely impurity free and the glass is formed slowly. Measurements have been made in this laboratory on several classes of compounds (azines, ketones, hydrocarbons) in hydrocarbon and EPA glasses with nearly identical results ($\Delta P = \pm 0.02$). The c.t. fluorescence emissions were too weak for polarization experiments even when excited into the c.t. band.

The phosphorescence emission was analyzed by HN-32 sheet polaroid and recorded on a photoelectric instrument (Perkin-Elmer Model 13U) with a constant slit width of 100–200 μ selected to resolve fully the bands. No polarization dependence on the slit width could be observed. Care was taken to correct for preferential polarization sensitivity in the optical arrangement. All measurements were repeated from 3–6 times and are

(3) J. N. Murrel, J. Am. Chem. Soc., **81**, 5037 (1959).

(4) A. C. Albrecht, J. Chem. Phys., **33**, 156 (1960).

(5) K. Nakamoto, J. Am. Chem. Soc., **74**, 1739 (1952).

(6) S. K. Lower, R. M. Hochstrasser, and C. Reid, Mol. Phys., **4**, 161 (1961).

(7) D. S. McClure and O. Schnepp, J. Chem. Phys., **23**, 1575 (1955).

(8) (a) S. P. McGlynn, ibid., **34**, 357 (1960); (b) G. Briegleb, J. Czekalla, W. Herre, and R. Glier, Z. Elektrochem., **61**, 537, 1053 (1957).
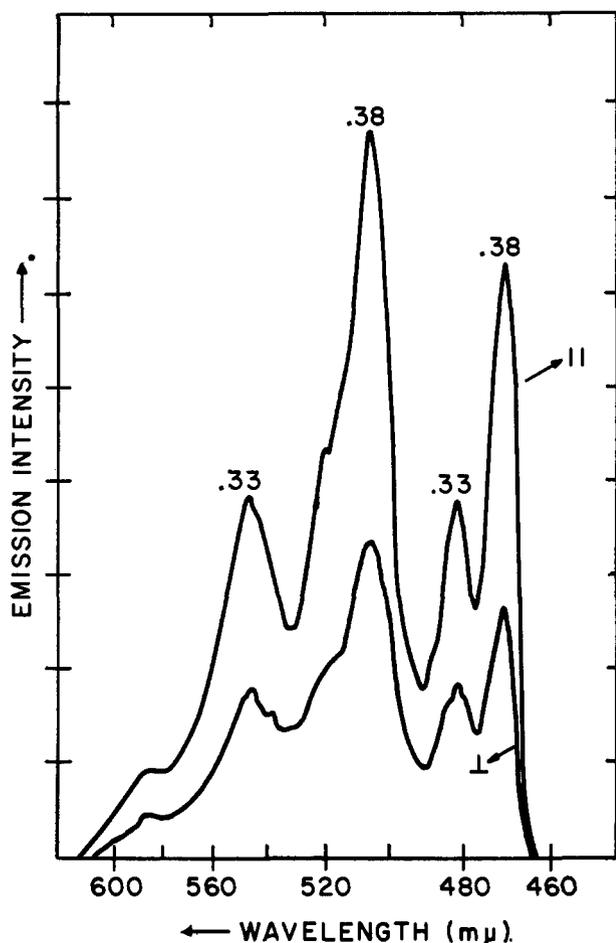
(9) C. Reid, J. Chem. Phys., **20**, 1212, 1214 (1952).

(10) (a) V. G. Krishna and L. Goodman, ibid., **37**, 912 (1962); (b) T. Azumi and S. P. McGlynn, ibid., **37**, 2413 (1962).

(11) (a) H. Gropper and F. Dörr, Ber. Bunsenges. Physik. Chem., **67**, 46 (1963); (b) F. Dörr and H. Gropper, ibid., **67**, 193 (1963).

(12) Defined as $P = (3\cos^2\alpha - 1)/(\cos^2\alpha + 3) = (I_\| - I_\perp)/(I_\| + I_\perp)$ where α is the angle between the transition moments in absorption and emission. The experimental quantities $I_\|$ and $I_\perp$ are, respectively, the intensities of emission with the analyzer oriented parallel and perpendicular to the electric vector of the exciting light.

(13) A. C. Albrecht, J. Mol. Spectry., **6**, 840 (1961).

(14) V. G. Krishna and L. Goodman, J. Chem. Phys., **36**, 2217 (1962).

Fig. 1.—Polarization of naphthalene phosphorescence emission in naphthalene–TCPA complex (concentrations: N 2.5 × 10⁻² M, TCPA 2.0 × 10⁻³ M) relative to excitation into the c.t. band (at 405 mμ). Degrees of polarization[12] are shown for the principal peaks.

reproducible within ±0.01 in the degree of polarization for the polycyclic hydrocarbon complexes.

The quinoline complex measurements were less precise than those on the polycyclic hydrocarbons owing to the necessity of using (because of breakage and malfunction) a 250-mm. B and L grating monochromator in conjunction with a round dewar.[15] The reproducibility in the degree of polarization for this case was only ±0.04.

TCPA (Eastman), naphthalene, phenanthrene (Fisher, purified), chrysene (Rutgerswerke Aktiengesellschaft), and quinoline (Eastman) were purified by recrystallization and vacuum sublimation. The donor concentration was near 2×10^{-2} M, and that of TCPA near 2×10^{-3} M. The donor/TCPA ratio was varied in all cases, but no appreciable change in degree of polarization was observed (e.g., naphthalene–TCPA complex, slit 200 μ[16]: N, 2.5 × 10⁻² M; N/TCPA = 13, P_{0-0} = 0.35; N/TCPA = 26, P_{0-0} = 0.34). If the concentrations approached 10^{-1} M a significant but still small depolarization was observed (e.g., N, 8.5 × 10⁻² M; N/TCPA = 42, P_{0-0} = 0.31). The spectrophotometer limiting sensitivity prevented measurements when donor concentrations were much less than 10^{-2} M.

Polycyclic Hydrocarbon–TCPA Complexes.—Figure 1 gives the parallel and perpendicular components of the polarized naphthalene phosphorescence spectra with respect to excitation into the c.t. band of naphthalene–TCPA complex (see Fig. 3). The observed degree of polarization of the 0–0 band of the naphthalene emission is +0.38, showing that the emitting light electric vector is essentially parallel to the exciting light electric vector. Since the naphthalene phosphorescence is polarized largely out-

(15) The particular round dewar utilized did not have a large degree of depolarization.

(16) In this case the slit is somewhat too wide to resolve fully the phosphorescence bands, resulting in slightly lower polarization than shown in Fig. 1, where a slit of 100 μ was utilized.
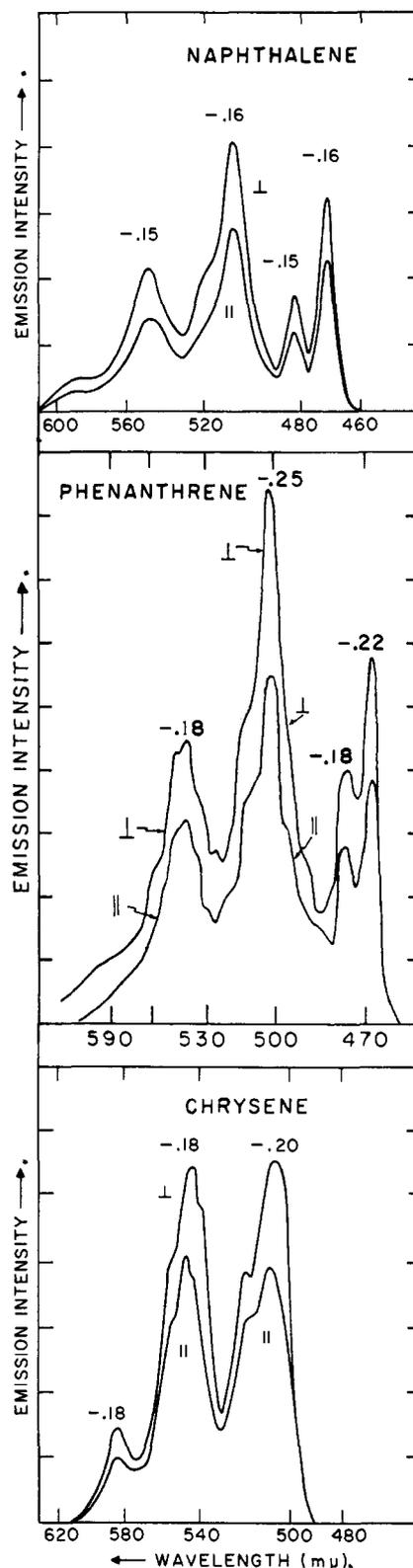

Fig. 2.—Polarization of free naphthalene, phenanthrene, and chrysene (in EPA) relative to 310 mμ excitation at 77°K.

of-plane,[10a] the c.t. band should therefore also be polarized essentially perpendicular to the molecular plane. Intermolecular energy transfer to free naphthalene is ruled out by the high degree of polarization shown in Fig. 3 for excitation into the c.t. band. One ambiguity is that T → S *gross* polarization in complexed naphthalene could be different from that in free naphthalene owing to the singlet–triplet transition borrowing intensity vibronically from complex or acceptor bands.[17] The intensity bor-

(17) H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).
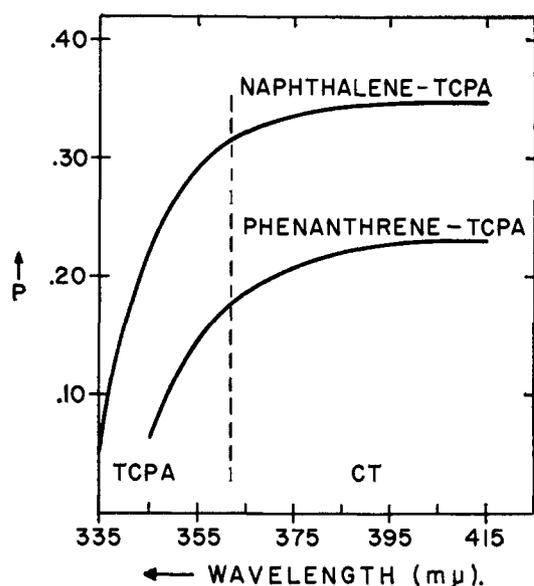
Fig. 3.—Variation of the degree of polarization,[12] P, with the wave length of excitation for naphthalene– and phenanthrene–TCPA complexes. The half-band width of the exciting radiation is 60 Å. The dotted line indicates onset of TCPA absorption; slit: 200 μ.[11]
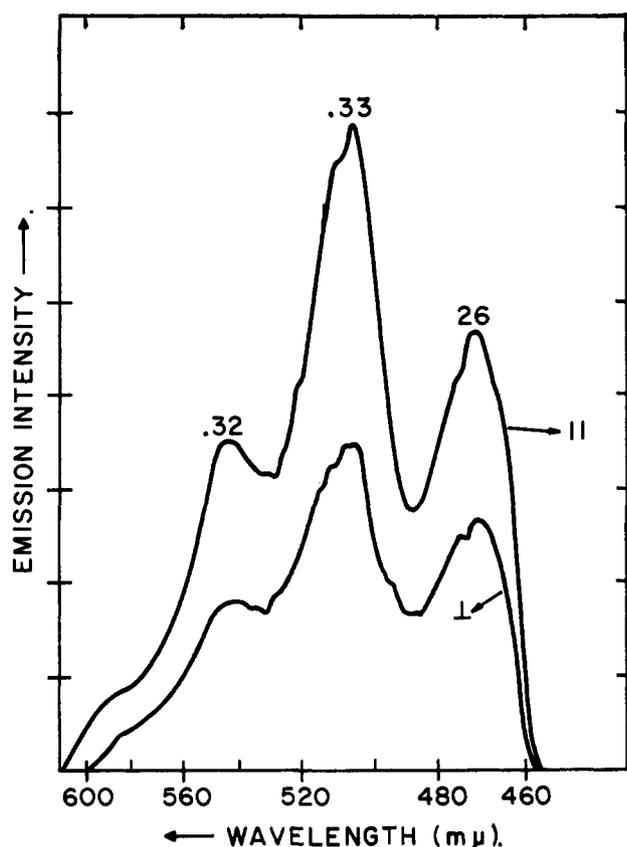

Fig. 4.—Polarization of phenanthrene phosphorescence emission in phenanthrene–TCPA complex (concentrations: P 2.0 × 10^{-2} M, TCPA 2.0 × 10^{-3} M) relative to excitation into the c.t. band (at 405 mμ).

rowing by the 0–0 band, however, will be possible only if both the bands are polarized in the same direction, hence we avoid any ambiguity by basing our conclusions on 0–0 band polarizations. Comparison of Fig. 1 with Fig. 2, where the polarization spectrum of free naphthalene phosphorescence emission is reproduced, shows that the vibrational features of the phosphorescence emission of complexed and free naphthalene (under similar conditions) are alike apart from some broadening in the complex, so that it is unlikely that the c.t. band contributes in a really major way to
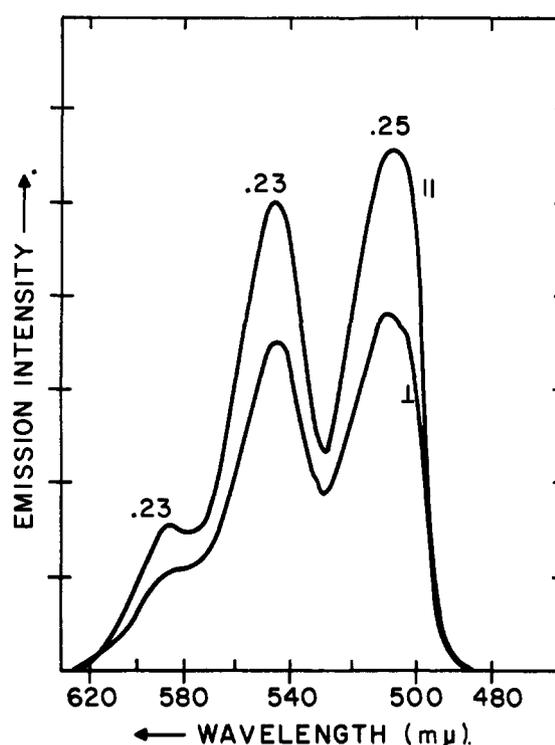

Fig. 5.—Polarization of chrysene phosphorescence emission in chrysene–TCPA complex (concentrations: C 2.5 × 10^{-2} M, TCPA 2.0 × 10^{-3} M) relative to excitation into the c.t. band (at 405 mμ).

the S–T transition probability. Comparison of the polarization of the individual vibrational bands in Fig. 1 and 2 shows that whereas the naphthalene emission is nearly uniformly polarized, naphthalene–TCPA complex has its highest polarization in the 0–0 band and then undergoes a strong alternation. This behavior is indicative of coupling of the triplet state in the complex with some other triplet(s) and thus does suggest additional sources for the S–T transition probability in complexed naphthalene. The decrease in radiative lifetime of the naphthalene emission of 2.6 to 1.4 sec. on complexation[8b] is consistent with this view, but could simply reflect the heavy atom effect.

As an explanation of anomalous equilibrium constant–intensity relationships in c.t. complexes, Orgel and Mulliken[18] suggested that a number of possible geometrical isomers may exist for c.t. complexes because of the small differences in energy between different configurations. In Fig. 3 the variation of the polarization for the naphthalene phosphorescence 0–0 band is shown as a function of excitation wave length. Throughout the c.t. band this is nearly constant but becomes depolarized in the donor and acceptor absorption regions consistent with intermolecular energy transfer between donor and complex. The high degree and uniformity of the polarization with respect to excitation throughout the c.t. band clearly shows that a complex of well-defined structure exists even in the excited state. Another explanation of the anomalous K–ϵ relationship, suggested by Orgel and Mulliken,[18] is that the c.t. transition may take place during momentary contacts between the acceptor and the donor. Such contact charge-transfer transitions are expected to be depolarized. The result shown in Fig. 3 indicates that contact transitions do not play significant roles in the intensity of these complexes, at least in the glassy state.

Figures 4 and 5 show the parallel and perpendicular components of the phosphorescence of phenanthrene and chrysene complex, respectively. Tne polarized phosphorescence emission of the free hydrocarbons are shown for comparison purposes in Fig. 2. The 0–0 band polarization is reduced from that of the naphthalene complex but is still high, $\sim$+0.25, showing again the predominantly out-of-plane nature of the c.t. transition. For the phenanthrene complex the second band is more highly polarized than the 0–0 band. In the naphthalene–TCPA complex both the partners contain two fused rings, and one fits exactly over the other. In the case of the phenanthrene complex, a reasonable

(18) L. E. Orgel and R. S. Mulliken, J. Am. Chem. Soc., 79, 4839 (1957)

speculation is that the TCPA overlaps two adjacent rings on one side of phenanthrene rather than forming a symmetrical complex with less overlap. X-Ray investigations show several examples of asymmetric organic π-molecular complexes.[19] If this asymmetry is true in these cases, the line joining the centroids of acceptor and donor orbitals will not be quite perpendicular to the plane of phenanthrene or chrysene (giving μ a parallel component) and hence the degree of polarization is expected to be somewhat reduced.

The parallel polarization of the donor T → S emission relative to the c.t. absorption observed in the above experiments clearly requires for these three polyacene–TCPA complexes a predominantly out-of-plane polarized c.t. band, and therefore these c.t. transitions cannot derive much intensity from the donor or acceptor transitions.

Quinoline–TCPA Complex.—The polarization of the quinoline phosphorescence was determined by Dörr and Gropper,[11b] using direct excitation, to be negative relative to both the ^1L_a and ^1L_b $\pi \rightarrow \pi^*$ excitations; they therefore concluded that the transition moment must be perpendicular to the plane of the molecule analogous to the phosphorescence polarization of the parent hydrocarbon.[10a]

Unfortunately, the absorption bands of quinoline are not distinct, and hence the polarization of the quinoline phosphorescence cannot be determined completely unambiguously by direct excitation. An extra band can be created, however, by forming a c.t. complex with TCPA, and the polarization of the T → S emission then determined by extending the hydrocarbon results to quinoline, i.e., assuming the c.t. band does not change polarization in going from naphthalene–TCPA to quinoline–TCPA. In quinoline–TCPA complex, the quinoline behaves as a π-donor, as shown by the close similarity of the c.t. band with that of the naphthalene–TCPA complex.[20] The diffuse π-acceptor orbital of TCPA can better overlap the π-donor orbital than the nitrogen n-orbital. Thus it is probable that the complex has a sandwich structure, with the c.t. band polarized out-of-plane analogous to that of naphthalene. Figure 6 shows that the degree of polarization of the phosphorescence is +0.35 with respect to excitation into the c.t. band of the complex, confirming Dörr and Gropper's direct excitation experiment and showing that the phosphorescence does not arise from an (n, π^*) triplet state. In this case the experiment does not rule out important contributions from donor (n → π^*) transitions to the c.t. intensity.

The above method of determining the polarization of phosphorescence by excitation into a c.t. band may be useful in cases where a direct excitation procedure is not possible. In order to utilize the method, the following conditions should be satisfied: (1) the c.t. band needs to be distinct from the absorption band of the complex components, (2) the triplet level of the donor should be below the c.t. triplet level, and (3) the radiationless deactivation rate should be low.

Conclusions and Summary

The strongly parallel polarization for c.t. excitation of the phosphorescence of the polyacene–TCPA com-

(19) S. C. Wallwork, *J. Chem. Soc.*, 494 (1961).
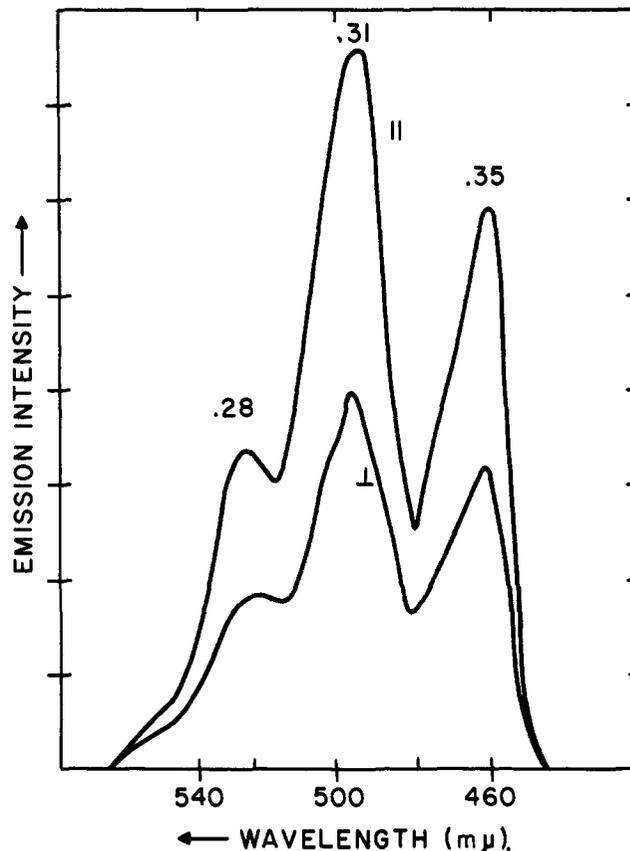(20) M. Chowdhury and S. Basu, *Trans. Faraday Soc.*, **56**, 335 (1960).

Fig. 6.—Polarization of quinoline phosphorescence emission in quinoline–TCPA complex relative to excitation into the c.t. band (at 405 mμ).

plexes requires a c.t. transition moment predominantly perpendicular to the donor and acceptor molecular planes, and thus strongly supports Mulliken's original ideas[2] on intensities of c.t. bands. It eliminates as major sources of intensification borrowing from the donor or acceptor bands and contact charge-transfer interactions. The kind of experiment described here should be applicable to structure determination of c.t. complexes in rigid solutions.