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Polarized Absorption Spectra of TCNNQ-Aromatic Hydrocarbon Molecular Complexes

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Polarized absorption spectra of TCNNQ and TCNNQ-anthracene, pyrene, phenanthrene (Group 1), 1,2-benzanthracene, chrysene and triphenylene (Group 2) molecular complexes were measured in the frequency range of 13.5—42 kK at room temperature and 80°K. The mole ratio of donor to acceptor was found to be 2 : 1 for Group 1 complexes and 1 : 1 for Group 2 complexes. Two broad bands observed in each spectrum of these complexes were assigned to be the first and the second charge-transfer (CT) bands. The CT bands were enhanced in intensity and displaced to the red at 80°K. The first CT bands were confirmed to be associated with the charge transfer from the highest occupied molecular orbital (HOMO) of donor to the lowest vacant molecular orbital (LVMO) of acceptor. The charge transfer mechanism for the second CT bands may be divided into two classes; for Group 1 complexes it is mainly due to the second LVMO of acceptor, while for Group 2 complexes, in addition to this, there is a possibility of the charge transfer from the second HOMO of donor to the LVMO of acceptor.

TCNNQ (11,11,12,12-tetracyano-1,4-naphthaquinodimethane) is a new cyanocarbon acceptor with the electron affinity 1.49 eV and is known to form sufficiently strong charge-transfer π-complexes with aromatic hydrocarbons.[2] In a previous paper,[2] we have presented a preliminary survey on the polarized absorption spectra of the molecular complexes which involve TCNNQ as an acceptor and anthracene, pyrene, phenanthrene, 1,2-benzanthracene, chrysene

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[1] S. Chatterjee, *J. Chem. Soc.*, *B*, **1967**, 1170.

[2] Y. J. I'Haya, T. Yunoki, and N. Suzuki, This Bulletin, **43**, 3636 (1970).

and triphenylene as donors. We have shown that the second charge-transfer (CT) bands of these complexes are mainly associated with a charge transfer from the highest occupied molecular orbital of donor to the *second* lowest vacant molecular orbital of acceptor.

In the present communication, we shall report the details of the polarized absorption spectra of TCNNQ and these TCNNQ molecular complexes observed at room temperature and liquid nitrogen temperature. To the authors' knowledge, there has been published no spectral datum of CT bands of a molecular complex observed at such a low temperature. We shall show that CT bands enhance their spectral intensities and disclose their vibrational structures at liquid nitrogen temperature. Using the low-temperature data, we re-examine the relationships between charge-transfer transition energies and highest occupied molecular orbital energies of donors.

Experimental

TCNNQ was synthesized by Chatterjee's method,[1] and purified by repetitive recrystallization from methanol and methylene chloride, followed by vacuum sublimation. Anthrancene, pyrene, phenanthrene, 1,2-benzanthracene, chrystene and triphenylene used as electron donors were of reagent grade from commercial sources and they were purified by recrystallization and sublimation. The molecular complex single crystals of microscopic size were prepared from the purified TCNNQ and donors by simultaneous sublimation onto a heated glass plate.

The absorption spectra of TCNNQ and its molecular complexes in solution were measured in methylene chloride by a JASCO ORD/UV-5 spectrophotometer. The mole ratio of donor to acceptor in each molecular complex was determined spectroscopically.

The polarized absorption spectra were measured with a specially designed microspectrophotometer. A 500 W high pressure xenon-arc lamp (Ushio Electric Co.) was used as a light source, which was operated with a 20A stabilized power supply. The light was passed through a grating monochrometer (Hitachi model 139), polarized by a Rochon prism, and focused onto a sample crystal mounted on a sample holder. The sample crystals, selected from among a number of sublimation flakes, were mounted between quartz objective slides which edges were sealed by Araldite cement in order to avoid sublimation of samples. The sample holder and two objectives of reflection type (Olympus Optical Co.) were set in a cryostat which had two cryogen containers. The section of the cryostat is shown in Fig. 1. Sample temperatures were measured with a copper-constantan thermocouple while spectra were being taken. An R-136 photomultiplier tube (Hamamatsu Television Co.) was used as the detector.

The directions of crystal axes were examined by the observation under a polarizing microscope. The crystal thickness was roughly estimated from birefringence and retardation using the polarizing microscope. The crystal spectra were observed from the direction normal to the developed face of a crystal for two polarizations, parallel and perpendicular to the crystal elongated axis which we hereafter call the *l*-axis. To each molecular complex, the spectral measurements were carried out for several crystals of different thicknesses. The position of each absorption maximum was found to be not dependent upon crystal thickness.

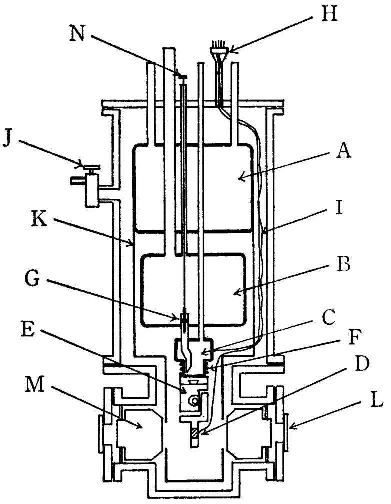

Fig. 1. Cryostat for Microspectrophotometry. A: Liquid nitrogen can; B,C: Liquid nitrogen or helium can; D: Sample holder; E: Vertical adjusting gear; F: Heater; G: Cryogen dropping valve; H: Connector; I: Thermocouple; J: Exhaust valve; K: Radiation shield; L: Fused quartz window; M: Reflection-type objective; N: Pin valve.

Results

1. *Crystal and Solution Spectra of TCNNQ.* The TCNNQ crystal is orthorhombic, space group *Pbca* with cell dimensions of a=13.210 Å, b=7.209 Å, and c=26.629 Å, eight molecules being contained in the unit cell. Fig. 2, the projection along the a-axis, shows that the TCNNQ molecule is non-polar in the crystal.[3] We have observed the b-axis and c-axis polarized spectra as well as the a- and b- polarized spectra, since we found the presence of two different crystal habits. They are shown in Figs. 3 and 4 together with the solution spectrum.

The solution spectrum in methylene chloride consists of two main bands, each having a few vibrational structures which maxima are estimated to be located at 25.3 kK (ε=33,000) and 34.7 kK (ε=6,900). Higher frequency bands have been observed at 45.2 kK and 48.1 kK.[4]

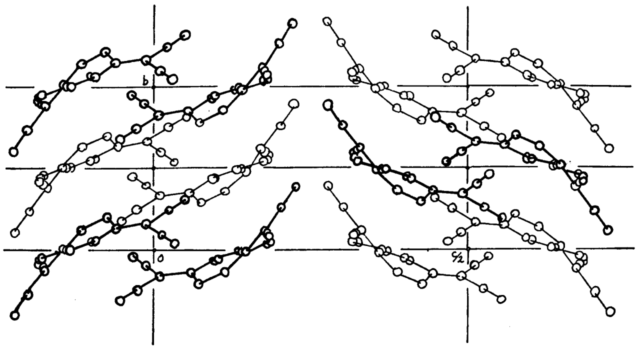

Fig. 2. Projection of the crystal structure of TCNNQ along the a-axis on the bc plane.

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[3] F. Iwasaki, private communication.

[4] N. Suzuki and Y. J. I'Haya, *Tetrahedron*, **26**, 5379. (1970).

The *a*-axis polarized spectrum in Fig. 3 has two absorption bands; one at 33.8 kK is rather narrow and the other in the 22—27 kK region is quite broad. The *b*-axis polarized spectrum in the same figure has one narrow band at 31.2 kK with an weak shoulder at 25.6 kK.

In the *bc*-face spectra (Fig. 4), the *b*-axis polarized spectrum has a peak at 30.9 kK and a weak shoulder at 26.0 kK, while the *c*-axis polarized spectrum has two peaks at 22.9 kK and 33.6 kK and a shoulder at 25.1 kK.

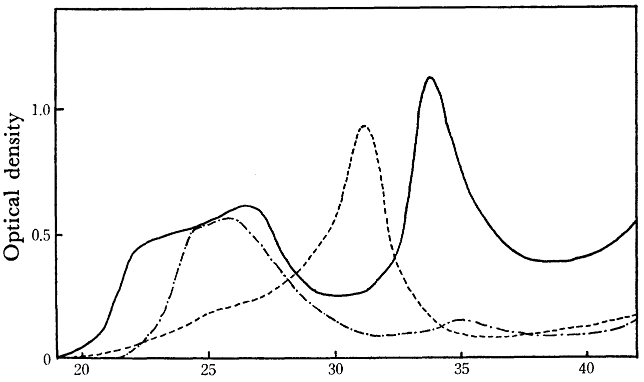

Fig. 3. Polarized absorption spectra of TCNNQ crystal observed from the *c*-axis at room temperature.
(—•—•— solution spectrum in methylene chloride)

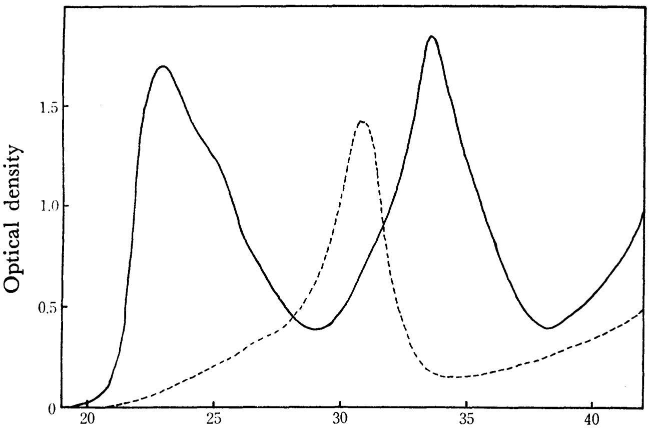

Fig. 4. Polarized absorption spectra of TCNNQ crystal observed from the *a*-axis at room temperature.

At liquid nitrogen temperature, we have not found any significant change in the overall spectrum of each polarization.

2. Composition and Solution Spectra of Molecular Complexes. The mole ratio of donor to acceptor was found to be 2 : 1 for anthracene-, pyrene-, and phenanthrene-TCNNQ complexes, while that for 1,2-benzanthracene-, chrysene-, and triphenylene-TCNNQ complexes was 1 : 1. The former is called Group 1 complexes and the latter Group 2 complexes in the following.

Measurement of the CT bands in a solution spectrum of each molecular complex was very difficult, because TCNNQ itself absorbed strongly in the longer wavelength side. The first CT bands were observed for all the complexes but second CT bands were not clearly observed in solution. The wave numbers of the first CT band maxima observed in solution are listed in the second column of Table 1.

3. Crystal Spectra of Molecular Complexes. Two broad bands were observed in each polarized absorption spectrum of all the molecular complexes studied, as shown in Figs. 5—10. These two bands (14—23 kK) are not local excitation bands but can be assigned to be the first and second CT bands, since the lowest transition of TCNNQ has an absorption maximum at 25 kK and those of electron donors appear at much shorter wavelength region. The wave numbers of these CT band maxima are listed in Table 1.

(a) Anthracene-TCNNQ (2 : 1) Complex: The first CT band appears at 14.3 kK in the room-temperature spectrum and is polarized in the *l*-axis, while the second CT band at 20.8 kK and polarized in a direction perpendicular to *l*. The polarization ratio, $I(//l)/I(\perp l)$, at each band maximum is 2.6 for the first CT band and 0.36 for the second CT band. When the crystal temperature is down to 80°K, the first CT band is displaced to the red by 600 cm^1 and the second CT band remains unshifted, both bands being remarkably enhanced in intensity. Furthermore, it is seen that the first CT band discloses a vibrational structure at 80°K. The broad band in the 25—30 kK region is a local excitation band associated mainly with the 25.9 kK transition of TCNNQ and partly with the 26.3 kK transition of anthracene.

TABLE 1. WAVE NUMBERS OF ABSORPTION PEAKS IN SOLUTION AND CRYSTAL CHARGE-TRANSFER (CT) SPECTRA OF AROMATIC HYDROCARBON-TCNNQ COMPLEXES (kK)

Donor molecule	Solution[a]	Crystal			
		Room temp.		Liq. N_2 temp.	
	CT	1 st CT	2 nd CT	1 st CT	2 nd CT
Anthracene	14.8	14.3	20.8	13.7	20.8
Pyrene	15.3	14.6	21.9	14.3	20.8
Phenanthrene	20.8	17.6	22.9	16.6	21.2
1,2-Benzanthracene	15.4	15.6	19.2	14.2	19.2
Chrysene	16.7	16.1	19.5	15.5	18.3
Triphenylene	21.7	18.5	21.6	18.1	21.3

a) Solvent: CH_2Cl_2. Only one CT band was observed in solution.

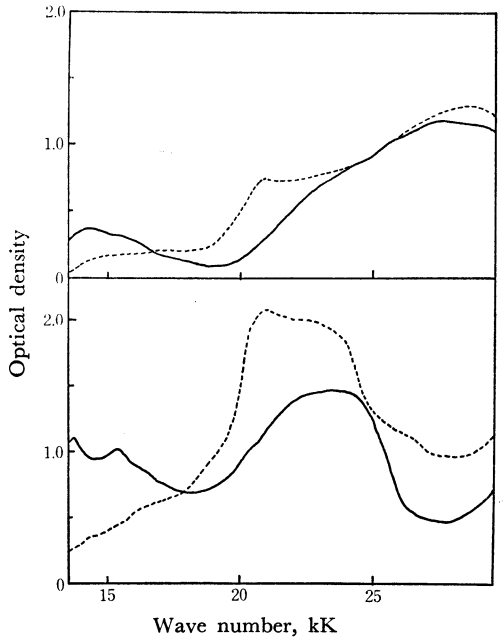

Fig. 5. Polarized absorption spectra of anthracene-TCNNQ complex at room temperature (above) and 80°K (below). Solid line: //*l* spectrum; Broken line: ⊥*l* spectrum.

(b) Pyrene-TCNNQ (2 : 1) Complex: The 14.6 kK and 21.9 kK absorption bands are assigned to be the first and the second CT bands, respectively, since they are enhanced in intensity at low temperature. The polarization ratio is 3.6 for the first CT band and is 0.46 for the second CT band. The longest wavelength absorption spectrum of TCNNQ and other local excitation bands are to appear around at 25 kK and/or in the frequency region higher than 25 kK. At 80°K, the first and the second CT bands are displaced by 300 cm^{-1} and 1,100 cm^{-1}, respectively, to the red compared with those taken at room temperature. Here again the low temperature spectrum has clear vibrational structure.

(c) Phenanthrene-TCNNQ (2 : 1) Complex: The polarized spectra of this complex resemble those of the anthracene- and pyrene-TCNNQ complexes described above. The first CT band located at 17.6 kK is polarized parallel to the *l*-axis and the second CT band at 22.9 kK perpendicular to *l*. The observed polarization ratios are 2.4 for the former and 0.43 for the latter. At 80°K, vibrational structures become clearer in both bands, while their longest wavelength peaks corresponding probably to 0,0 transitions are shifted

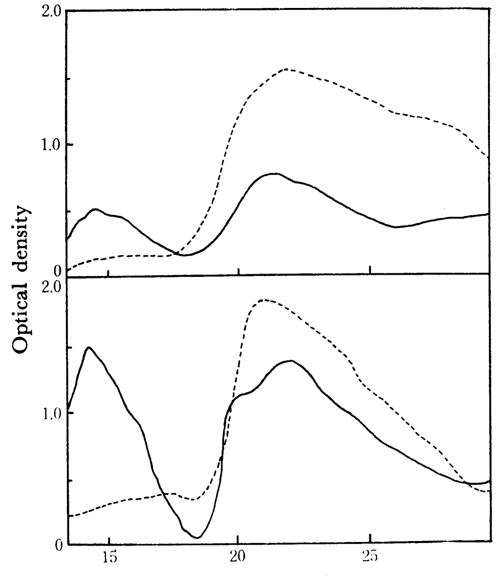

Fig. 6. Polarized absorption spectra of pyrene-TCNNQ complex at room temperature (above) and 80°K (below). Solid line: //*l* spectrum; Broken line: ⊥*l* spectrum.

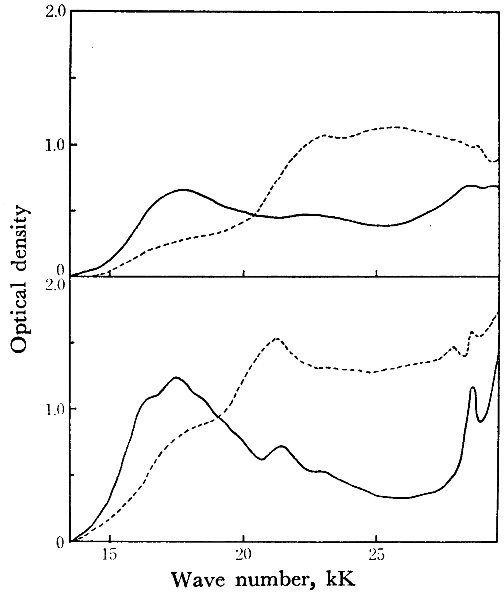

Fig. 7. Polarized absorption spectra of phenanthrene-TCNNQ complex at room temperature (above) and 80°K (below). Solid line: //*l* spectrum; Broken line: ⊥*l* spectrum.

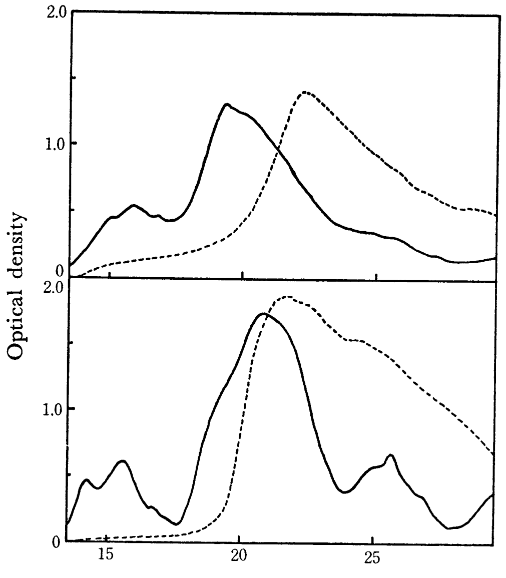

Fig. 8. Polarized absorption spectra of 1,2-benzanthracene-TCNNQ complex at room temperature (above) and 80°K (below). Solid line: //*l* spectrum: Broken line: ⊥*l* spectrum.

to the red. The sharp absorption bands appearing around at 28.5 kK are due to phenanthrene.

(d) 1,2-Benzanthracene-TCNNQ (1 : 1) Complex: The spectrum of the complex is quite different from those three described above. The first and the second CT bands appear at 15.6 kK and 19.2 kK, respectively, both being polarized along the *l*-axis. At 80°K, the vibrational structure of the first CT band becomes clear-cut and the lowest frequency peak, probably a 0,0 band, is displaced by 1,400 cm^{-1} to the red. There has not frequently been observed an intermolecular CT spectrum that shows such a clear vibrational structure. On the other side, the lowest frequency peak of the second CT band appears as a shoulder of the corresponding band in the low-temperature spectrum, no spectral shift being observed.

Moreover, we have observed another absorption band which is polarized perpendicular to the *l*-axis and the absorption peak of which is located at 22.1 kK. The band is enhanced in intensity and displaced to the red by 500 cm^{-1} at 80°K. The band can not be attributed to any local excitation and is tentatively assigned to be the third CT band. The polarization ratio for this band is 0.61, while those for the first and the second CT bands are 5.2 and 3.9, respectively. Around at 25 kK, there appear the local excitation bands of 1,2-benzanthracene and TCNNQ.

(e) Chrysene-TCNNQ (1 : 1) Complex: The spectrum of the complex is rather broad in both polarization directions, parallel and perpendicular to the *l*-axis. The absorption shoulder at 16.1 kK can be assigned as the first CT band. The *l*-polarized spectrum has a peak at 19.5 kK which may be regarded as the second CT band. The polarization ratios are 2.2 and 1.2, respectively, for the first and the second CT bands. These broad bands become somewhat narrow at low temperature. The 16.1 kK shoulder is still not resolved well and shifted to 15.5 kK, while the 19.5 kK peak appears more clearly at 18.3 kK. The absorption band appearing around at 27 kK is evidently due to the local excitation associated with the *p*-band of chrysene (27.2 kK).

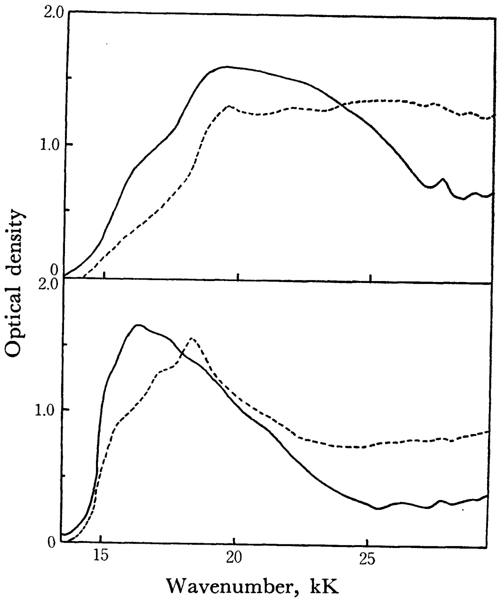

Fig. 9. Polarized absorption spectra of chrysene-TCNNQ complex at room temperature (above) and 80°K (below). Solid line: //*l* spectrum; Brolen line: ⊥*l* spectrum.

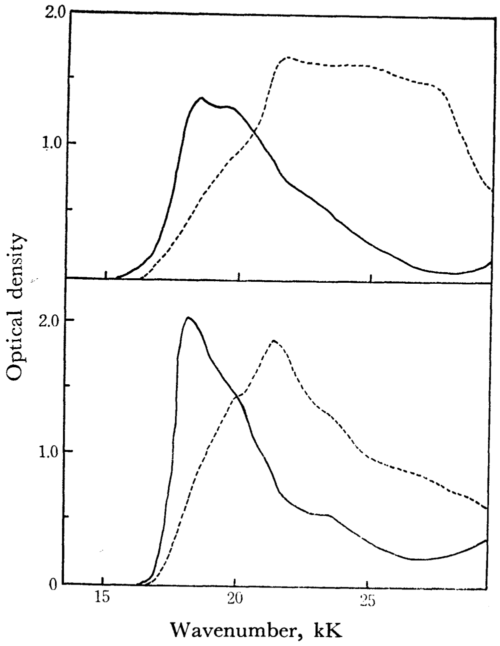

Fig. 10. Polarized absorption spectra of triphenylene-TCNNQ complex at room temperature (above) and 80°K (below). Solid line: //*l* spectrum; Broken line: ⊥*l* spectrum.

(f) Triphenylene-TCNNQ (1 : 1) Complex: The first CT band is found at 18.5 kK with an *l*-axis polarization and the second CT band at 21.6 kK with a polarization perpendicular to *l*. The broad absorption band in the 23—28 kK region is due to the local excitation associated with the TCNNQ transition and the 28.6 kK transition of triphenylene. At 80°K, both bands become considerably sharp, enhance their intensities, and shift to the red by 900 cm^{-1} and 300 cm^{-1}, respectively. The polarization ratios are 2.2 and 0.46, respectively, for the first and the second CT bands.

Discussion

Our previous calculation of the electronic spectrum of TCNNQ, assuming the molecule to be planar, has shown that in solution the 25.3 kK absorption band corresponds to the lowest B_2 transition polarized along the molecular longer axis and the weak 34.7 kK band to the next to the lowest A_1 transition polarized along the molecular short axis.[4] In the crystalline state, the bands are markedly intensified and broadened compared with the solution spectrum. The fact that the molecular structure of TCNNQ is non-planar in crystal puzzles us how to explain the observed crystal spectra and their polarization. Though a theoretical estimate of optically allowed exciton levels has to be carried out on the basis of the actual molecular structure, we may attribute the 33.8 kK (*a*-polarized) and 31.2 kK (*b*-polarized) bands in Fig. 3 to the two components of the 34.7 kK A_1 transition. The A_1 transition may be split and intensified through an interaction with the strong B_2 transition. Similarly, the 33.6 kK (*c*-polarized) and 30.9 kK (*b*-polarized) bands appearing in the *bc*-face spectra (Fig. 4) may be attributed to the components of the same 34.7 kK transition. The broad bands in the 22—27 kK region in both the *ab*- and *bc*-face spectra are ascribed to the 25.3 kK B_2 transition of the free molecule.

Unlike the TCNQ- and TCNE-polycyclic aromatic hydrocarbon complexes, there exist two kinds of composition for the TCNNQ complexes as mentioned before, that is those of the mole ratios of donor to acceptor 2 : 1 and 1 : 1. Though the molecular sizes of Group 1 hydrocarbons are certainly smaller than those of Group 2 hydrocarbons, the difference in molecular size is not great enough to explain the existence of the two forms. A similar situation was found in some *p*-benzoquinone complexes.[5] This is probably due to the non-planar structure of the TCNNQ molecule, above and below which conditions for charge transfer interaction may be different.

As shown before, the TCNNQ molecular complexes studied exhibit two broad absorption bands, with the exception of the 1,2-benzanthracene-TCNNQ complex which shows three bands, in the spectral region where no local excitation band is expected to appear. We have assigned them to be the first and the second CT bands. In Group 1 complexes, the first CT bands are clearly polarized along the crystal elongated *l*-axes and the second CT bands are perpendicular to them. The two CT bands of Group 2 complexes, however, have both polarization components, except for the triphenylene-TCNNQ complex which exhibits polarization ratios of the first and the second CT bands quite similar to Group 1 complexes.

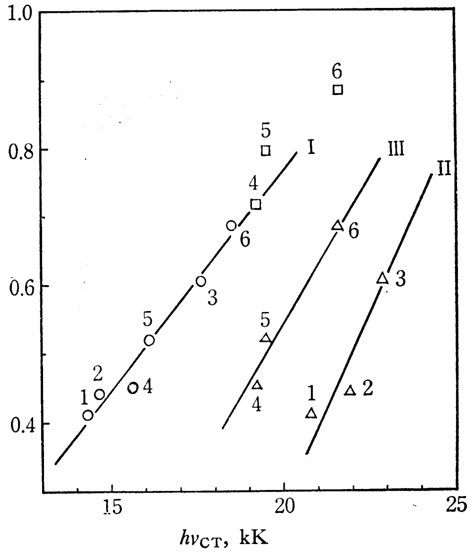

Fig. 11. Charge-transfer transition energies (room temperature) *vs* the Hückel molecular oribtal energy coefficients, χ_i, of the polycyclic aromatic donors. O: lst CT band, Δ: 2nd CT band; 1: anthracene, 2: pyrene, 3: phenanthrene, 4: 1,2-benzanthracene, 5: chrysene, 6: triphenylene-TCNNQ complexes. □ is a plot of 2nd CT band against 2nd HOMO energy of donor.

The wave numbers of the absorption maxima of the first and the second CT bands, $h\nu_{\mathrm{CT1}}$ and $h\nu_{\mathrm{CT2}}$, are plotted in Fig. 11 against the highest occupied molecular orbital (HOMO) energies of the corresponding polycyclic aromatic donors. The values of these HOMO energies are taken from the results of the Hückel molecular orbital calculations (the overlap integrals neglected)[7] and appear as χ_i on the ordinate of Fig. 11. Actual *i*th orbital energy is $\alpha+\chi_i\beta$ where α is the Coulomb integral for carbon and β is the carbon-carbon resonance integral. For the first CT bands, a straight line can be drawn (line I) as usual cases, so that these bands are most probably associated with the charge transfer from the HOMO of donor to the lowest vacant molecular orbital (LVMO) of acceptor. We have found that the energies of the first CT states of these complexes can be well expressed in terms of the ionization potentials, I_p, of the donor molecules as (in eV)

$$h\nu_{\mathrm{CT1}} = 0.69\,I_p - 3.29.$$

The 25 kK band of TCNNQ, assigned to be the B_2 transition polarized along the molecular longer axis, appears as a local excitation band polarized perpendicular to the *l*-axis which coincides with the polarization direction of the first CT bands in all Group 1 complexes. The donor molecules and TCNNQ are therefore supposed to be alternately stacked along the *l*-axis in Group 1 complex crystals.

A plot of $h\nu_{\mathrm{CT2}}$ *versus* the HOMO energy of donor products two linear relationships, Line II for Group 1 complexes and Line III for Group 2 complexes. The charge transfer mechanism for the second CT bands of these complexes may, therefore, be divided into two classes depending upon the mole ratio of donor to acceptor. A current explanation for the origin of a second CT band is that the band is mainly associated with a charge transfer from the second HOMO of a donor molecule to the LVMO of an acceptor molecule.[7] If we assume such a charge transfer mechanism for Group 1 complexes, the magnitude of $h\nu_{\mathrm{CT2}}$ turns out to be in the order anthracene—pyrene—phenanthrene, which is entirely in the reverse order compared with the present observation.

We tentatively conclude, therefore, that the second CT bands of Group 1 complexes may be associated mainly with the charge transfer from the HOMO of donor to the *second* LVMO of acceptor. A similar explanation was given by Iwata, Tanaka, and Nagakura for the 1,2,4,5-tetracyanobenzene-aromatic donor complexes.[8] As they pointed out, Line II should be drawn parallel with Line I in Fig. 11, if a simple relationship is assumed for both first and second CT

$$h\nu_{\mathrm{CT}} = I_p - E_A - C$$

bands. Here E_A is the electron affinity for the lowest and/or the second lowest vacant orbital of acceptor and C the sum of several terms including electrostatic

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[5] T. Amano, H. Kuroda, and H. Akamatu, This Bulletin, **42**, 671 (1969).

[6] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations", W. H. Freeman and Co., San Francisco (1965).

[7] H. Kuroda, I. Ikemoto, and H. Akamatu, This Bulletin, **39**, 1842 (1966) and subsequent papers.

interaction energy, which may be supposed to be approximately constant for a given acceptor. The reason why this is not the case is just uncertain.

On the other side, a plot $h\nu_{CT2}$ of Group 2 complexes against the second HOMO energy of donor (the squares drawn in Fig. 11) suggests that there is a roughly linear relationship between them. Thus in this case, we can not exclude the possibility of a charge transfer from the second HOMO of donor. Our tentative conclusion is that the second CT bands of Group 2 complexes may be due to a mixed charge transfer mechanism, one from the HOMO of donor to the second LVMO of acceptor and the other from the second HOMO of donor to the LVMO of acceptor.

As mentioned before, the second CT band in each crystal spectrum is polarized in the direction almost perpendicular to the polarization direction of the corresponding first CT band. This fact suggests that the donor molecule and TCNNQ are alternately and slantly stacked along the *l*-axis so that charge transfer can occur in two directions, almost parallel and perpendicular to the *l*-axis.

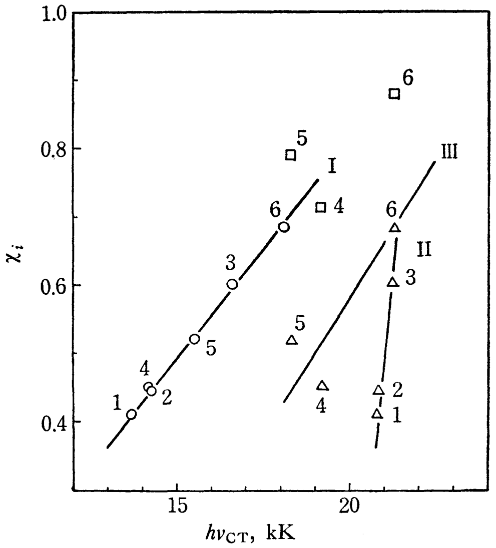

Fig. 12. Charge-transfer transition energies (80°K) *vs.* the Hückel molecular oribtal energy coefficients, χ_i, of the polycyclic aromatic donors. Symbols are the same as in Fig. 11.

The data taken at 80°K are plotted in Fig. 12 in exactly the same manner of Fig. 11. It is seen that the linear relationship for the first CT bands holds more precisely than in the room-temperature data. Line I of Fig. 12 is in parallel with Line I of Fig. 11 and is displaced to the red by 700 cm^{-1} compared with the latter. Line II strongly suggests that the second CT bands of Group 1 complexes are due to the charge transfer from the HOMO of donor to the second LVMO of acceptor, but the situation that its slope is so steep is again puzzling. Plots of $h\nu_{CT_2}$ of Group 2 complexes against the HOMO energy of donor (triangles in Fig. 12) and the second HOMO energy of donor (squares in Fig. 12) both deviate considerably from linearity. Rather the datum for the triphenylene-TCNNQ complex seems to join with those for Group 1 complexes, namely Line II. Originally the crystal spectra of the triphenylene-TCNNQ complex taken at room temperature and at 80°K resemble those of Group 1 complexes in regard to their polarizations.

Thus the low-temperature data clearly support our conclusion on the charge transfer mechanism of these complexes obtained from the room-temperature data. On the other side, we can not say anything in detail about the polarization and intensity of these CT bands since the crystal structures of these complexes have not been analysed. Specifically, it is hard to understand that the intensity of each CT spectrum is as large as that of the strong TCNNQ local excitation. A series of studies along such requests is being planned, together with a theoretical estimate of optically allowed exciton levels of the TCNNQ crystal.

This work was supported in part by a grant of Ministry of Education.

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[8] S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).

[9] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe", Springer-Verlag, Berlin-Göttingen-Heidelberg (1961), p. 75.