Charge-Transfer Bands of the Mixed Molecular Complex, (Anthracene)$_{1-x}$(Phenanthrene)$_x$(1,2,4,5-Tetracyanobenzene)

John D. WRIGHT,* Toshiaki OHTA, and Haruo KURODA

Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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A series of crystalline mixed molecular complexes of composition, (anthracene)$_{1-x}$(phenanthrene)$_x$(TCNB), with $0.17 \leq x \leq 0.63$, has been prepared from solutions containing mixtures of the three components. A linear relationship is observed between solution and solid composition, and the melting point data and powder X-ray diffraction patterns suggest the formation of a continuous series of mixed molecular complexes of closely related crystal structure. Polarized crystal spectra of these crystals show two charge-transfer bands characteristic of the interaction between anthracene and TCNB and that between phenanthrene and TCNB, respectively. Their intensity ratio is linearly dependent on composition, and constant for different crystals of the same composition. Discussion is given on these results by using the results of semi-empirical SCF-MO-CI calculations on the three-molecule model, anthracene/TCNB/phenanthrene.

Although physical properties of mixed molecular crystal composed of aromatic hydrocarbons have been widely studied, relatively little work has been reported[1,2] on crystals of mixed molecular complexes of the type (Donor 1)$_x$(Donor 2)$_{1-x}$(Acceptor). Extensive studies of the crystal structures of molecular complexes suggest that the relative orientation of donor and acceptor is influenced by lattice packing requirements in addition to intermolecular attractive forces.[3] Therefore, for a given donor/acceptor pair, the relative orientation of the donor and acceptor molecules can be different from the one found in the crystal of the pure molecular complex, if the pair is incorporated in the crystal lattice of mixed molecular complex. Thus, one could examine the effects of relative orientation of donor and acceptor on charge-transfer interaction by comparing the structures and properties of the crystals of mixed molecular complexes with those of pure molecular complexes.

The present work is an investigation of the crystal spectra and other physical properties of the mixed molecular complex system which involves anthracene and phenanthrene as the donors and 1,2,4,5-tetracyanobenzene (TCNB) as the acceptor, undertaken primarily to elucidate the nature of this mixed complex system. We were able to confirm that anthracene–TCNB and phenanthrene–TCNB complexes form a homogeneous solid-solution over the whole composition range. Discussion will be given on the nature of the charge-transfer bands which were observed in the single crystals of mixed molecular complexes.

Experimental

Anthracene was purified by chromatography and multiple zone refining. Phenanthrene, purified by successive treatment with maleic anhydride, KOH and sodium, followed by sublimation and multiple zone-refining,[4] was kindly supplied by Professor Y. Matsunaga. TCNB was synthesized from pyromellitic dianhydride,[5] and purified by recrystallization and sublimation. Crystals of the anthracene–TCNB and phenanthrene–TCNB (pure) complexes were grown by slow cooling of glacial acetic acid and 2-methoxyethanol solutions, respectively, containing 100 mg of each component in 5 ml of solvent. Crystalline powders of the apparent compositions, (anthracene)$_x$(phenanthrene)$_{1-x}$(TCNB) with $0.17 \leq x \leq 0.63$, were obtained from 2-methoxyethanol solutions containing 100 mg TCNB with varying ratios of anthracene and phenanthrene. The anthracene and phenanthrene contents of those powders were determined by ultraviolet spectrophotometry of their ethanol solutions: The optical densities of several solutions of different known concentrations in ethanol were measured at 356, 339, and 282 nm, for each sample of mixed complex, using a Hitachi EPS-3 recording spectrophotometer, and the data were interpreted assuming 1 : 1 mol ratio of (phenanthrene+anthracene)/TCNB, using previously determined values of the extinction coefficients of anthracene, phenanthrene and TCNB at these wavelengths.

X-Ray powder diffraction patterns were recorded for all samples using a diffractometer, Geigerflex, quartz being used as the internal standard. Differential scanning calorimetry (DSC) was carried out by means of a Rigaku TG-DSC apparatus on powdered samples sealed in small aluminium capsules.

The polarized absorption spectra in the visible region, were measured on small plate crystals, typically 20×10 μ in size and less than 1 μ thick, by using a microspectrophotometer, Olympus MSP-IV. The details of the apparatus and the procedures of measurement were described elsewhere.[6]

Results and Discussion

Structural Aspects of the Mixed Molecular Complex. The anthracene/phenanthrene ratio of a crystalline powder of mixed complex varied depending on the anthracene/phenanthrene ratio initially mixed in the solution from which the sample was prepared. In Fig. 1, we have plotted the mol fraction of anthracene, $x = [\text{anthracene}]/\{[\text{anthracene}]+[\text{phenanthrene}]\}$, in the powder sample against the corresponding value for the solution. This plot shows a linear relationship, indicating that anthracene and phenanthrene form a continuous series of mixed molecular complexes with TCNB, with no particularly stable phase of fixed stoichiometric ratio of two donors.

In Fig. 2, the melting point is plotted against the composition. Accurate determination of melting point was not possible because of the thermal decomposition which was apparent at temperatures far below the melting point. The data shown in Fig. 2 were obtained by means of a conventional method of melting-point measurement with visual observation using a rapid heating

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* On leave from University of Kent at Canterbury, Canterbury, Kent CT2 7NH, U. K.

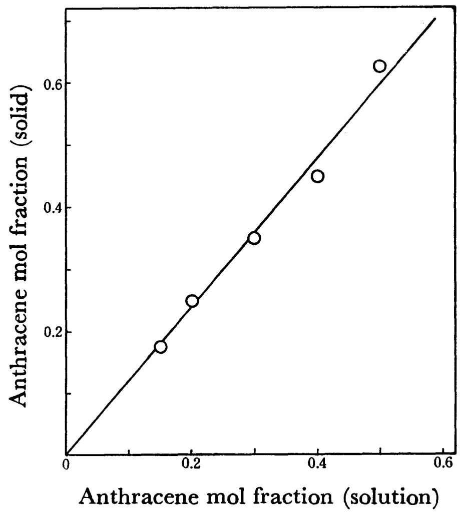

Fig. 1. Mol fraction of anthracene of mixed crystalline complexes, $(\text{Anthracene})_x(\text{phenanthrene})_{1-x}(\text{TCNB})$, as a function of composition of the solutions used to obtain the complexes.

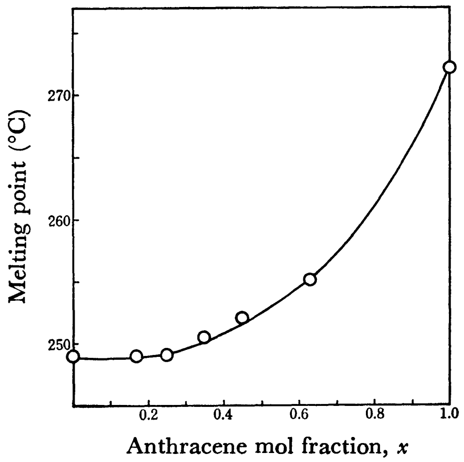

Fig. 2. Dependence of melting point on composition.

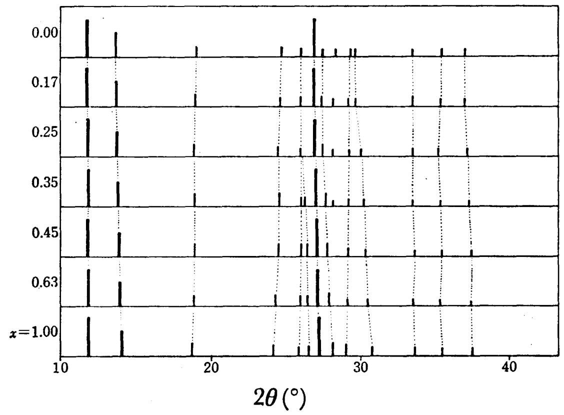

Fig. 3. X-Ray powder diffraction patterns of mixed complexes.

condition to minimize thermal decomposition. For each sample, melting occurred rapidly over a temperature range of about 1 °C, suggesting that all crystals in a given sample of mixed complex have almost identical composition. The plot of melting point *vs.* composition is a smooth curve, as shown in Fig. 2, with no evidence for a eutectic. None of the samples of (anthracene, phenanthrene)/TCNB showed any indication of a phase transition in their DSC curves, at least in the range above room temperature. Melting point can be determined also from DSC curves. The melting point data obtained by this method were 2—4 °C higher than those shown in Fig. 2, but their dependence on composition was essentially the same as found for the latter.

The X-ray powder diffraction patterns of mixed complexes and those of the two pure complexes are all very similar (see Fig. 3). Although the positions and intensities of several diffraction peaks are dependent on the composition, they vary continuously with the anthracene/phenanthrene ratio without showing any indication of discrete change of crystal lattice. We can also conclude from the X-ray powder diffraction patterns that each powder sample of mixed complex in a given preparation is composed of crystals of almost uniform composition and structure.

All of the results mentioned above indicate that the $(\text{anthracene})_x(\text{phenanthrene})_{1-x}(\text{TCNB})$ system is indeed a homogeneous solid solution over the whole composition range, $0 \leq x \leq 1$.

The crystal structure of anthracene–TCNB complex was determined by Tsuchiya *et al.*[7] The crystal is monoclinic with space group Cm, the lattice parameters being $a=9.505$ Å, $b=12.748$ Å, $c=7.417$ Å, and $\beta=92.45°$. Anthracene and TCNB molecules are alternately stacked on each other to form molecular columns parallel to the c-axis. It was pointed out that there exists a disorder concerning the orientation of anthracene molecule; Anthracene molecules are taking, with equal probability, one of the two orientations rotated by $\pm 8.6°$ within their molecular plane from the mean position. We are currently determining the crystal structure of phenanthrene–TCNB complex. The crystal data have been found to be as follows: monoclinic with possible space group $C2/m$ or $C2$ and the lattice parameters, $a=9.413$ Å, $b=13.104$ Å, $c=7.260$ Å, and $\beta=93.06°$. Phenanthrene and TCNB molecules are alternately stacked along the c-axis and phenanthrene molecules are disordered so as to conform to the apparent site symmetry required for the space groups mentioned above. Thus the crystal lattice of phenanthrene–TCNB is very similar to that of anthracene–TCNB. This similarity of lattice structures suggests that the donor sites in the mixed complexes can be occupied with equal facility by anthracene or phenanthrene, and this may be a requirement for the formation of a continuous series of mixed molecular complexes.

Crystal Spectra of Anthracene–TCNB and Phenanthrene–TCNB. The polarized absorption spectra of single crystals of the two pure complexes are shown in Fig. 4.[8] In the crystal spectrum of anthracene–TCNB (Fig. 4a), the first absorption band at $20.5 \times 10^3\ \text{cm}^{-1}$ is almost completely polarized in the direction parallel to the c-axis, along which anthracene and TCNB are alternately stacked on each other. This absorption band can be assigned to the charge transfer from the highest occupied orbital of anthracene to the lowest vacant orbital of

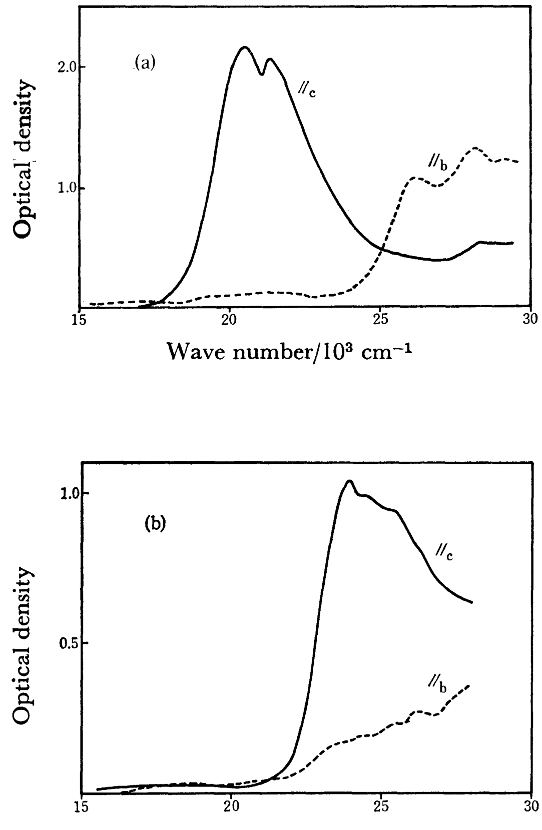

Fig. 4. Polarized absorption spectra of single crystals of pure complexes; (a) Anthracene–TCNB, (b) Phenanthrene–TCNB

TCNB. Incidentally, the corresponding charge-transfer band appears at 20.1×10^3 cm^{-1} in the case of the anthracene–TCNB (1:1) complex in chloroform solution.[9] In the crystal spectrum shown in Fig. 4a, there is another absorption band, polarized in the b-axis direction in the region above 25×10^3 cm^{-1}. This absorption band can be attributed to the local-excitation band mainly associated with the $^1B_{2u}\leftarrow{}^1A_g$ (short-axis polarized) transition of anthracene. Since the short-axis of the anthracene molecule is almost parallel to the b-axis, the above absorption band is expected to be strongly polarized in the b-axis direction. This is consistent with the observed results.

In the case of phenanthrene–TCNB, only one absorption band is found in the observed region (below 28×10^3 cm^{-1}) of crystal spectrum (see Fig. 4b). This absorption band shows its maximum at 23.8×10^3 cm^{-1}, and is strongly polarized in the c-axis direction. Since no local-excitation band is expected to appear in this region, we can safely attribute it to a charge-transfer band. The phenanthrene–TCNB (1:1) complex in chloroform solution exhibits a charge-transfer band at 25.0×10^3 cm^{-1}.[9] When it is compared with the charge transfer band of the anthracene–TCNB (1:1) complex in chloroform solution, the energy difference between them, 0.41 eV, closely agrees with the difference of the first ionization potentials of phenanthrene and anthracene, which have been determined as 7.86 and 7.47 eV, respectively, by means of photoelectron spectroscopy.[10] Thus the 25.0×10^3 cm^{-1} band of the solution spectrum of phenanthrene–TCNB complex can be assigned to the charge transfer from the highest occupied orbital of phenanthrene to the lowest vacant orbital of TCNB, although, in phenanthrene, the second highest occupied orbital is located rather close to the highest occupied orbital. Seemingly, the 23.8×10^3 cm^{-1} band of the crystal of phenanthrene–TCNB complex is also attributable to the charge transfer from the highest occupied orbital of phenanthrene to TCNB.

In measuring the crystal spectra of anthracene–TCNB and phenanthrene–TCNB complexes, we noted that the extinction coefficient of the charge-transfer band is very much lower in the latter than in the former, although we were not able to carry out a quantitative comparison because of the difficulty of determining crystal thickness. As we will describe later, this was confirmed to be the case from the studies of the crystal spectra of mixed molecular complexes.

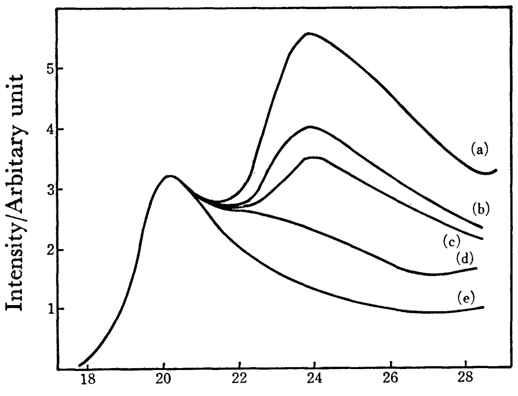

Fig. 5. Charge-transfer bands in the single-crystal spectra of mixed complexes, (Anthracene)$_x$(Phenanthrene)$_{1-x}$(TCNB); (a) $x=0.17$, (b) $x=0.25$, (c) $x=0.35$, (d) $x=0.45$, (e) $x=0.63$.

Charge-transfer Bands of Mixed Complexes. The crystals of mixed complexes all show broad absorption bands extending from 18×10^3 to 28×10^3 cm^{-1}, when the spectra are measured with light polarized parallel to the elongated direction of crystal, which is the crystal axis along which donor and acceptor molecules are alternately stacked on each other. The observed spectra are shown in Fig. 5, where the ordinate (optical density) has been scaled so that all spectra coincide in the region of the first absorption maximum (at about 20×10^3 cm^{-1}). As can be seen in Fig. 5, the observed spectra exhibit two absorption maxima, one at about 20×10^3 cm^{-1} and the other at about 24×10^3 cm^{-1}, and their intensity ratio varies as a function of anthracene/phenanthrene ratio. We have confirmed that the above intensity ratio is almost the same for all crystals in a given preparation of mixed complex. The intensity ratios observed for three different crystals taken from the crystalline powder whose apparent composition is (anthracene)$_{0.25}$(phenanthrene)$_{0.75}$(TCNB), agreed within 5%, indicating that the composition of the crystals in any given preparation is indeed uniform.

The positions of the two absorption maxima mention-

Table 1. Intensity ratios of the two charge-transfer bands in the crystal spectra of mixed complexes, (Anthracene)$_x$-(Phenanthrene)$_{1-x}$(TCNB)

Composition x	Melting point [°C]	Intensity ratio[a] I_2/I_1
0.17	249	1.47
0.25	249	0.94
0.35	251	0.82
0.45	252	0.38
0.63	255	0.18

a) I_1 and I_2 are the integrated intensities of the 20×10^3 cm^{-1} and 24×10^3 cm^{-1} bands, respectively (see text).

ed above correspond closely to those of the first charge-transfer bands of the two pure complexes. This fact, together with the dependence of their intensity ratio on composition, suggests that the 20×10^3 cm^{-1} maximum is due to the charge transfer from anthracene to TCNB, and the 24×10^3 cm^{-1} maximum is due to the charge transfer from phenanthrene to TCNB. The observed charge-transfer bands of the mixed complexes can be reproduced well by superposing the charge-transfer bands of the crystals of the two pure complexes, assuming an appropriate intensity ratio. Table 1 includes the intensity ratios of the two bands of mixed complexes, obtained by the graphical decomposition of observed spectra.

If we assume that the intensities of the two charge-transfer bands of a mixed complex are simply proportional to the probabilities of finding anthracene/TCNB and phenanthrene/TCNB pairs in the crystal, the following relation is expected for the intesnity ratio,

$$\frac{I_2}{I_1} = \frac{I_{\text{phen/TCNB}}}{I_{\text{anth/TCNB}}} \cdot \frac{1-x}{x} \tag{1}$$

where I_1 and I_2 are the intensities of the bands at 20×10^3 and 24×10^3 cm^{-1}, respectively, and $I_{\text{anth/TCNB}}$ and $I_{\text{phen/TCNB}}$ are the constants corresponding to the extinction coefficients of the charge-transfer bands of anthracene/TCNB and phenanthrene/TCNB pairs, respectively. In Fig. 6, we have plotted the observed intensity ratio against $(1-x)/x$. The points can be fitted well by a single straight line, showing that the intensity ratio is actually proportional to the phenanthrene/anthracene ratio, with $I_{\text{phen/TCNB}}/I_{\text{anth/TCNB}}=0.3$.

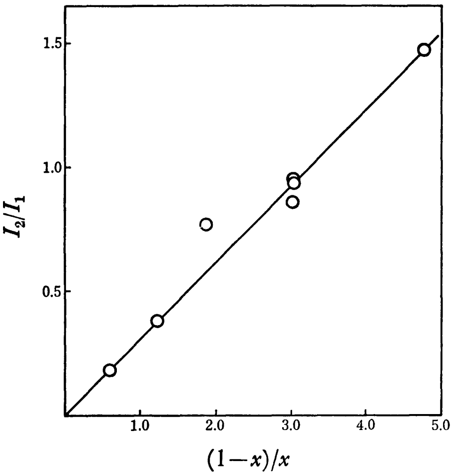

Fig. 6. Intensity ratio of the two charge transfer bands as a function of mol ratio of the two donors.

Molecular-orbital Calculations. Since the oscillator strength of a charge-transfer transition is usually quite small, charge-transfer excitons in a molecular complex crystal can be regarded as rather localized in nature, so that one may neglect the effects of long-range interaction between them. However, it should be noted that, in the crystal of mixed complex, there are sites where an acceptor molecule is sandwiched between two different donors, and, at those sites, the charge-transfer states associated with the two donors could appreciably interact with each other. Therefore, a crystal of mixed molecular complex could exhibit charge-transfer bands considerably different from those observed in pure complexes. However, the crystals of mixed complexes show two charge-transfer bands corresponding very well to those of anthracene–TCNB and phenanthrene–TCNB complexes, and their intensity ratio is simply proportional to the anthracene/phenanthrene ratio.

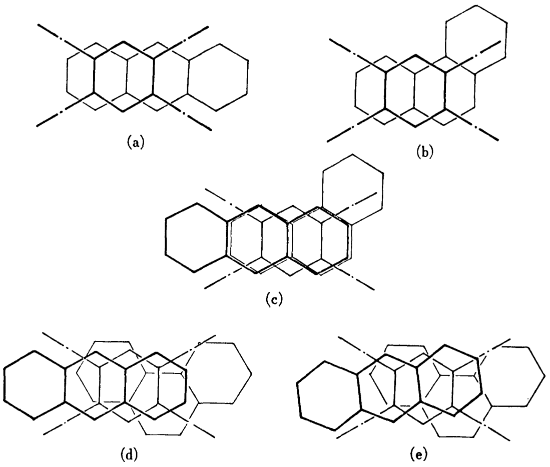

Fig. 7. Relative orientations of donor and acceptor, assumed for the models used in MO calculations. (The mean interplanar spacing between electron donor and acceptor molecules is 3.43 Å in all cases).

In order to examine the nature of charge-transfer bands of the crystals of (anthracene, phenanthrene)/TCNB mixed complexes, we carried out molecular-orbital calculations. Since the main purpose is to examine the short-range interactions of donor and acceptor molecules, calculations were made on simplified models, which are the three-molecule system, anthracene/TCNB/phenanthrene, and the two-molecule systems, anthracene/TCNB and phenanthrene/TCNB. The relative arrangements of donor and acceptor molecules assumed for these models are shown in Fig. 7. For the anthracene/TCNB pair (Fig. 7(a)) the relative orientation and mean separation were taken as those found in the crystal structure analysis of anthracene-TCNB complex, with the anthracene molecule occupying a position corresponding to the mean of the observed disordered arrangement. A model for the phenanthrene/TCNB pair (Fig. 7(b)) retained an orientation of TCNB relative to two of the aromatic rings of phenanthrene similar to that in the crystal of anthracene–TCNB complex, with the same intermolecular spacing. The first trial model for anthracene/TCNB/phenanthrene (the model (c) in Fig. 7) consists of a combination of the models (a) and (b). However, since the experimental data suggest that anthracene and phenanthrene can be readily interchanged without appreciably disturbing the crystal lattice, two further models (d) and (e) (see Fig. 7) were adopted, in which phenanthrene molecule was rotated and translated so as to occupy a space as similar as possible to that occupied by the anthracene molecule. The two models, (d) and (e), differ only in that the latter contains anthracene occupying one of its extreme positions in the disordered model, rotated in the molecular plane by 8.6° from the orientation in model (d). Seemingly, model (e) is the most realistic one for the relative arrangement of molecules in the crystal of mixed complex.

We carried out calculations on the models described above, by the semiempirical molecular orbital method which was essentially the same as that previously described by Ohta, Kuroda, and Kunii,[11] but extended to permit calculation of a three-molecule system. In this calculation, the orbitals of the system composed of three molecules, D_1, A, and D_2, are calculated as linear combinations of 2p AO's of the atoms in the system as follows;

$$\phi_i = \sum_{\mu}^{(D_1)} c_{i\mu}\phi_\mu + \sum_{\mu'}^{(A)} c_{i\mu'}\phi_{\mu'} + \sum_{\mu''}^{(D_2)} c_{i\mu''}\phi_{\mu''} \tag{2}$$

where the first, second and third summations are those over the AO's in D_1, A and D_2, respectively. In order to see the character of each orbital, we calculated the following quantities;

$$D_1^{(i)} = \sum_{\mu}^{(D_1)} c_{i\mu}^2, \quad A^{(i)} = \sum_{\mu'}^{(A)} c_{i\mu'}^2, \quad D_2^{(i)} = \sum_{\mu''}^{(D_2)} c_{i\mu''}^2 \tag{3}$$

These show the contribution of each molecule in the i-th orbital of the system. The results of the calculation on model (e) are partly listed in Table 2. It should be noted that the highest three occupied orbitals are strongly localized on one of the three constituent molecules, although deeper occupied orbitals are considerably delocalized over the whole system. We can see also that vacant orbitals are localized on individual molecules. Similar results were obtained for other models.

Table 2. Characters of molecular orbitals of the three-molecule system, anthracene/TCNB/phenanthrene (Model (e))

Orbital number	Character of MO's[a]				Orbital energy (eV)
	TCNB	Anthracene	Phenanthrene		
12	0.133	0.615	0.253	Occupied	−11.924
13	0.117	0.315	0.568		−11.395
14	0.202	0.321	0.477		−10.757
15	0.131	0.414	0.455		−10.217
16	0.567	0.170	0.263		−9.939
17	0.052	0.923	0.024		−9.711
18	0.328	0.489	0.183		−9.666
19	0.027	0.002	0.971		−9.037
20	0.014	0.006	0.980		−8.655
21	0.034	0.958	0.008		−8.120
22	0.951	0.035	0.014	Vacant	−3.763
23	0.949	0.039	0.013		−2.868
24	0.902	0.060	0.038		−2.656
25	0.082	0.912	0.005		−2.310
26	0.957	0.006	0.037		−1.808
27	0.062	0.003	0.935		−1.693
28	0.043	0.001	0.957		−1.362
29	0.013	0.986	0.001		−0.965
30	0.837	0.126	0.037		−0.834
31	0.120	0.876	0.004		−0.713

a) Defined by Eq. 3 in the text.

We calculated the transitions in the three-molecule system by taking into account the lowest forty singly-excited configurations in the configuration interaction calculation. The results obtained for charge-transfer transitions using different models are compared in Table 3. For the three models of anthracene/TCNB/phenanthrene, (models (c), (d), and (e) of Fig. 7), the calculations gave nearly the same results. In all cases, the lowest-energy transition is predicted at 17.1×10^3—17.7×10^3 cm^{-1} with the character almost entirely associated with the charge transfer from the highest occupied orbital of anthracene to the lowest vacant orbital of TCNB, and the next transition is predicted at about 21×10^3 cm^{-1} with the character of the charge transfer from the highest occupied orbital of phenanthrene to the lowest vacant orbital of TCNB. There is little interac-

Table 3. Energies and oscillator strengths of charge-transfer bands, obtained from the calculations for different models

Model[a]	$\bar{\nu}$ 10^3 cm^{-1}	f[b]	Contribution of HOMO(A)→LUMO(T)[c] %	$\bar{\nu}$ 10^3 cm^{-1}	f[d]	Contribution of HOMO(P)→LUMO(T)[e] %
(a)	17.13	0.155(0.144)	97.9			
(b)				20.64	0.055	97.4
(c)	17.72	0.174(0.161)	97.9	21.57	0.041	97.2
(d)	17.45	0.164(0.155)	97.9	21.11	0.024	97.6
(e)	17.12	0.146(0.133)	98.0	20.99	0.028	97.1

(a) See Fig. 7. b) The transition moment of this transition has a small component (5—10%) parallel to the short-axis of anthracene molecule. The oscillator-strength component perpendicular to the molecular plane is given in the parenthesis. c) Contribution of the charge transfer from HOMO of anthracene to LUMO of TCNB, estimated by the procedure given in Ref. 11. d) The component parallel to the molecular plane is negligible. e) Contribution of the charge transfer from HOMO of phenanthrene to LUMO of TCNB.

tion between these two charge-transfer states.

Since model (c) has been formed simply by combining model (a) of the anthracene/TCNB pair and model (b) of the phenanthrene/TCNB pair, it is interesting to compare the results obtained for model (c) with those obtained separately for models (a) and (b). We can see in Table 3, that the two charge-transfer transitions predicted for model (c) of the anthracene/TCNB/phenanthrene very closely correspond to the charge-transfer transition predicted for the anthracene/TCNB pair and that for the phenanthrene/TCNB pair, respectively, although there are small differences as regards the predicted energies and oscillator strengths.

All of the results of the above calculations suggest that the nature of charge-transfer transitions in the mixed complex system should not differ appreciably from those found in the crystals of pure complexes.

Table 4. $I_{\text{phen·TCNB}}/I_{\text{anth·TCNB}}$ estimated from the calculations on the two- and three-molecule models

	$I_{\text{phen·TCNB}}/I_{\text{anth·TCNB}}$
Model (b)/Model (a)	0.38
Model (c)	0.25
Model (d)	0.15
Model (e)	0.20
Expl.	0.30

The intensity ratio of the two charge-transfer bands of anthracene/TCNB/phenanthrene system can be calculated from the predicted oscillator strengths. As shown in Table 4, the predicted ratios[12] fall in the range of 0.15—0.25. If the intensity ratio is estimated by using the results calculated separately for the anthracene/TCNB and phenanthrene/TCNB pairs, (models (a) and (b) of Fig. 7), it becomes 0.38, which is a little larger than the values obtained by the calculations on the three-molecule models. The intensity ratios mentioned above correspond to $I_{\text{phen/TCNB}}/I_{\text{anth/TCNB}}$ in Eq. 3. As we have already mentioned, we obtained 0.3 as the experimental value of $I_{\text{phen/TCNB}}/I_{\text{anth/TCNB}}$ from the observed linear relationship between intensity ratio of two charge-transfer bands and composition of mixed complex. This experimental value is in reasonable agreement with the results of calculations.

Conclusion. The studies reported above show that anthracene and phenanthrene form a particularly ideal series of mixed molecular complexes with TCNB. This may be a consequence of the similar overall size of the three molecules. One interesting consequence of this ideality of (anthracene, phenanthrene)/TCNB solid solution is that it is possible to introduce a large amount of second donor, having different electronic properties, into the crystal lattice of a molecular complex without introducing appreciable lattice perturbations. In this respect the crystals of (anthracene, phenanthrene)/TCNB mixed complex seem to be of particular interest for the purpose of investigating energy transfer and electron transfer in molecular crystals. Studies of the electrical conductivity of this mixed molecular complex are now planned from the above point of view.

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12) These are the values obtained by using the oscillator-strength components perpendicular to the molecular plane.