Absorption and Fluorescence Spectra of Anthracene-*s*-Trinitrobenzene Complex Crystal[*1]

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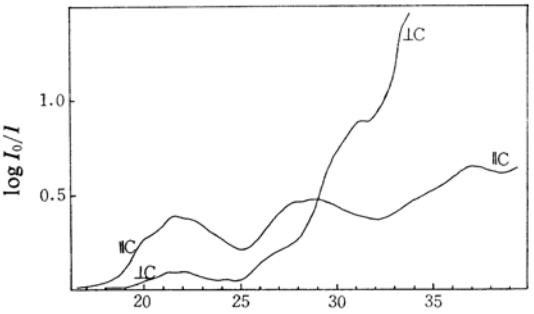
The electronic spectra of a crystal of a charge-transfer type molecular complex is of particular interest since the mechanism of the electronic interaction between the electron donor and the acceptor can be elucidated by the aid of polarization measurements. Nakamoto1) measured the polarized absorption spectra of charge-transfer complexes such as quinhydrone and showed that the charge transfer absorption is stronger along the direction out of the plane of the benzene ring. The absorption spectra of the crystal formed between anthracene and 1, 3, 5-trinitrobenzene (TNB) was also studied by Lawer, Hochstrasser and Reid,2) and the fluorescence and phosphorescence of this system was investigated by Czekalla et al.3) and McGlynn and his co-workers.4) According to these studies, the fluorescence is to be ascribed to a reverse process of charge transfer absorption, since a linear relationship was found between the absorption and the fluorescence for various systems having TNB as an electron acceptor. The theoretical analysis of the charge resonance interaction is facilitated by crystal studies, and the structure of the crystal has been recently determined by Wallwork and his co-workers.5)

In this paper a polarization measurement of the absorption and fluorescence spectra of the crystal will be reported with the view of obtaining detailed information on the electronic interaction between the electron donor and the acceptor. The electric conductivity of the crystal has already been reported on by Kuroda, Yoshihara and Akamatu.6)

Experimental

Anthracene was purified by recrystallization from a xylene solution, followed by chromatography and sublimation in vacuo. TNB was obtained after recrystallization from an ethanol solution. The crystal for the measurement of the fluorescence of the complex was grown from a carbon tetrachloride solution. The thin flakes of single crystals obtained by sublimation were used for the absorption measurement. The crystal elongates along the c-axis.

The absorption spectrum shown in Fig. 1 was measured by using the light polarized parallel to and perpendicular to the c-axis and by using the ultraviolet microspectrophotometer described in a previous paper.7) The measurement was made at room temperature.



Wave number ×10⁻³, cm⁻¹

Fig. 1. Absorption spectrum of anthracene-TNB complex.

TABLE I. BAND POSITIONS OF ABSORPTION AND FLUORESCENCE OF CRYSTAL
(Value in wave number)

Absorption		Fluorescence		
C∥	C⊥	Room temp.	Liq. N_2 temp.	Liq. He temp.
20050	20260	18300	18335	18350
21500	21200	17000	17095	17040
22600	22200	15300	15600	15748
27500	26200			
28800				
	29800			
	31300			
37000				

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1) K. Nakamoto, *J. Am. Chem. Soc.*, **74**, 1739 (1952); This Bulletin, **26**, 70 (1953).

2) S. K. Lawer, R. M. Hochstrasser and C. Reid, *Mol. Phys.*, **4**, 162 (1961); *J. Chem. Phys.*, to be published.

3) J. Czekalla, A. Schmillen and K. J. Mager, *Z. Eelektrochem.*, **61**, 1053 (1957); **63**, 623 (1959).

4) S. P. McGlynn and J. D. Boggus, *J. Am. Chem. Soc.*, **80**, 5096 (1958); *J. Chem. Phys.*, **32**, 357 (1960); N. Christodouleas and S. P. McGlynn, to be published.

5) D. S. Brown, S. C. Wallwork and A. Wilson, *Acta Cryst.*, **17**, 168 (1964); S. C. Wallwork, ibid., **7**, 648 (1954).

6) H. Kuroda, K. Yoshihara and H. Akamatu, This Bulletin, **35**, 1604 (1962).

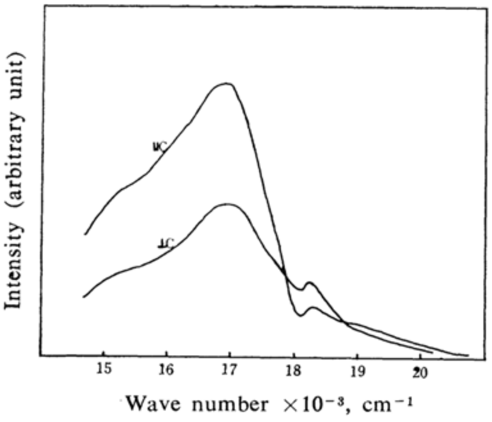
7) J. Tanaka, ibid., **36**, 833 (1963).

TABLE II. LCAO MO

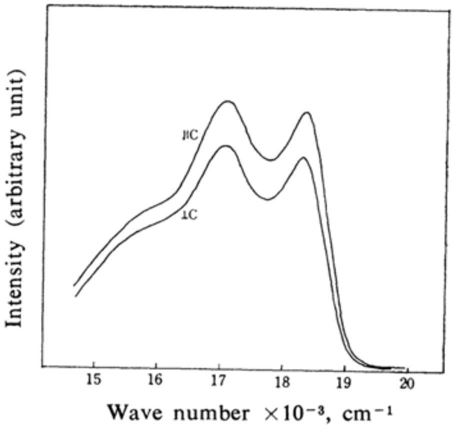
Symmetry	energy ($-\beta$)	C_1	C_2	C_3	C_4	C_5	C_6
A_2''	2.52	0.2570	0.2570	0.2570	0.1976	0.1976	0.1976
E''(s)	2.39	0.2102	−0.1051	−0.1051	−0.2096	0.1048	0.1048
(a)	2.39	0	0.1821	−0.1821	0	0.0741	−0.0741
A_2''	1.75	−0.3136	−0.3136	−0.3136	−0.3463	−0.3463	−0.3463
A_1''	1.20	0	0	0	0	0	0
E''(s)	1.14	0	0	0	0	0	0
(a)	1.14	0	0	0	0	0	0
E''(s)	0.98	−0.5158	0.2579	0.2579	0.4946	−0.2473	−0.2473
(a)	0.98	0	−0.4468	0.4468	0	0.4248	−0.4248
A_2''	0.25	0.0206	0.0206	0.0206	0.135	0.135	0.135
E''(s)	0.20	0.0968	−0.0484	−0.0484	−0.3722	0.1861	0.1861
(a)	0.20	0	0.0838	−0.0838	0	−0.3223	0.3223
E''(s)	−1.18	0.5886	−0.2943	−0.2943	0.5252	−0.2626	−0.2626
(a)	−1.18	0	0.5099	−0.5099	0	0.4549	−0.4549
A_2''	−2.14	−0.4104	−0.4104	−0.4104	0.3951	0.3951	0.3951

The Hückel molecular orbital of trinitrobenzene has been calculated using the parameters as
The numbering of atoms is shown in Fig. 4.

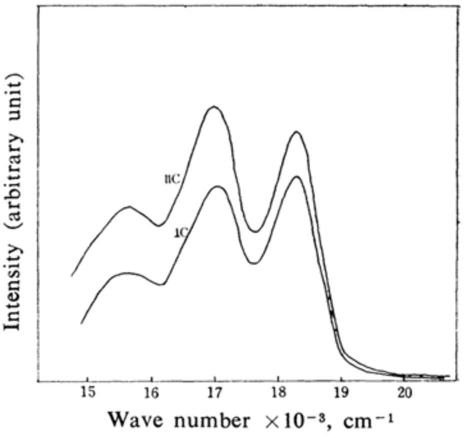
The fluorescence spectrum was measured by a recording spectrofluorometer.* The crystal was excited by a high pressure mercury lamp combined with a Toshiba UVD2 filter in order to obtain the 3650 Å radiation. A calcite Glan-Thompson type polarizer of the Olympus Optical Co. was used for the polarization measurement. The spectrofluorometer consists of a Kipp double monochrometer, a RCA 1P22 photomultiplier, and an amplifier in series. The slit width was kept constant at 0.2 mm. during all measurements. The characteristic sensitivity and polarization properties of the instrument were calibrated using a standard light source. The fluorescence spectra at room temperature and at the temperature of liquid helium, and of liquid nitrogen are shown in Fig. 2, and all results are summarized in Table I.



(a) room temperature



(b) liquid nitrogen temperature



(c) liquid helium temperature

Fig. 2. Fluorescence spectrum of anthracene-TNB complex.

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OF TRINITROBENZENE

Coefficients								
N_1	N_2	N_3	O_1	O_2	O_3	O_4	O_5	O_6
0.3901	0.3901	0.3901	0.1949	0.1949	0.1949	0.1949	0.1949	0.1949
0.6162	−0.3081	−0.3081	0.3428	−0.1714	−0.1714	0.3428	−0.1714	−0.1714
0	0.5337	−0.5337	0	0.2970	−0.2970	0	0.2970	−0.2970
0.1781	0.1781	0.1781	0.2040	0.2040	0.2040	0.2040	0.2040	0.2040
0	0	0	0.4080	−0.4080	0.4080	−0.4080	0.4080	−0.4080
0	0	0	0.5772	−0.2886	−0.2886	0.5772	−0.2886	−0.2886
0	0	0	0	0.500	−0.500	0	0.500	−0.500
−0.0618	0.0309	0.0309	0.2754	−0.1377	−0.1377	0.2754	−0.1377	−0.1377
0	−0.0535	0.0535	0	0.2386	−0.2386	0	0.2386	−0.2386
−0.376	−0.376	−0.376	0.294	0.294	0.294	0.294	0.294	0.294
−0.4958	0.2479	0.2479	0.3692	−0.1846	−0.1846	0.3692	−0.1846	−0.1846
0	−0.4293	0.4293	0	0.3198	−0.3198	0	0.3198	−0.3198
−0.1926	−0.0963	−0.0963	0.0580	−0.0290	−0.0290	0.0580	−0.0290	−0.0290
0	−0.1669	0.1669	0	0.0503	−0.0503	0	0.0503	−0.0503
0.0893	0.0893	0.0893	−0.0191	−0.0191	−0.0191	−0.0191	−0.0191	−0.0191

follows: $\alpha_O=\alpha_C+1.2\beta_{C-C}$ $\alpha_N=\alpha_C+1.44\beta_{C-C}$ $\beta_{NO}=0.7\beta_{C-C}$ $\beta_{NC}=0.7\beta_{C-C}$ $\alpha_C=4.1\beta_{C-C}$

Results and Discussion

(1) Theoretical Consideration.—The charge transfer resonance interaction between the highest occupied orbital of anthracene and the lower vacant orbitals of TNB is considered. The LCAO MO calculation of TNB has been made, and it has been found that the three lowest vacant orbitals are nearly degenerate. The results of calculation are shown in Table II, where it may be seen that the lower vacant orbitals are composed mainly of nitro groups. The nitro groups have a three-fold symmetry, and the vacant orbitals of these groups are split by mutual interactions into one orbital of the lowest energy of the totally symmetric and two orbitals of a slightly higher energy of E″ symmetry. According to these calculations, the lowest symmetric vacant orbital may have a larger electron affinity than the other two orbitals, about 0.05β, where β is the exchange integral (-2—-3 eV.).* However, under the influence of an electron donor or foreign ions on one particular nitro group, the lowest charge transfer state will occur when an electron is transferred into an E″ orbital where the charge density is concentrated on particular nitro groups. For instance, the ESR spectra of the TNB negative ion produced by metallic and photo-reduction shows that the excess electron is accommodated into the E″(s) orbital.[8]

The crystal structure analysis data shows that one nitro group is placed close to anthracene (Fig. 3). The electrostatic energies between partial charges on TNB and positive holes on anthracene have been calculated for molecular separations from 2.8 to 4.0 Å, whereby the geometrical planar configuration is unchanged, as in Fig. 3. The charge density of TNB is taken as those of A_2'', E″(s) and E″(a) orbitals, and three different orientations are considered for the calculation with E″ orbitals since the energy is dependent on the local charge densities on particular atoms (cf. Table III). The results are given in Table III, where it is found that E″(s2), E″(a1) and E″(s3) states are most stabilized by an electrostatic force. Other states are higher in energy by about 0.1—0.2 eV.

The theoretical foundation of the charge-transfer type molecular complex was given by Mulliken,[9] and the wave functions for the ground state and the charge transfer state may be given as follows:

$$\Phi_G=\varphi(D\cdot A)+\lambda_1\varphi(D^+\cdot A^-)$$
$$\Phi_C=\varphi(D^+\cdot A^-)+\delta_1\varphi(D\cdot A)+\delta_2\varphi(D^*\cdot A) \quad (1)$$

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* Fischer and McDowell (private communication) have made a similar calculation of the Hückel MO of TNB using different parameters. They found a different sequence of energy levels as regards the lowest vacant A and E orbitals, where the A_2'' is slightly more unstable than E″. Therefore, these three levels are considered to be nearly degenerate, since the simple Hückel MO result is greatly dependent on the choice of parameters.

[8] Although Ward had observed the characteristic of the E″ orbital in accommodating an excess electron, Fischer and McDowell (private communication) have found that by the electrolytic reduction a symmetric anion is formed on which an electron is put in the totally symmetric orbital. See R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1961); *J. Chem. Phys.*, **38**, 2588 (1963).

[9] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

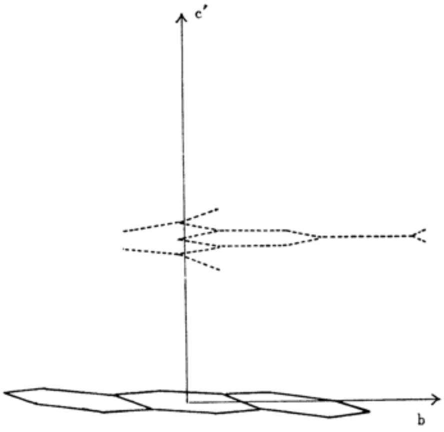


Fig. 3a

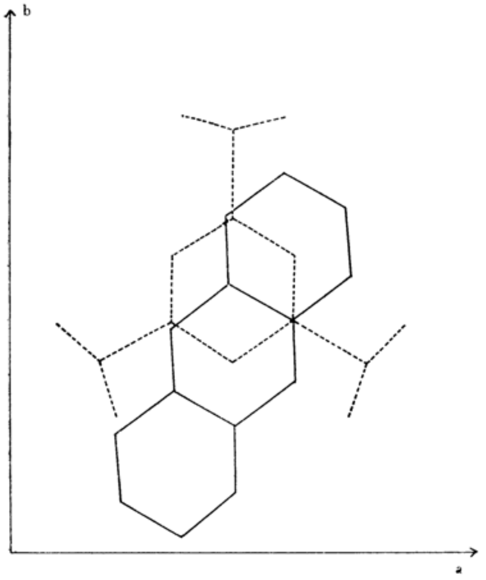


Fig. 3b

Fig. 3. Projections of molecules in the crystal.

where $\varphi(\mathrm{D}\cdot\mathrm{A})$, $\varphi(\mathrm{D}^+\cdot\mathrm{A}^-)$ and $\varphi(\mathrm{D}^*\cdot\mathrm{A})$ represent wave functions of a no-bond structure, the charge transfer structure and the local excited state of the donor. The perturbation coefficients are given by:

$$\lambda_1=\frac{\int\varphi^*(\mathrm{D}^+\cdot\mathrm{A}^-)\mathbf{H}\varphi(\mathrm{D}\cdot\mathrm{A})\mathrm{d}\tau}{E_{\mathrm{CT}}-E_{\mathrm{G}}} \tag{2}$$

$$\delta_1\simeq-\lambda_1$$

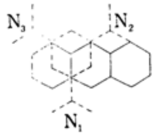
$$\delta_2=\frac{\int\varphi^*(\mathrm{D}^*\cdot\mathrm{A})\mathbf{H}\varphi(\mathrm{D}^+\cdot\mathrm{A}^-)\mathrm{d}\tau}{E_{\mathrm{D}^*\cdot\mathrm{A}}-E_{\mathrm{CT}}} \tag{3}$$

The integrals in Eqs. 2 and 3 might be proportional to the overlap integrals between them, so the overlap integrals have been evaluated between the highest occupied and the lowest vacant orbitals of anthracene with the lower vacant orbitals of TNB, using a common orbital exponent for all atoms at $\xi=Z/n=1.4$[10] and taking into account the overlap between direct-opposite and next-neighbor atoms. The results are shown in Table IV, where it is shown that E″(s2) is the most favorable orbital and configuration since the overlap has the same sign for both ground and excited states and since it increases at a shorter molecular separation. This means that both ground and

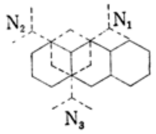
TABLE III. ELECTROSTATIC ENERGY BETWEEN (Anthracene)$^+$(TNB)$^-$, (eV.)

Molecular separation (Å)	A_2''	E″(a1)	E″(a2)	E″(a3)*
2.8	3.055	3.227	3.027	3.052
3.0	2.961	3.118	2.932	2.954
3.5	2.745	2.869	2.714	2.730
4.0	2.554	2.652	2.521	2.533
		E″(s1)	E″(s2)	E″(s3)*
2.8		3.037	3.240	3.211
3.0		2.943	3.131	3.105
3.5		2.726	2.883	2.864
4.0		2.534	2.667	2.652

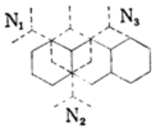
* There are three possible orientations of orbitals for the E″ type. We have distinguished them by 1, 2, and 3.



(1)



(2)



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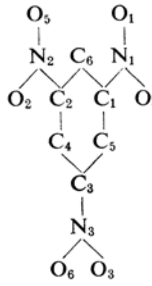

Fig. 4. Numbering of atoms in the TNB molecule.

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[10] J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).

TABLE IV. OVERLAP INTEGRALS BETWEEN THE ORBITALS OF ANTHRACENE AND TNB

Vacant orbitals of TNB	Orbitals of* anthracene	Overlap integral	
		2.8	3.5 (Å)
A_2''	1	0.0035	0.0016
	2	−0.0039	−0.0012
E″(a1)	1	0.0115	0.00554
	2	0.0039	0.00152
E″(a2)	1	−0.00073	−0.00017
	2	−0.00403	−0.00121
E″(a3)	1	0.01424	0.00665
	2	0.00438	−0.00033
E″(s1)	1	−0.0040	−0.0014
	2	−0.0045	−0.0017
E″(s2)	1	−0.01266	−0.00417
	2	−0.05026	−0.01721
E″(s3)	1	0.02799	−0.00545
	2	0.0039	0.01464

* Highest occupied orbital of anthracene is denoted by 1 and the lowest vacant orbital by 2.

excited states are stabilized by charge resonance interaction, particularly at a shorter molecular separation. The molecular separation of 3.28 Å found by X-ray analysis is apparently shorter than the normal van der Waals radii, and the charge transfer resonance force might be responsible for the shortening of the molecular distance. The stabilization of the excited state is demonstrated by a shift of the fluorescence band (loc. cit.).

Since we are concerned with the lowest charge transfer state, we will pay particular attention to a state in which an electron is transferred into the E″(s) orbital. Other states are less convenient from the points of view of electrostatic energy and electron overlap; for instance, the charge transfer state into the E″(a2) orbital is 0.2 eV. higher in electrostatic energy and 1/10 smaller in electron overlap effect.

The energy of the charge transfer state, E_{CT}, is estimated by Eq. 4:

$$E_{\mathrm{CT}} = I_p - E_A - \sum_{i,j} q_i q_j / R_{ij} \tag{4}$$

where I_p is the ionization potential of anthracene, E_A is the electron affinity of TNB, and the last term is the electrostatic energy at 3.28 Å separation, where q_i and q_j indicate partial charges on *i*-th and *j*-th atoms. Using values of $I_p = 7.4$ eV.[11] and $E_A = 1.86$ eV.[12] and electrostatic energy for the E″(s2) orbital, E_{CT} is estimated as 2.54 eV. The local excited state of anthracene is the lowest singlet excited state of ^1L_a at 3.40 eV. Although it is very difficult to estimate the numerical value of the integrals quantitatively, we will tentatively assign −0.10 eV. for the integral in Eq. 2 and −0.40 eV. for Eq. 3. The perturbation coefficient is estimated as $\lambda_1 = 0.04$.

For the excited state, the perturbation treatment is not accurate enough because the E_{CT} and $E_{\mathrm{D^*\cdot A}}$ are close to each other; hence, we have solved a secular equation and found two energies and wave functions as follows:

$$\begin{aligned} &2.39\ \text{eV.}:\ 0.94\,\varphi(\mathrm{D^+\cdot A^-}) + 0.33\,\varphi(\mathrm{D^*\cdot A}) \\ &3.55\ \text{eV.}:\ 0.33\,\varphi(\mathrm{D^+\cdot A^-}) - 0.94\,\varphi(\mathrm{D^*\cdot A}) \end{aligned} \tag{5}$$

The stabilization of the ground state is 0.004 eV. Although this figure is too small to explain the stability of the complex, a much larger energy will arise from charge-transfer interactions of other filled orbitals. Those results will be discussed in a later section.

(2) Absorption Spectrum.—The general feature of the spectrum coincides with the findings of Lawer et al.[2] on the longer wavelength side, but the present results show more bands in the shorter ultraviolet region. Three bands are observed along the c-axis, as Fig. 1 shows. This axis is the direction out of the benzene rings, and the charge transfer resonance interaction might occur along this axis since the electron overlap between molecules is larger for this direction (cf. Fig. 3). Three bands, at about 20000 cm^{-1}, 28000 cm^{-1} and 37000 cm^{-1}, are assigned to the intermolecular charge transfer from anthracene to TNB. The energy of the first band (2.48 eV.) is nearly in agreement with the calculated value (2.39 eV.).

The transitions to A_2'' and E″(a2) orbitals might occur in the same energy region, but their intensities will be rather smaller than to E″(s2) since the interaction matrix is smaller. The second and the third charge transfer bands might be ascribed to transitions from the second or third occupied orbital of anthracene to TNB, since the same sort of second and third charge transfer bands were observed in the case of anthracene-tetracyanoethylene complex.[13] The energy difference between the first and second band is 8000 cm^{-1} in both cases. Of course, the possibility cannot be excluded that the second and third bands arise from transitions to higher vacant orbitals of the acceptor. The band at 26500 cm^{-1} observed in the direction perpendicular to the c-axis might be ascribed to the same origin of the transition to the state observed at 27500 cm^{-1} along the c-axis, since the intensity is weaker in the direction perpendicular to the c-axis. It is remarkable that these extra charge transfer bands, which are difficult to see in a

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[11] G. Briegleb and J. Czekalla, *Z. phys. Chem., N. F.*, **24**, 37 (1960).

[12] M. Bertley and L. E. Lyons, *Nature*, **196**, 573 (1962).

[13] G. Briegleb, J. Czekalla and G. Reuss, *Z. phys. Chem., N. F.*, **30**, 316 (1961).

solution's spectra, appear distinctly in the crystal spectrum since the polarization is different from the $\pi-\pi^*$ transition of the parent molecules. Three vibrational progressions are observed even at room temperature for the 20000 cm^{-1} system, and they are in perfect agreement with the values of Lawer et al.[2)]

The electronic transitions of parent molecules will be weaker in the direction parallel to the c-axis, because the transition moment of the $\pi-\pi^*$ transition is in the plane of the benzene ring. The bands at 29800 cm^{-1} and 31300 cm^{-1} are considered to be the ^1L_a bands of anthracene shifted by the interaction with TNB. They appear at 26730 cm^{-1} in a solution and at 25400 cm^{-1} in a crystal. The calculated value mentioned in the previous section is 28500 cm^{-1} (3.55 eV.), so it explains the blue shift of the ^1L_a band.

The intensity of the charge transfer transition has been discussed by Murrell[14)] in pointing out the important contribution of the donor's local excited configuration. The transition moment integral which is proportional to the coefficients, λ_1 and δ_2, is given by Eq. 6 by neglecting the electron overlap between A and D and the ground state dipole:

$$\begin{aligned}\mu&=\int\Phi^*_{\mathrm{CT}}\mathbf{r}\Phi_{\mathrm{G}}\mathrm{d}\tau\\&=\lambda_1\langle \mathrm{D}^+\cdot\mathrm{A}^-|\mathbf{r}|\mathrm{D}^+\cdot\mathrm{A}^-\rangle+\delta_2\langle \mathrm{D}\cdot\mathrm{A}|\mathbf{r}|\mathrm{D}^*\cdot\mathrm{A}\rangle\end{aligned}\tag{6}$$

The first bracket is approximately given by a vector connecting the point charge placed on the center of the E$''$(s2) orbital of TNB and a point-positive charge placed on the center of anthracene. The vector has components about 1 Å along the [110] and 3.3 Å along the [001] directions. The second bracket denotes the transition moment of the ^1L_a state of anthracene directed along the short axis of anthracene, in a direction opposite to that of the $\mathbf{r}(\mathrm{D}^+\mathrm{A}^-)$ vector.

The intensity of the first charge transfer band has been determined by McGlynn et al. as $\varepsilon_{max}=1600$. Using the width of the half-intensity of about 4700 cm^{-1}, the oscillator strength, f, is obtained as 0.032.* By the use of this value, the magnitude of the transition moment is determined to be 0.36 Å.

The dichroic ratio observed in Fig. 1 is $D_{\mathrm{C}\parallel}:D_{\mathrm{C}\perp}=5:1$; this value may be related to the vector components in Eq. 6 as follows:

$$\frac{D_{\mathrm{C}\parallel}}{D_{\mathrm{C}\perp}}=\frac{(\lambda_1\langle \mathrm{D}^+\cdot\mathrm{A}^-|\mathbf{r}|\mathrm{D}^+\cdot\mathrm{A}^-\rangle_{\mathrm{C}\parallel})^2}{(\delta_2\langle \mathrm{D}\cdot\mathrm{A}|\mathbf{r}|\mathrm{D}^*\cdot\mathrm{A}\rangle+\lambda_1\langle \mathrm{D}^+\cdot\mathrm{A}|\mathbf{r}|\mathrm{D}^+\cdot\mathrm{A}^-\rangle_{\mathrm{C}\perp})^2}\tag{7}$$

If we use values of $\lambda_1=0.09$—0.10 and $\lambda_2=0.33$, then the calculated value is in agreement with the observed values. The value of λ_1 determined from these results is nearly twice as large as the value estimated in the previous section; this discrepancy might be ascribed to uncertainity in the estimation of the integral in Eq. 2, to the point charge approximation for the $\mathbf{r}(\mathrm{D}^+\cdot\mathrm{A}^-)$ vector, and to the deviation of the intensity from the oriented gas model of the crystal.

(3) The Fluorescence Spectrum.—The fluorescence spectrum of the TNB-anthracene system has been ascribed to the reverse process of the charge transfer absorption.[3,4)] The shift of the 0–0 band from absorption to emission (Franck-Condon gap) is 1700 cm^{-1} in this experiment, while a value of 7000 cm^{-1} was given by McGlynn et al.[4)] The 0–0 emission band may clearly be seen at the temperature of liquid helium.

The fluorescence spectrum shown in Fig. 2 exhibits some unusual characteristics in that the shape of the bands changes markedly with a change in temperature and in that the dichroic ratio is reduced from that of the absorption. The change in the dichroic ratio cannot be understood unless we have assumed a change in the fluorescence state or configuration from that of the absorption. The big change in emission shape caused by the change in temperature will be due to a frequent thermal motion in a shallow potential, which will lead to the reduction of the vibrational overlap integral for the 0–0 transition in the Franck-Condon integral.

The relatively larger shift of the fluorescence of 1700 cm^{-1} will be ascribed to the shortening of the molecular separation after the excitation, since the potential for the excited state is lower in energy at a shorter distance. However, if we ascribe the shift solely to an increase in electrostatic stabilization caused by closing, it will require an unreasonably larger value of the shortening of 0.43 Å to explain the 1700 cm^{-1} shift. Therefore, it is most reasonable that the interaction term in Eq. 3 increases rapidly when the molecular separation is closed. In fact, the overlap integral increases for the excited state from -0.025 to -0.035 by a shortening of 0.20 Å, and this may correspond to an increase in the integral from -0.40 eV. to -0.56 eV. by assuming a proportionality of the energy to the overlap

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[14)] J. N. Murrell, *J. Am. Chem. Soc.*, **81**, 5037 (1959).

* This value is smaller than the value suggested by Briegleb. We have used as a formula for oscillator strength:

$$f=4.32\times10^{-9}\int\varepsilon_\nu \mathrm{d}_\nu$$

integral. By the use of the electrostatic energy at 3.1 Å of 3.09 eV., the excited state wave functions are given as follows:

$$\begin{aligned}&2.19\,\text{eV.}: 0.905\varphi(\mathrm{D}^+\cdot\mathrm{A}^-)+0.42\varphi(\mathrm{D}^*\cdot\mathrm{A})\\&3.67\,\text{eV.}: 0.42\varphi(\mathrm{D}^+\cdot\mathrm{A}^-)-0.905\varphi(\mathrm{D}^*\cdot\mathrm{A})\end{aligned}\qquad(8)$$

The excited state is stabilized about 1600 cm^{-1} by this interaction. Of course, the repulsive potential in the ground state might be responsible for some part of the shift of the fiuorescence.

Equation 8 involves a larger contribution of the $\varphi(\mathrm{D}^*\cdot\mathrm{A})$ state. The dichroic ratio for this emission is calculated, by using Eq. 7 as:

$$D_{\mathrm{C}\parallel} : D_{\mathrm{C}\perp}=1.5 : 1.0$$

The observed value is 1.2 : 1.0 at the temperature of liquid nitrogen, and 1.4 : 1.0 at the temperature of liquid helium. The calculated value is nearly in agreement with the observed values.

Therefore, the molecules in the complex are considered to be displaced to a closer position by about 0.2 Å after the excitation, the 0–0 state is stabilized about 1700 cm^{-1}, and the dichroic ratio is changed from 5 : 1 in absorption to 1.4 : 1 in fluorescence by an increase of the component of the locally-excited $^1\mathrm{L_a}$ state of anthracene. The shallow intermolecular potential for this molecular motion is reflected in the emission spectrum at room temperature, where the 0–0 band decreases in intensity. The vibrational progression of 1300 cm^{-1} might be due to a skeletal vibration of TNB coupled with intermolecular vibration.

Summary

The electronic absorption and fluorescence spectra of the single crystal of the anthracene-*s*-trinitrobenzene complex have been measured, and the polarization property of electronic transitions has been discussed in terms of interaction between the no-bond structure, the charge transfer and the locally-excited state of anthracene.

It has been shown that molecules in a pair are displaced to a closer position after the excitation, whereby the mixing of the donor-excited level occurs more than in the ground state (Frank-Condon state), and the fluorescence involves a larger contribution from the in-plane transition of anthracene.

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