Molecular Complexes between 1,2,4,5-Tetracyanobenzene and Some Aromatic Electron Donors

Suehiro Iwata, Jiro Tanaka,[1] and Saburo Nagakura

Contribution from the Institute for Solid State Physics, University of Tokyo, Azabu-shinryudo-cho, Minato-ku, Tokyo. *Received August 16, 1965*

Abstract: The charge-transfer (CT) complexes of 1,2,4,5-tetracyanobenzene (TCNB) with substituted benzenes were studied by measuring electronic absorption spectra in solution and in crystal. Two CT absorption bands were observed for the TCNB complexes with mesitylene, hexamethylbenzene, dimethylaniline, and N,N,N′,N′-tetramethyl-*p*-phenylenediamine. The separation between the two CT bands was found to be almost constant for these TCNB complexes. From this together with the other experimental and theoretical facts, it was concluded that the appearance of the two CT bands is due to the two closely located vacant orbitals of TCNB. From the measurement of the polarized absorption spectrum of the single crystal, the 31,200-cm^{-1} band of TCNB was found to shift toward shorter wavelengths by 3600 cm^{-1} by the complex formation with mesitylene. This blue shift can be explained by the interaction of the locally (within TCNB) excited configuration with the CT configurations. A theoretical study was made by considering the configuration interaction among ground, CT, and locally excited configurations. It was theoretically demonstrated that the center of one of the benzene rings is located above the carbon atom or C–C bond of the other benzene ring in the stable geometrical configuration.

Recently 1,2,4,5-tetracyanobenzene (TCNB) has been found to be one of typical electron acceptors and to form stable charge-transfer (abbreviated hereafter to CT) complexes[2] with aromatic compounds.[3–5] Zweig, *et al.*,[3] measured the absorption spectra of CT complexes of polycyclic aromatic hydrocarbons with TCNB and found a linear relationship between the transition energies corresponding to the CT absorption maxima and the highest occupied molecular orbitals of the donors. Bailey, *et al.*,[4] obtained the CT absorption maxima and the association constants for the TCNB complexes with pyrene and dimethylaniline in chloroform solution. Foster and Thomson[5] determined the association constants and stabilization energies of N,N,N′,N′-tetramethyl-*p*-phenylenediamine (TMPD) complexes with polycyanobenzenes in chloroform and compared the results with those of similar polynitrobenzene complexes.

In the present paper, spectrophotometric studies have been made with CT complexes of various substituted benzenes with TCNB, special attention being paid to the appearance of two CT bands due to the closely located two vacant orbitals of the electron acceptor, and to the change in the absorption spectrum of TCNB itself. The polarized absorption spectrum of the single crystal was measured with the TCNB–mesitylene complex, in order to obtain some knowledge concerning these two points. Theoretical consideration has also been carried out with some TCNB complexes by a method combining LCAO–MO with configuration interaction. The stable geometrical configuration and the observed spectrophotometric behaviors of the complexes were discussed on the basis of the theoretical results.

Experimental Section

TCNB, prepared by Ishitani and Maruyama of our laboratory,[6] was purified by recrystallization from ethanol. The melting point, 258° in sealed tube (turning blue), agrees well with the value in the literature.[7]

Hexamethylbenzene (HMB) and TMPD were purified by recrystallization followed by sublimation. Benzene, toluene, *m*-xylene, and mesitylene were shaken with concentrated sulfuric acid, washed with water, dried over calcium chloride, and finally distilled. Aniline and *o*-, *m*-, and *p*-toluidine were purified by the vacuum distillation. Methylene chloride and tetrachloroethane, which were used as solvents for spectral measurements, were dried over calcium chloride and carefully distilled.

The absorption spectra of the solutions were measured with a Cary recording spectrophotometer Model 14 M. Solutions containing components were mixed separately with each other immediately before measurement. The concentrations of electron donors were taken to be in excess up to 20–100 times that of TCNB. The temperature of the cell compartment of the spectrophotometer was kept constant by a heater with a thermister. A microspectrophotometer constructed by Tanaka[8] was used for the polarized ultraviolet absorption measurement of single crystals of the TCNB–mesitylene complex which was obtained from the TCNB solution of mesitylene. The crystal showed a rectangular face, and the axis of elongation coincides with an extinction position. This means that the elongated axis or the axis perpendicular to it is the crystalline *b* axis in a monoclinic crystal or one of the axes in an orthorhombic crystal.

Results and Discussion

The Absorption Spectra of the Solutions Containing TCNB and Some Electron Donors. New absorption bands due neither to electron donor nor electron acceptor appear in the near-ultraviolet and visible regions for the mixed solution containing TCNB and such aromatic molecules as HMB, N,N-dimethylaniline, and TMPD, which are shown in Figure 1. For example, the TCNB–TMPD system[9] shows two new bands at 13,900 and 20,300 cm^{-1}. These bands may be regarded as the CT bands characteristic of the interaction between electron donor and acceptor.

---

(1) Department of Chemistry, Faculty of Science, Nagoya University.

(2) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952); *J. Am. Chem. Soc.*, 74, 811 (1952).

(3) A. Zweig, J. E. Lehnsen, W. G. Hodgson, and W. H. Jura, *ibid.*, **85**, 3937 (1963).

(4) A. S. Bailey, B. R. Henn, and J. M. Langton, *Tetrahedron*, **19**, 161 (1963).

(5) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 2287 (1963).

(6) The authors wish to thank Mr. A. Ishitani and Miss Y. Maruyama for offering TCNB.

(7) E. A. Lawton and D. D. McRichie, *J. Org. Chem.*, 24, 26 (1959).

(8) J. Tanaka, *Bull. Chem. Soc. Japan*, 36, 833 (1963).

(9) TCNB itself has the absorption band at 31,600 cm^{-1} in tetrachloroethane and TMPD itself at 31,550 cm^{-1}.

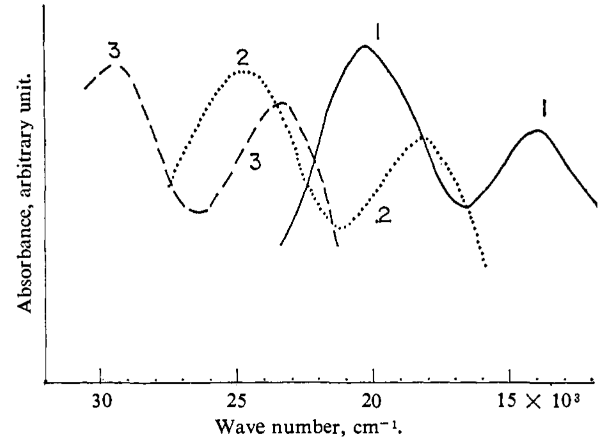


Figure 1. Spectra of the TCNB complexes with (1) TMPD in $C_2H_2Cl_4$; (2) dimethylaniline in $C_2H_2Cl_4$; (3) hexamethylbenzene in CH_2Cl_2.

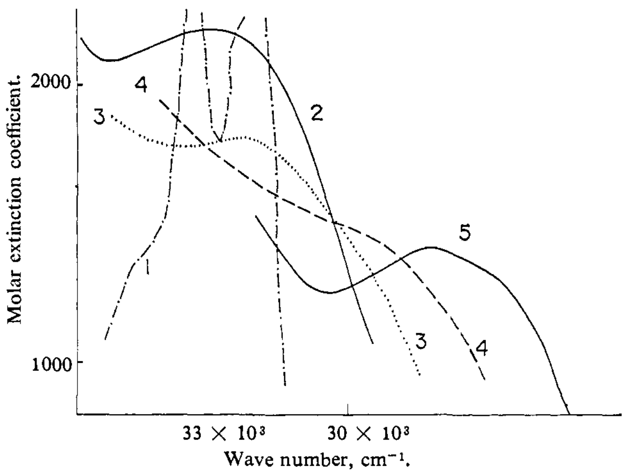


Figure 2. Spectra of TCNB in various solvents: (1) in $C_2H_2Cl_4$, (2) in benzene, (3) in toluene, (4) in *m*-xylene, (5) in mesitylene.

As for the benzene–TCNB system, a new absorption maximum is difficult to find by the usual procedure of dissolving the component molecules in tetrachloroethane. This is because the new band overlaps with that pertinent to TCNB itself (see Figure 2) and because this complex has a small equilibrium constant. Therefore, we dissolved TCNB in pure benzene and found that the new absorption maximum appears at 32,500 cm⁻¹ (see Figure 2). The absorption bands were also measured by dissolving TCNB in pure donors like toluene, *m*-xylene, and mesitylene. The results are shown in Figure 2.

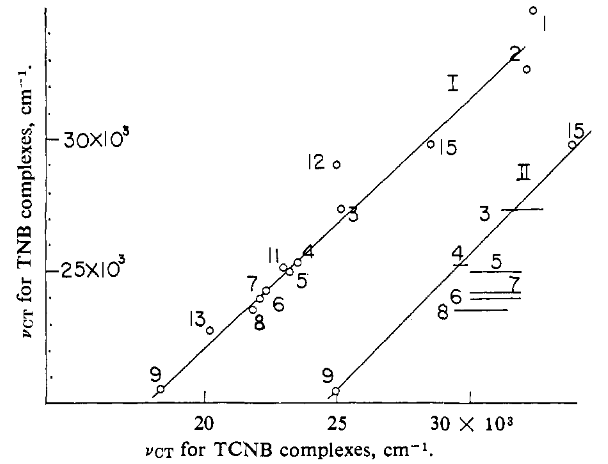


Figure 3. Plot of ν_{max} for the TCNB complexes with various donors against those for the corresponding 1,3,5-trinitrobenzene complexes.

Table I. CT Bands of the π-Complexes of TCNB with Some Aromatic Donors

Donors	No. in Figure 3	Frequency, cm⁻¹ First CT band (ν_1)	Frequency, cm⁻¹ Second CT band (ν_2)
Benzene[a]	1	32,500	
Toluene[a]	2	31,800	
HMB[b]	3	23,500	29,900
Naphthalene[b]	4	25,000	>31,300
Aniline	5	23,300	>30,300
o-Toluidine	6	22,200	>30,300
m-Toluidine	7	22,500	>31,300
p-Toluidine	8	21,700	>29,400
N,N-Dimethylaniline[b]	9	18,300	25,000
TMPD[b]	10	13,900	20,300
p-Dimethoxybenzene	11	23,000	
Durene	12	25,000	
Pyrene[c]	13	20,200	
Mesitylene[d]	15	28,300	33,700

[a] Absorption maximum in the pure liquid of donor. [b] Foster and Thomson[5] reported ν_1 23,400, 24,700, 18,600, and 13,600 cm⁻¹ for the HMB, naphthalene, N,N-dimethylaniline, and TMPD complexes, respectively. Furthermore, they found the second CT band at 19,600 cm⁻¹ for the TMPD-TCNB complex. Their measurements were made with the chloroform solutions. [c] Taken from ref 4. [d] Absorption maxima measured with the single crystal.

The peak wavelengths observed by the present authors are summarized in Table I. From the results given in this table, it may be inferred that the maximum wavelengths of the new bands shift toward longer wavelengths with the lower ionization potentials of the donors. In order to check this point more quantitatively, we plotted the maximum frequencies of the new bands observed with TCNB complexes against those observed with 1,3,5-trinitrobenzene (TNB) complexes. As is shown in Figure 3, the points fit well to two straight lines. One of them (line I) corresponds to the first CT bands and the other (line II) to the second CT bands.

The Polarized Absorption Spectrum of the TCNB–Mesitylene Crystal. The polarized absorption spectrum of the TCNB–mesitylene single crystal was measured in the direction parallel (||) and perpendicular (⊥) to the elongated axis of the crystal. The results are shown in Figure 4. As is easily seen in Figure 4, three absorption peaks were found at 28,300, 33,700, and 34,800 cm⁻¹, and a strong absorption tail was observed in the higher-frequency region than 37,000 cm⁻¹.

The first absorption peak[10] observed with the single crystal undoubtedly corresponds to the first CT band which appears at 28,400 cm⁻¹ in solution. The absorption intensity is stronger in the direction parallel to the elongated axis of the crystal than in the perpendicular direction. Since the CT band may be

---

(10) Figure 4 shows that this band seems to split by 700 cm⁻¹ in the single crystal. The splitting cannot be observed with the solution.

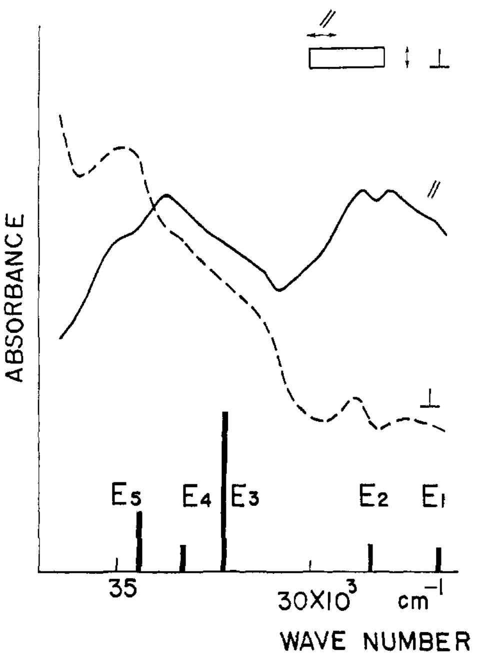


Figure 4. Polarized absorption spectrum observed with the single crystal of the TCNB-mesitylene complex: ———, with the polarized light parallel to the elongation axis; ---------, with the polarized light perpendicular to the elongation axis. The vertical lines $E_1, \ldots, E_5$ show the calculated transition energies and oscillator strengths.

polarized perpendicular to the benzene rings of the electron donor and acceptor, the observed dichroism of the first band shows that the donor and the acceptor are stacked with each other in the single crystal in such a way that the benzene ring planes are almost perpendicular to the elongated axis.[11]

The second and third absorption bands observed with the single crystal may conceivably correspond to the absorption tail observed with the solution in the higher-frequency region than 31,000 cm^{-1}. The intensity of the second band is stronger in the direction parallel to the elongated axis of the crystal. Therefore, the band may be regarded as the second CT band. The separation between the first and the second bands is 5400 cm^{-1}. This agrees considerably well with the separation between the two CT bands observed with the TCNB–HMB and TCNB–TMPD complexes in solution. This point will be discussed later.

The dichroic intensity ratio of the first CT band is somewhat different from that of the second CT band. That is to say, the observed dichroic ratio $(D_{\|}:D_{\perp})$ is 2.78 and 1.15 for the first and second bands, respectively. This will be explained by the mixing of the CT configurations with the locally excited configurations. In fact, the dichroic ratio $(M_z^2/(M_x^2 + M_y^2))$ calculated by considering the configuration interaction between the CT and locally excited configurations is 3.47 and 0.87 for the first and second bands, respectively.

The dichroic intensity relation of the third band at 34,800 cm^{-1} is the reverse of those of the above-mentioned two bands. This means that the band is polarized in the direction parallel to the ring plane,

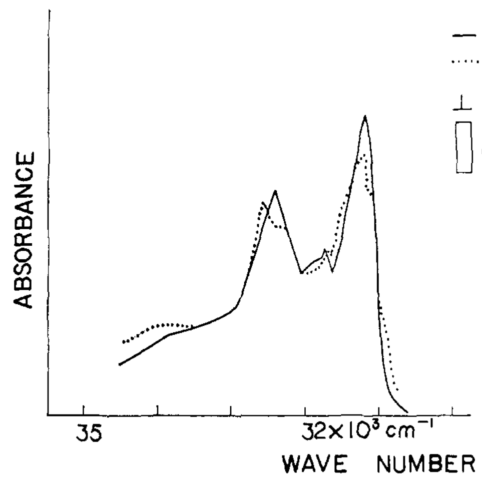


Figure 5. Polarized absorption spectrum of the TCNB single crystal: ———, with the polarized light perpendicular to the elongation axis; . . . . , with the polarized light parallel to the elongation axis.

and therefore it may be regarded as a shifted band of the 31,200-cm^{-1} band of TCNB. The spectrum of the single crystal of TCNB itself was measured for the purpose of obtaining a quantitative knowledge about the shift. The result given in Figure 5 shows that the absorption maximum of the single crystal appears at 31,200 cm^{-1}, *i.e.*, at the same position as that of the solution spectrum. Thus it is concluded that the band of TCNB shifts toward shorter wavelengths by the complex formation and the magnitude of the shift amounts to 3600 cm^{-1}.

Appearance of the Two CT Absorption Bands. The absorption peaks of the two CT bands were clearly observed for the TCNB complexes with HMB, TMPD, and N,N-dimethylaniline (Figure 1).[12] A shoulder due to the second CT transition was observed for the TCNB complexes with naphthalene, aniline, and *o*-, *m*-, and *p*-toluidines.

Multi-CT absorption bands have been found for the CT complexes containing strong electron acceptors such as chloranil, bromanil, and tetracyanoethylene (TCNE).[13] The origin of the multi-CT bands hitherto observed was explained by the existence of two closely located occupied orbitals of the donor.[13] In this case, the frequency difference $(\Delta\nu_{CT})$ between the two CT bands is approximately equal to the energy difference in the first and the second highest occupied orbitals of the donor. The $\Delta\nu_{CT}$ values for the chloranil and TCNE complexes, which are given in the third and fourth columns of Table II, respectively, are nearly coincident with each other for the respective donors.

The $\Delta\nu_{CT}$ values for the TCNB complexes are summarized in the second column of Table II. The $\Delta\nu_{CT}$ value for the TCNE–TMPD complex is greater than twice that of the TCNB–TMPD complex. This seems to mean that the appearance of the two CT bands for the TCNB complexes cannot be explained

---

(11) This geometrical orientation may be thought to be supported by the observation that the refractive index of the crystal is greater in the direction perpendicular to the elongated axis than in the direction parallel to it.

(12) There is a possibility of observing CT bands more than two for the TCNB complex with TMPD or N,N-dimethylaniline, because the CT band splits by the two ionization potentials of the electron donor as well as by the two electron affinities of TCNB. The third CT band, however, could not actually be observed. This is because it may appear in the shorter wavelength side than the measurable region.

(13) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

Table II. The Frequency Difference ($\Delta\nu_{CT}$) between the Two CT Bands (cm^{-1})

Donors	Acceptors TCNB	 TCNE^a	 Chloranil^a
HMB	6400	. . .	. . .
Mesitylene	5400^b	. . .	. . .
TMPD	6400	13,100	. . .
N,N-Dimethylaniline	6700	. . .	. . .
Naphthalene	6300	5,200	5,100
Anisole	. . .	6,300	6,900
Pyrene	. . .	6,500	6,500
p-Dimethoxybenzene	. . .	10,200	10,600

^{a} Taken from ref 13. ^{b} Obtained with the single crystal.

by the same mechanism as that for the TCNE or chloranil complexes. In this connection, it is to be noticed that the $\Delta\nu_{CT}$ values for the TCNB complexes are almost constant (6200 cm^{-1}), independent from the electron donors. Furthermore, the observed $\Delta\nu_{CT}$ values are very close to the calculated energy difference ($\Delta\nu$) between the lowest and the second lowest vacant orbitals of TCNB; *i.e.*, the observed $\Delta\nu_{CT}$ and the theoretical $\Delta\nu$ are 6200 and 5500 cm^{-1}, respectively. The details of the calculation of the $\Delta\nu$ value will be described in the theoretical part of the present paper. The above-mentioned facts lead to the conclusion that the two closely located vacant orbitals of the electron acceptor play an important role in the appearance of the two CT bands for the case of the TCNB complexes.

The above conclusion is also supported by the fact that the TCNB complex with hexamethylbenzene as an electron donor, which has the same symmetry as benzene and therefore whose two highest occupied orbitals are doubly degenerated, shows the two CT bands (see Figure 1). The present experimental result may be the first finding of the two CT bands due to the two closely located vacant orbitals of electron acceptor.

Molar Extinction Coefficients of TCNB Complexes. On the assumption that all the TCNB molecules form complexes when they are dissolved in pure liquids of benzene,[14] toluene, and mesitylene, the peak molar extinction coefficients of the CT bands (ϵ_{max}) can be obtained as is shown in Table III. In this table, the

Table III. Molar Extinction Coefficients (ϵ_{max}) of the CT Bands

Donors	ϵ_{max} TCNB	 TNB^b	I_p,^{c} ev
Benzene	2200^a 3300 (in tetrachloroethane)	5855	9.245
Toluene	1800^a	3540	8.82
Mesitylene	1400^a		8.40
HMB	1000 (in methylene chloride)	2150	7.85

^{a} The values in pure liquid of donors. ^{b} The values in CCl_4: G Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955). ^{c} Ionization potentials of the donors obtained from ref 18.

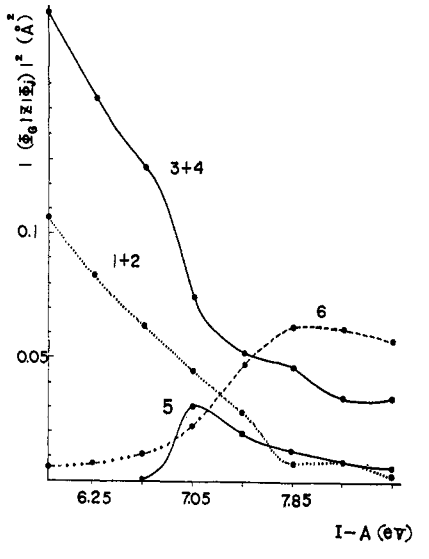


Figure 6a. Calculated transition moments: $M_{zj}^2 \equiv (\Psi_G|Z|\Psi_j)^2$. $(1 + 2) = M_{z1}^2 + M_{z2}^2$; $(3 + 4) = M_{z3}^2 + M_{z4}^2$.

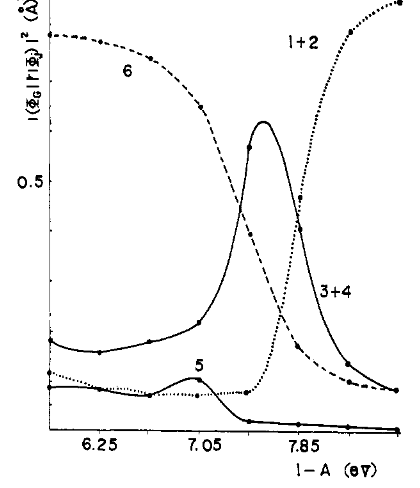


Figure 6b. Calculated transition moments: $M_j^2 \equiv (\Psi_G|r|\Psi_j)^2$. $(1 + 2) = M_1^2 + M_2^2$; $(3 + 4) = M_3^2 + M_4^2$.

ϵ_{max} values for the TNB complexes were also shown for the purpose of comparison. The ϵ_{max} value for the HMB-TCNB complex was evaluated by the aid of the equilibrium constant, the determination of which will be described in a later part of the present paper. The ϵ_{max} value of the benzene–TCNB complex was also evaluated by the aid of the equilibrium constant as well as from the data of the TCNB in pure benzene. As is seen in Table III, a discrepancy exists between these two ϵ_{max} values. This might be due partly to the difference in the dielectric constants of the solvents.

Table III shows that the CT band intensity increases with the decreasing donor ability, *i.e.*, with the higher ionization potentials (I_p) of the donors. This may be explained by considering the configuration interaction between the CT configuration and locally (within TCNB) excited configuration. The present theoretical consideration, the details of which will be described in the Theoretical Part, shows that the mixing of the locally

---

(14) Strictly speaking, this assumption is not correct. The equilibrium constant of the benzene–TCNB complex given in Table IV shows that the complex formation amounts to ~80% when TCNB is dissolved in pure benzene. However, this gives only a small effect to the evaluated ϵ_{max} value because the free TCNB molecule has also an absorption in the wavelength region under consideration.

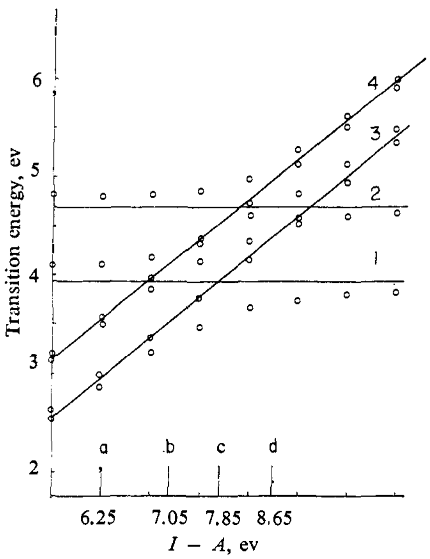


Figure 7. Calculated transition energies in $R_x = 1.20$, $R_y = 0.695$, and $R_z = 3.4$ Å. The open circles represent the calculated transition energies for the TCNB complexes with various $I - A$ values. The straight lines 1 and 2 show the energies of the locally (within TCNB) excited configuration Φ_{L1} and Φ_{L2}, respectively. The straight lines 3 and 4 show the energies of the CT configurations Φ_{CT_1} and Φ_{CT_2}, and Φ_{CT_2} and Φ_{CT_4}, respectively. a, b, c, and d are respectively the $I - A$ values corresponding to the HMB, mesitylene, toluene, and benzene complexes.

(within the acceptor) excited configuration with the CT configurations is important for the CT band intensity; that is to say, the second term of eq 13 in the Theoretical Part shows that the CT absorption bands borrow the intensity from the acceptor excitation. This effect becomes more important when the energy of the CT configuration ($E(D^+A^-)$) becomes higher and is closer to the energy of the locally excited configuration ($E(DA^*)$). The theoretical relation between the donor ability and the CT band intensity is shown in Figure 6b. The abscissa of this figure, $I - A$, represents the difference between the ionization potentials of the donors and the electron affinity of the acceptor, TCNB. Curve (1 + 2) in the figure, which represents the square of the transition moment for the first CT band, rises steeply with the increment of the $I - A$ values. Thus it may be possible to explain the fact that the CT band intensity increases with the higher ionization potentials of the donors.

Orgel and Mulliken[15] discussed the intensity borrowing for the contact-pair mechanism for TNB complexes. The present experimental and theoretical results indicate that the similar phenomenon is also important for the stable CT complex.

Murrell[16] discussed the intensity borrowing of the CT bands from donor excitations. In the present study, we have shown that the intensity donation also occurs from acceptor excitations to the CT bands.

Comparison of the Observed and Theoretical Transition Energies. The transition energies of TCNB complexes were calculated by the present authors by considering the configurational interaction among the ground, two locally (within TCNB) excited, and four CT configurations. The transition energies evaluated for various $I - A$ values are given in Figure 7. For the donor molecules with small ionization potentials, the two CT absorption bands corresponding to the transitions to the lowest four excited states[17] are expected to appear in the visible and near-ultraviolet regions. The actual appearance of the two CT bands has already been discussed in the present paper. The transition energies of the HMB–TCNB complex were calculated to be 2.93 and 3.51 ev on the assumption of $I - A = 6.25$ ev. These values may be said to agree well with the observed values, 2.91 and 3.65 ev. Since the ionization potential of HMB is 7.85 ev,[18] the electron affinity of TCNB was determined to be 1.60 ev.[19]

Using the above value of electron affinity and the ionization potential of mesitylene, $I = 8.40$ ev,[18] the transition energies for the mesitylene–TCNB complex were calculated to be 3.44, 4.06, and 4.25 ev.[20] These values are well coincident with the transition energies observed with the crystal, 3.51, 4.18, and 4.34 ev. In Figure 4, which shows the polarized absorption spectrum of the mesitylene–TCNB complex crystal, the calculated transition energies are shown by vertical lines, E_1, E_2, E_3, E_4, and E_5. E_1, E_2, E_3, E_4, and E_5 mean respectively the transition energies for the $W_0 \rightarrow W_1$, $W_0 \rightarrow W_2$, $W_0 \rightarrow W_3$, $W_0 \rightarrow W_4$, and $W_0 \rightarrow W_5$ transitions given in Table VIII in the Theoretical Part. The first CT band corresponds to E_1 and E_2 transitions and the second CT band to the E_3 and E_4 transitions. The doublet characters of these transitions are caused by the doubly degenerate highest occupied orbitals of mesitylene. The broadness of the first and the second CT bands may be due to the above-mentioned doublet characters. A similar calculation was also made for benzene and toluene complexes. The calculated transition energies to the lowest excited states are 3.70 and 3.55 ev for the benzene and toluene complexes, respectively, while the observed values are 4.03 and 3.94 ev.

Equilibrium Constants. The equilibrium constant (K) for the benzene–TCNB complex was determined in tetrachloroethane. The concentration of benzene was varied between 0 and 5.05 mole/l., while that of TCNB was taken nearly constant (order of 10^{-4} mole/l.). TCNB has an absorption tail at 30,300 cm^{-1} where the equilibrium constant for the benzene–TCNB complex was measured. Therefore, we determined the equilibrium constant by the following equation which was derived by considering the change in the absorption spectrum of TCNB due to the complex formation at the wavelength under investigation[21]

$$\epsilon^* - \epsilon_A = \frac{\epsilon - \epsilon_A}{1 + \dfrac{1}{KC_D}} \qquad (1)$$

---

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

(16) J. N. Murrell, *ibid.*, **81**, 4839 (1959).

(17) These four excited states are separated into two sets, each of which consists of two closely located states.

(18) F. I. Vilesov, *Soviet Phys. Usp.*, **6**, 888 (1964); *Usp. Fiz. Nauk*, **81**, 669 (1963).

(19) The electron affinity of TCNB is estimated as 0.4 ev by Briegleb. The value of the Coulomb attraction energy which was used in his review on the electron affinity (G. Briegleb, *Angew. Chem. Intern. Ed. Engl.*, **3**, 617 (1964)) is 4.3 ev. This value of the Coulomb attraction energy is apparently overestimated. Our Coulomb attraction energies are 3.30 ~3.45 ev as will be described later. Therefore his value of the electron affinity is smaller than ours by about 1 ev.

(20) The average values for the corresponding two transitions are 3.44 and 4.06 ev, respectively.

where ϵ^* ($\equiv D/C_Al$) is the apparent molar extinction coefficient of the solution, ϵ_A and ϵ are the molar extinction coefficients of TCNB and the complex, respectively, C_A and C_D are respectively the concentrations of TCNB and benzene, D is the absorbance, and l is the light path length of a cell in cm. The equilibrium constants were determined at 30,300 cm^{-1} using the least-squares method, and the results are given in Table IV.

Table IV. Equilibrium Constants (K), Molar Extinction Coefficients (ϵ) of the CT Band, Heat of Formation (ΔH), and Entropy Change (ΔS) for the Benzene–TCNB Complex in $C_2H_2Cl_4$

Temp, °C	K, l./mole	$\epsilon_{30,300\ \text{cm}^{-1}}$
24	0.25	2400
28	0.23	2500
32	0.22	2500
	$\Delta H = -0.4$ kcal/mole	
	$\Delta S = -0.9$ eu	

The equilibrium constant of the hexamethylbenzene–TCNB complex in methylene chloride was determined to be 3.0 l./mole at 22.4° by applying the Benesi–Hildebrand[22] method to the absorbance values observed at 23,500 cm^{-1}.

Heats of Formation. The heat of formation of the benzene–TCNB system was determined to be about 0.4 kcal/mole from the temperature dependence of the equilibrium constants given in Table IV. On the other hand, the heat of formation of the TMPD–TCNB complex was measured by Foster and Thomson to be about 3.6 kcal/mole[5] in chloroform solution.

The stabilization energy due to the CT interaction was calculated by the method described in the Theoretical Part to be 0.03 ev (0.7 kcal/mole) and 0.06 ev (1.4 kcal/mole) for the ($I - A$) values of 8.65 and 5.85 ev, respectively. The stabilization energy largely depends on the relative orientation of the electron donor and acceptor. The above values were evaluated for the stable conformation (model 2 described in the Theoretical Part).

The observed heat of formation of the complex may conceivably include the contributions of the electrostatic and dispersion forces in addition to the abovementioned CT force. Furthermore, as is well known, it is difficult to get an accurate result in the calculation of the stabilization energy, especially in this case, because of the ambiguity in the geometry of the complex. Therefore, the quantitative comparison of the calculated CT energy with the observed heat of formation might be rather meaningless. However, theoretical evaluation of the CT force may be helpful for the consideration of the stable conformation of the complex, because the CT force may conceivably be sensitive to the relative orientation of the donor to the acceptor, compared with the other forces.

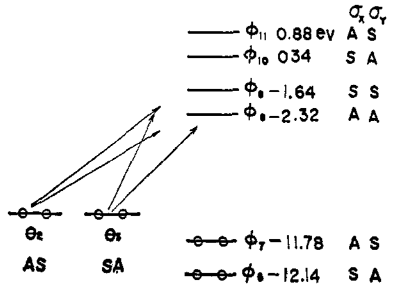


Figure 8. Molecular orbitals and their symmetries of TCNB and benzene.

Theoretical Part

The electronic structures of the π–π type CT complexes between benzene or methyl-substituted benzenes as electron donors and TCNB as electron acceptor were calculated by considering the configuration interaction among the ground (or no bond), CT (or dative), and locally excited configurations.

The electronic structures of the CT complexes are usually described in terms of the "no bond structure" and the "dative structure" as follows.

$$\Psi_G = a\Phi(DA) + b\Phi(D^+A^-)$$

$$\Psi_E = b'\Phi(DA) - a'\Phi(D^+A^-)$$

Mulliken,[23] however, pointed out that the other configurations like the back CT configurations and locally excited configurations are important in some cases. Hosoya and Nagakura[24] demonstrated that the lowest excited state of the complex between cyclohexene and the silver cation has the mixing character of CT and donor Rydberg excitation. Furthermore, our experimental results suggest that the mixing of locally excited configurations $\Phi(D^*A)$ and $\Phi(DA^*)$ is important, in particular, in excited states. Here $\Phi(D^*A)$ and $\Phi(DA^*)$ mean the excited configurations caused by the excitation within the donor and the acceptor, respectively. In the present calculation we took into account the interaction among the ground, locally excited, and CT configurations.

First of all, the molecular orbitals of TCNB, ϕ_1, ϕ_2, $\ldots$, ϕ_{14} were calculated with the results given in Table V and Figure 8. The details of MO calculations are given in the Appendix. As for the molecular orbitals of methyl-substituted benzenes, we have used those of benzene which are represented by θ_1, θ_2, $\ldots$, θ_6. This is because the small change in the shape of the MO may not give significant influence to the present results.

The wave function of the ground configuration is given by a Slater determinant

$$\Phi_G = |\theta_1\bar{\theta}_1\cdots\theta_3\bar{\theta}_3\phi_1\bar{\phi}_1\cdots\phi_7\bar{\phi}_7| \tag{5}$$

---

(21) From the relation among D, ϵ_A, ϵ, C_A, and the concentration of the complex C_{AD}, we can obtain the following equation

$$D/C_Al \equiv \epsilon^* = (1 - x)\epsilon_A + x\epsilon \tag{2}$$

where $x = C_{AD}/C_A$. By solving this equation

$$x = (\epsilon^* - \epsilon_A)/(\epsilon - \epsilon_A) \tag{3}$$

In the case of $C_A \ll C_D$, the equilibrium constant K is related with x as

$$K = C_{AD}/[(C_A - C_{AD})C_C] = x/(1 - x)C_D \tag{4}$$

By inserting eq 3 into eq 4, eq 1 is easily derived.

(22) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

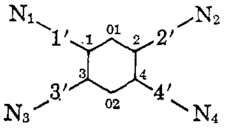
(23) K. S. Mulliken, *J. Chim. Phys.*, **61**, 20 (1963).

(24) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Japan*, **37**, 249 (1964).

Table V. Molecular Orbitals of TCNB[a,b]

	Orbital energy, ev	Wave function			
1	−16.594	$0.3108\varphi_0^{ss}$	$+0.3583\varphi_1^{ss}$	$+0.2129\varphi_{1'}^{ss}$	$+0.1680\varphi_N^{ss}$
2	−15.441	0	$-0.2565\varphi_1^{sa}$	$-0.3068\varphi_{1'}^{sa}$	$-0.3002\varphi_N^{sa}$
3	−14.975	$0.1686\varphi_0^{as}$	$+0.1451\varphi_1^{as}$	$+0.3168\varphi_{1'}^{as}$	$+0.3382\varphi_N^{as}$
4	−14.749	0	$-0.0821\varphi_1^{aa}$	$-0.3280\varphi_{1'}^{aa}$	$-0.3682\varphi_N^{aa}$
5	−13.742	$-0.2585\varphi_0^{ss}$	$-0.1940\varphi_1^{ss}$	$+0.2422\varphi_{1'}^{ss}$	$+0.3468\varphi_N^{ss}$
6	−12.143	$-0.5489\varphi_0^{as}$	$-0.2520\varphi_1^{as}$	$+0.0768\varphi_{1'}^{as}$	$+0.1730\varphi_N^{as}$
7	−11.782	0	$-0.4171\varphi_1^{sa}$	$+0.0958\varphi_{1'}^{sa}$	$+0.2585\varphi_N^{sa}$
8	−2.318	0	$-0.4029\varphi_1^{aa}$	$-0.1707\varphi_{1'}^{aa}$	$+0.2419\varphi_N^{aa}$
9	−1.637	$-0.5419\varphi_0^{ss}$	$+0.2314\varphi_1^{ss}$	$+0.1420\varphi_{1'}^{ss}$	$+0.1717\varphi_N^{ss}$
10	−0.345	$0.2673\varphi_0^{as}$	$-0.1802\varphi_1^{as}$	$-0.3058\varphi_{1'}^{as}$	$+0.2971\varphi_N^{as}$
11	0.825	0	$-0.1011\varphi_1^{sa}$	$+0.3830\varphi_{1'}^{sa}$	$-0.3051\varphi_N^{sa}$
12	1.155	$-0.2072\varphi_0^{ss}$	$+0.1744\varphi_1^{ss}$	$-0.3551\varphi_{1'}^{ss}$	$+0.2684\varphi_N^{ss}$
13	1.721	0	$+0.2844\varphi_1^{aa}$	$-0.3365\varphi_{1'}^{aa}$	$+0.2363\varphi_N^{aa}$
14	2.993	$-0.3143\varphi_0^{as}$	$+0.3646\varphi_1^{as}$	$-0.2241\varphi_{1'}^{as}$	$+0.1319\varphi_N^{as}$

[a] $\varphi_0^{ss} = \chi_{01} + \chi_{02}$, $\varphi_0^{as} = \chi_{01} - \chi_{02}$: $\varphi_1^{ss} = \chi_1 + \chi_2 + \chi_3 + \chi_4$; $\varphi_1^{sa} = \chi_1 - \chi_2 + \chi_3 - \chi_4$; $\varphi_1^{as} = \chi_1 + \chi_2 - \chi_3 - \chi_4$; $\varphi_1^{aa} = \chi_1 - \chi_2 - \chi_3 + \chi_4$; φ_1' consists of χ_1', χ_2', χ_3', and χ_4' instead of χ_1, χ_2, χ_3, and χ_4, respectively, in the corresponding φ_1 orbital. φ_N consists of χ_{N1}, χ_{N2}, χ_{N3}, and χ_{N4} instead of χ_1, χ_2, χ_3, and χ_4, respectively, in the corresponding φ_1 orbital. [b] The atoms of TCNB are marked as follows



The locally (in TCNB) excited configurations are given by[25]

$$\Phi_{L1} = a\Phi(\phi_6{}^{-1}\phi_8) + b\Phi(\phi_7{}^{-1}\phi_9)$$
$$a = 0.7878,\ b = 0.6159 \qquad (6)$$
$$\Phi_{L2} = c\Phi(\phi_6{}^{-1}\phi_9) + d\Phi(\phi_7{}^{-1}\phi_8)$$
$$c = -0.5032,\ d = 0.8642$$

where

$$\Phi(\phi_i{}^{-1}\phi_k) = {}^1/_2\{|\theta_1\ldots\phi_i\bar{\phi}_k\ldots\bar{\phi}_7| + |\theta_1\ldots\phi_k\bar{\phi}_i\ldots\bar{\phi}_7|\}$$

The wave functions Φ_{L1} and Φ_{L2} can be represented by a linear combination of configurations caused by one-electron excitation, the coefficients *a*, *b*, *c*, and *d* being determined by the configuration interaction calculation for TCNB itself. The four CT configurations are as follows.

$$\begin{aligned}\Phi_{CT_1} &= \Phi(\theta_2{}^{-1}\phi_8)\\ \Phi_{CT_2} &= \Phi(\theta_2{}^{-1}\phi_9)\\ \Phi_{CT_3} &= \Phi(\theta_3{}^{-1}\phi_8)\\ \Phi_{CT_4} &= \Phi(\theta_3{}^{-1}\phi_9)\end{aligned} \qquad (7)$$

In order to consider the configuration interaction among the above-mentioned seven electron configurations, we must evaluate the energies of these configurations and the off-diagonal elements of the total electronic Hamiltonian for the system.

The energies of the excited configurations are evaluated by taking the energy of the ground configurations as the standard. The energies for the Φ_{L1} and Φ_{L2} configurations are taken from the transition energies observed with TCNB.

$$\begin{aligned}E_G &= 0 \text{ ev}\\ E_{L1} &= 3.93 \text{ ev}\\ E_{L2} &= 4.70 \text{ ev}\end{aligned} \qquad (8)$$

The energies of the CT configurations can be estimated as

$$\begin{aligned}E_{CT_1} &= I - A - C_{28}\\ E_{CT_2} &= I - A' - C_{29} \simeq I - A - 0.68 - C_{29}\\ E_{CT_3} &= I - A - C_{38}\\ E_{CT_4} &= I - A' - C_{39} \simeq I - A - 0.68 - C_{39}\end{aligned} \qquad (9)$$

where *I* is the ionization potential of the donor, *A* and *A′* are the electron affinities for the first and the second lowest vacant orbitals, the difference of which is assumed to be the same as the difference between the SCF orbital energies, ϵ_8 and ϵ_9. The electron affinity *A* is taken as one of the parameters. The Coulomb integrals

$$C_{ij} = \int \theta^*_i(1)\theta_i(1)\frac{e^2}{r_{12}}\phi_j^*(2)\phi_j(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

are evaluated with the point-charge approximation

$$C_{ij} \cong \sum_p \sum_q c_{ip}{}^2 c_{jq}{}^2 \int \chi_p^*(1)\chi_p(1) \times \frac{e^2}{r_{12}}\chi_q^*(2)\chi_q(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \cong \sum_p \sum_q c_{ip}{}^2 c_{jq}{}^2 \frac{e^2}{R_{pq}} \qquad (10)$$

where χ_p and χ_q are the atomic orbitals on *p* and *q* atoms of donor and acceptor, respectively, and R_{pq} is the distance between them. In eq 9 we have neglected the electrostatic interaction between the donor and the acceptor in the ground configuration.

The off-diagonal terms of the CT configurations with the ground and excited configurations are given in

---

[25] Locally excited configuration with higher energies are not considered in the present calculation. In particular it may be noticed that the locally excited configurations of the donor corresponding to the $A_{1g} \rightarrow B_{2u}$, $A_{1g} \rightarrow B_{1u}$, and $A_{1g} \rightarrow E_{1u}$ transitions of benzene are disregarded. This is because the locally excited configurations of donors are higher than the lowest locally excited configuration of the acceptor (TCNB), and because the interaction of the CT configurations with locally excited configurations of the donor is small in the stable form of the complex, as is revealed from the overlap integral values given in Table VII.

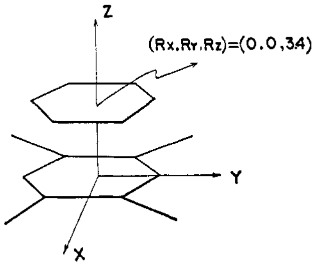


Figure 9. One of the models assumed for the TCNB–benzene complex.

Table VI. They are given in terms of the following integral

$$(H^c)_{ij} \equiv \int \theta_i(1) H^c(1) \phi_j(1) d\tau$$

Table VI. The Matrix Elements between the CT Configurations and the Ground and the Locally Excited Configurations

	Φ_G	Φ_{L1}	Φ_{L2}
$\Phi(\theta_2^{-1}\phi_8)$	$\sqrt{2}(H^c)_{28}$	$a(H^c)_{26}$	$d(H^c)_{27}$
$\Phi(\theta_2^{-1}\phi_9)$	$\sqrt{2}(H^c)_{29}$	$b(H^c)_{27}$	$c(H^c)_{26}$
$\Phi(\theta_3^{-1}\phi_8)$	$\sqrt{2}(H^c)_{38}$	$a(H^c)_{36}$	$d(H^c)_{37}$
$\Phi(\theta_3^{-1}\phi_9)$	$\sqrt{2}(H^c)_{39}$	$b(H^c)_{37}$	$c(H^c)_{36}$

Here H^c is the core attraction term of the total electronic Hamiltonian of the system. The integral is assumed to be proportional to the overlap integral

$$(\theta_i | H^c | \phi_j) = -KS_{ij} \quad (11)$$

where $S_{ij} = \int \theta_i(1)\phi_j(1)d\tau$

The constant K is taken as one of the experimental parameters. The matrix elements between the CT configurations are shown to be very small by an evaluation with the point charge approximation.

For calculating the overlap integrals,[26] two types of carbon atomic orbital functions were employed: one is the minimal Slater-type orbital with the orbital exponent 1.568[27] and the other, Roothaan's expanded Hartree–Fock atomic orbitals.[27] The values evaluated by the latter atomic orbitals are two or three times larger than those by the former atomic orbitals.[28]

The calculation was made on the basis of the geometrical models shown in Figure 9, where the center of one benzene ring is taken as an origin of the coordinate system and R_x, R_y, and R_z are the coordinates of the center of the other benzene ring. For the sake of simplicity the separation between the two benzene rings is fixed as R_z = 3.4 Å, and only the displacement along the x and y axes is taken into account.

Model 1; R_x = 0 and R_y = 0. In this case, the overlap integrals S_{28}, S_{29}, S_{38}, and S_{39}, which are related to the stabilization of the ground state, become zero from the symmetry of the molecular orbitals.[29] Therefore the lower CT configurations do not contribute to the stabilization of the ground state. This seems to mean that the displaced conformation, model 2, may be more favorable for the formation of the stable complex than model 1.

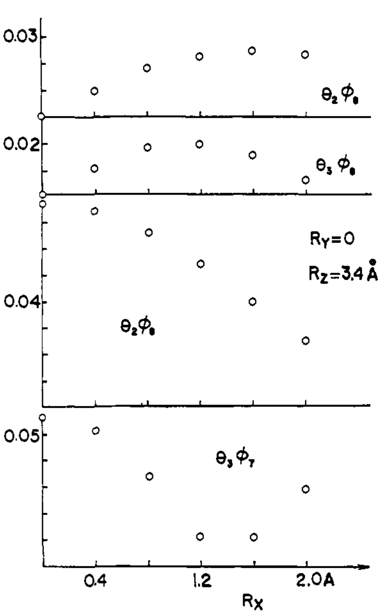


Figure 10. The values of the overlap integrals in R_y = 0, R_z = 3.4, and R_x = 0–2.0 Å.

In model 1 the higher CT configurations interact with the ground configuration through the overlap integrals S_{19}, $S_{2,10}$, and $S_{3,11}$. These overlap integrals are given in Table VII.

Model 2; $R_x \neq 0$ or $R_y \neq 0$. Since the overlap integrals between the occupied orbitals of the donor and the vacant orbitals of the acceptor are an important factor in considering the stabilization of the complex, they were calculated for some typical structures, with the results given in Table VII and Figure 10. The inspection of the results shows that these overlap integrals have the maximum values in the structure where a center of one benzene ring is located above a C–C bond of the other ring.

The stabilization energy of the ground state and the transition energies for excited states are tentatively evaluated and compared with the experimental results. The secular equations have been solved for two cases: (a) R_x = 1.2035, R_y = 0.695, and R_z = 3.4 Å; (b) R_x = 1.2035, R_y = 0, and R_z = 3.4 Å.

The Coulomb terms (ev) in the CT diagonal energies are obtained as follows.

$$C_{28} = \text{(a) } 3.294 \text{ (b) } 3.326 \quad C_{29} = \text{(a) } 3.406 \text{ (b) } 3.439$$

$$C_{38} = \text{(a) } 3.316 \text{ (b) } 3.353 \quad C_{39} = \text{(a) } 3.411 \text{ (b) } 3.445$$

We must determine two parameters, $I - A$ and K. $I - A$ has been selected in the range from 8.65 to 6.25 ev. When the Hartree–Fock atomic orbitals are used, the value of K is settled to 10, the magnitude of which might be reasonable from the comparison with the case of benzene, where $\beta_{C-C}/S_{C-C} = -9.6$. However, by the single Slater-type orbital for calculation between molecules, a much larger K value, 20–30, is used since the overlap integral is underestimated by this procedure.

---

(26) Calculations of the overlap integrals and the secular equations were performed by the aid of an electronic computer FACOM 202 in our institute. The authors acknowledge the assistance of Mr. H. Takahashi for making the program.

(27) T. L. Gilbert, private communication.

(28) Through our calculation we have used common atomic orbitals for constructing the vacant and occupied molecular orbitals, because the shape of the vacant π orbital may be less deformed in the case of π complexes than in the case of the acceptor orbital of iodine complexes.[15,16]

(29) Even if the rotation of one of the benzene rings around the Z axis is allowed, S_{28}, S_{29}, S_{38}, and S_{39} are still equal to zero, because the orbitals θ_2 and θ_3 of benzene are doubly degenerate.

Table VII. The Overlap Integrals between Benzene and TCNB Orbitals

R_x, Å	R_y, Å	R_z, Å	S_{28}	S_{29}	S_{38}	S_{39}	$S_{2,10}$	$S_{3,11}$	S_{26}	S_{37}	S_{58}[a]	S_{49}[a]
0	0	3.4	0	0	0	0	−0.0043	0.0133	−0.0773	−0.0570	−0.0234	−0.0238
0.40	0	3.4	0.0096	0	0	−0.0111	−0.0052	0.0135	−0.0745	−0.0509	−0.0214	−0.0209
0.80	0	3.4	0.0177	0	0	−0.0185	−0.0076	0.0136	0.0664	−0.0342	−0.0160	−0.0135
1.20	0	3.4	0.0229	0	0	−0.0199	−0.0105	0.0125	−0.0544	−0.0116	−0.0082	−0.0050
1.60	0	3.4	0.0245	0	0	−0.0155	−0.0126	0.0092	−0.0400	−0.0113	0.0002	0.0015
0	0.46	3.4	0	−0.0091	−0.0110	0	−0.0032	0.0133	−0.0693	−0.0543	−0.0200	−0.0215
0	0.93	3.4	0	−0.0144	−0.0195	0	−0.0006	0.0133	−0.0480	−0.0469	−0.0107	−0.0158
0	1.39	3.4	0	−0.0140	−0.0239	0	+0.0021	0.0130	−0.0204	−0.0365	−0.0006	−0.0095
1.20	0.695	3.4	0.0167	−0.0132	−0.0051	−0.0198	...	...	−0.0417	−0.0089	...	...
1.20	0.695	2.8	0.0356	−0.0275	−0.0106	−0.0421	...	...	−0.0776	−0.0159	...	...

[a] Overlap integrals concerning the interaction between CT configurations and lower locally excited configurations of benzene.

Table VIII. Calculated Wave Functions and Energies for the Mesitylene–TCNB Complex[a]

	W_i, ev		Φ_G[b]	Φ_{L1}[c]	Φ_{L2}[c]	Φ_{CT_1}[d]	Φ_{CT_2}[d]	Φ_{CT_3}[d]	Φ_{CT_4}[d]
W_0	−0.05	Ψ_0	0.9941	0.0026	0.0052	0.0665	−0.0449	−0.0201	−0.0699
W_1	3.28	Ψ_1	−0.0358	0.5013	0.0837	0.7244	0.0568	0.4595	−0.0353
W_2	3.49	Ψ_2	0.0491	−0.0510	0.0072	−0.5037	−0.0596	0.8588	0.0087
W_3	3.96	Ψ_3	0.0710	0.4039	−0.3131	−0.2619	0.7590	−0.0813	0.2872
W_4	4.07	Ψ_4	0.0451	0.0892	−0.0304	−0.0324	−0.4212	−0.0543	0.8987
W_5	4.21	Ψ_5	−0.0199	0.7582	0.1009	−0.3681	−0.4006	−0.1955	−0.2836
W_6	4.80	Ψ_6	0.0245	0.0117	0.9401	−0.1098	0.2779	−0.0552	0.1523

[a] The calculation was made for the following geometrical parameters and the $I - A$ value: $R_x = 1.20$, $R_y = 0.695$, $R_z = 3.4$ Å, and $I - A = 6.80$ ev. [b] Φ_G is the wave function of the ground configuration shown in eq 5. [c] Φ_1 and Φ_2 are the wave functions of the locally excited configurations of TCNB shown in eq 6. [d] Φ_{CT_1}, Φ_{CT_2}, Φ_{CT_3}, and Φ_{CT_4} are the wave functions of the CT configurations shown in eq 7.

Figure 7 shows the transition energies calculated for case a, the Hartree–Fock atomic orbital being used. The evaluated wave functions of the ground and excited states of the TCNB–mesitylene complex as an example are tabulated in Table VIII.

By the use of the resultant wave functions, we calculated the transition probability between the ground and the excited states. Writing the ground and the excited states as

$$\begin{aligned}\Psi_G &= a\Phi_G + \Sigma b_i\Phi_i(D^+A^-) + \Sigma c_i\Phi_i(DA^*)\\ \Psi_E &= a'\Phi_G + \Sigma b'_i\Phi_i(D^+A^-) + \Sigma c_i'\Phi_i(DA)^*\end{aligned} \tag{12}$$

the transition moment is approximately represented as

$$(\Psi_G|er|\Psi_E) \simeq b_ib_i'(\Phi_i(D^+A^-)|en|\Phi_i(D^+A^-)) + \Sigma(ac_i' + c_ia')(\Phi_i(DA^*)|er|\Phi(DA)) + \Sigma(ab_i' + b_ia')(\Phi_i(D^+A^-)|er|\Phi(DA)) \tag{13}$$

where the second term of the right-hand side was taken from the experimental values. The first and the third terms are estimated as

$$(\Phi(D^+A^-)|er|\Phi(D^+A^-)) \cong e(R_A - R_D)$$

$$(\Phi(D^+A^-)|er|\Phi(DA)) \simeq \sqrt{2}\sum_{pq}c_{Ap}c_{Dq} \times \int \chi_p(1)er\chi_q(1)d\tau \simeq \sqrt{2}\sum_{pq}c_{Ap}c_{Dq}[(R_p + R_q)S_{pq}]/2 \tag{14}$$

The second term in eq 13 appears only for the x and y directions in the molecular plane, while the first and third terms might have components in the z direction as well as in the x and y directions. In Figures 6a and 6b, $(\Psi_G|ez|\Psi_{Ej})^2$ and $(\Psi_G|ex|\Psi_{Ej})^2 + (\Psi_G|ey|\Psi_{Ej})^2 + |(\Psi_G|ez|\Psi_{Ej})|^2$ are shown for each transition.

In view of the ambiguity in the geometrical structure of the TCNB complexes under consideration, too much importance should not be attached to the present theoretical results, especially to the calculated stabilization energy. However, they might be important in giving a qualitative or semiquantitative explanation to the observed phenomena, in particular, to the appearance of the two CT bands, the decrease in the absorption intensities of the first bands of the TCNB complexes with the decrease in the ionization potentials of electron donors, and the polarization of the first and second CT bands.

Appendix

By the aid of the electronic computer program of SCF–CI calculation based on the Pariser–Parr–Pople approximation,[30,31] we calculated the molecular orbitals and the transition energies of TCNB and some other polycyanobenzenes. The results for $\beta_{CN} = -3.28$ ev and $\beta_{CC} = -2.39$ ev are given in Tables V and IX.

Table IX. Calculated and Observed Transition Energies and Oscillator Strengths

Calcd		Obsd	
Transition energies, v	Oscillator strength	Transition energies, ev	Oscillator strength
4.45	0.01	3.93	0.03
4.59	0.17	4.66	0.34
5.90	2.11	5.56	
6.15	1.18		

---

(30) R. Pariser and R. G. Parr *J. Chem. Phys.*, **21**, 466 (1953).
(31) J. A. Pople, *Proc. Phys. Soc.* (London), **A68**, 81 (1955).