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The Triplet States of 1,3,5-Tricyanobenzene Complexes with Methyl Substituted Benzenes

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Triplet-triplet absorption, phosphorescence, and ESR spectra have been measured on the 1,3,5-tricyanobenzene complexes with toluene, mesitylene, durene, and hexamethylbenzene. Four triplet-triplet absorption bands were commonly observed in the wave number region of 10000—30000 cm^{-1} for all the complexes. The observed phosphorescence and T-T absorption spectra could be understood systematically by considering the interaction among zero-order charge-transfer triplet states and zero-order locally (within the acceptor) excited triplet states. From an analysis of the zero-field splitting values obtained from the observed ESR spectra, the contribution of the zero-order charge-transfer triplet state to the lowest triplet state was determined to be 76, 65, 25, and 9% for the 1,3,5-tricyanobenzene complexes with hexamethylbenzene, durene, mesitylene, and toluene, respectively. From the consideration on the results obtained for various polycyanobenzene complexes, the phosphorescence lifetime was found to decrease remarkably for the complexes with the charge-transfer character higher than 50% in their lowest triplet states.

The triplet states of electron donor-acceptor (EDA) complexes have been studied in detail through measurements of the phosphorescence and ESR spectra.[1–7] In particular, concerning the TCNB complexes with benzene and methyl substituted benzenes, the nature of their lowest triplet states was investigated quantitatively and the appearance of the charge-transfer (CT) phosphorescence characteristic of the electron donor-acceptor interaction was confirmed.[4,5]

Triplet-triplet (T-T) absorption spectra have been measured with some EDA complexes.[8–12] The analysis of the results on the TCNB complexes with methyl substituted benzenes supports the conclusions obtained from the phosphorescence and ESR spectra.[10,12]

In the present paper, for the purpose of studying the effects of the electron accepting ability and molecular symmetry of the acceptor upon the triplet states of EDA complexes, we have undertaken a study of the phosphorescence, ESR, and T-T absorption spectra of the 1,3,5-tricyanobenzene complexes with toluene, mesitylene, durene, and hexamethylbenzene.

Experimental

1,3,5-Tricyanobenzene (TRCNB) used as electron acceptor was prepared and purified by the method described in literature.[13,14]

Hexamethylbenzene (HMB), durene, mesitylene, and toluene were used as electron donors. HMB and durene were recrystallized from ethanol. Mesitylene was shaken with concentrated sulfuric acid, washed with water, dried over calcium chloride, and finally distilled. Toluene (Dotite spectrosol grade) was used without further purification.

T-T absorption spectra were measured at 77 K for the TRCNB–toluene complex in a toluene–ethyl ether (1:1) mixed solvent and for the other TRCNB complexes in an ethyl ether–isopentane (1:1) mixed solvent (EP). The samples were excited by a 500 W super-high pressure mercury lamp combined with a Toshiba UV-D 25 filter. The details of the measurement were described in a previous paper.[12]

The electronic absorption spectra as shown in Fig. 2 were measured with a Cary recording spectrophotometer model 14M. Phosphorescence spectra were measured with a phosphoroscope and a grating monochromator (Spex 1700-111) attached with an EMI 9558 QB photomultiplier, and excitation of the samples was effected with a 100 W high pressure mercury lamp.

ESR spectra of the phosphorescent states were measured in rigid solutions at 77 K with a JEOL ME 3X spectrometer (9225.9 MHz, 100 kHz magnetic field modulation), the samples being excited with a 500 W super-high pressure mercury lamp. The microwave magnetic field was perpendicular to the external field.

Theoretical

In order to assign the observed T-T absorption spectra and clarify the nature of the triplet states of the complexes, theoretical studies were made by considering the interaction among the zero-order CT triplet states and the zero-order locally (within TRCNB) excited (LE) triplet states. The details of the method were described in the previous paper.[12] In actuality, we took six zero-order CT triplet states and three zero-order LE triplet states shown in Table 1.

The molecular orbitals of TRCNB were calculated by the Pariser-Parr-Pople SCF MO method,[15,16] the same parameters as those used for TCNB[17] being adopted. The results are shown in Table 2. The zero-order CT triplet states in Table 1, ${}^3\Phi_{\mathrm{CT}_1}({}^3\Phi_{\mathrm{CT}_2})$, ${}^3\Phi_{\mathrm{CT}_3}({}^3\Phi_{\mathrm{CT}_4})$, and ${}^3\Phi_{\mathrm{CT}_5}({}^3\Phi_{\mathrm{CT}_6})$, correspond to the electron transfer from the highest occupied orbital of the donor, $\theta_2(\theta_3)$, to the lowest three vacant orbitals of TRCNB, ϕ_7, ϕ_8, and ϕ_9, respectively. The zero-order LE triplet states, ${}^3\Phi_{\mathrm{LE}_1}$, ${}^3\Phi_{\mathrm{LE}_2}$, and ${}^3\Phi_{\mathrm{LE}_3}$ are represented as follows:

$$\begin{aligned}{}^3\Phi_{\mathrm{LE}_1} = {} & -0.64638\,{}^3\Psi_{6\to7}+0.64719\,{}^3\Psi_{5\to8}+0.00040\,{}^3\Psi_{5\to9}\\ & -0.00081\,{}^3\Psi_{4\to8}+\cdots\\ {}^3\Phi_{\mathrm{LE}_2} = {} & 0.52383\,{}^3\Psi_{6\to7}+0.52037\,{}^3\Psi_{5\to8}+0.33223\,{}^3\Psi_{5\to9}\\ & -0.31785\,{}^3\Psi_{4\to8}+\cdots\\ {}^3\Phi_{\mathrm{LE}_3} = {} & -0.02656\,{}^3\Psi_{6\to7}-0.02695\,{}^3\Psi_{5\to8}-0.44357\,{}^3\Psi_{5\to9}\\ & +0.31901\,{}^3\Psi_{4\to8}+\cdots\end{aligned}$$

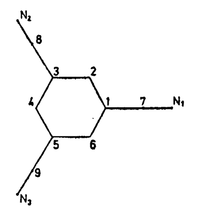
Table 1. Configurations and their estimated energies used in the calculation for the TRCNB–HMB complex

Configuration	$^3\Phi_{\mathrm{CT}_1}$	$^3\Phi_{\mathrm{CT}_2}$	$^3\Phi_{\mathrm{CT}_3}$	$^3\Phi_{\mathrm{CT}_4}$	$^3\Phi_{\mathrm{CT}_5}$	$^3\Phi_{\mathrm{CT}_6}$	$^3\Phi_{\mathrm{LE}_1}$	$^3\Phi_{\mathrm{LE}_2}$	$^3\Phi_{\mathrm{LE}_3}$
Energy (eV)	3.0	3.0	3.0	3.0	5.25	5.25	3.20	3.92	5.11

Table 2. Orbital energies and their wave functions of TRCNB

Orbital energy (eV)		Wave function[a]
ϕ_1	−14.430	$0.3704\chi_1+0.3262\chi_2+0.3715\chi_3+0.3267\chi_4+0.3715\chi_5+0.3262\chi_6+0.2377\chi_7+0.2340\chi_8+0.2340\chi_9+0.1774\chi_{\mathrm{N}_1}+0.1793\chi_{\mathrm{N}_2}+0.1793\chi_{\mathrm{N}_3}$
ϕ_2	−13.148	$-0.0009\chi_1+0.1600\chi_2+0.2811\chi_3+0.0005\chi_4-0.2802\chi_5-0.1605\chi_6-0.0014\chi_7+0.4522\chi_8-0.4508\chi_9-0.0014\chi_{\mathrm{N}_1}+0.4358\chi_{\mathrm{N}2}-0.4372\chi_{\mathrm{N}3}$
ϕ_3	−13.142	$0.3255\chi_1+0.0945\chi_2-0.1600\chi_3-0.1839\chi_4-0.1616\chi_5+0.0937\chi_6+0.5210\chi_7-0.2593\chi_8-0.2620\chi_9+0.5050\chi_{\mathrm{N}_1}-0.2521\chi_{\mathrm{N}_2}-0.2544\chi_{\mathrm{N}_3}$
ϕ_4	−11.857	$0.1708\chi_1+0.2399\chi_2+0.1721\chi_3+0.2409\chi_4+0.1721\chi_5+0.2399\chi_6-0.2991\chi_7-0.2973\chi_8-0.2973\chi_9-0.3979\chi_{\mathrm{N}1}-0.3963\chi_{\mathrm{N}_2}-0.3963\chi_{\mathrm{N}_3}$
ϕ_5	−10.208	$-0.4827\chi_1-0.2622\chi_2+0.2464\chi_3+0.5356\chi_4+0.2362\chi_5-0.2735\chi_6+0.1483\chi_7-0.0754\chi_8-0.0723\chi_9+0.3534\chi_{\mathrm{N}_1}-0.1803\chi_{\mathrm{N}_2}-0.1729\chi_{\mathrm{N}_3}$
ϕ_6	−10.208	$-0.0059\chi_1-0.4672\chi_2-0.4151\chi_3+0.0065\chi_4+0.4210\chi_5+0.4607\chi_6+0.0018\chi_7+0.1271\chi_8-0.1289\chi_9+0.0043\chi_{\mathrm{N}_1}+0.3037\chi_{\mathrm{N}_2}-0.3080\chi_{\mathrm{N}_3}$
ϕ_7	−1.669	$0.1570\chi_1-0.5328\chi_2+0.2605\chi_3+0.2003\chi_4-0.4174\chi_5+0.3324\chi_6+0.1016\chi_7+0.1680\chi_8-0.2693\chi_9-0.1319\chi_{\mathrm{N}_1}-0.2185\chi_{\mathrm{N}_2}+0.3502\chi_{\mathrm{N}_3}$
ϕ_8	−1.669	$-0.3912\chi_1+0.0761\chi_2+0.3315\chi_3-0.4992\chi_4+0.0596\chi_5+0.4233\chi_6-0.2532\chi_7+0.2139\chi_8+0.0384\chi_9+0.3288\chi_{\mathrm{N}_1}-0.2782\chi_{\mathrm{N}_2}-0.0500\chi_{\mathrm{N}_3}$
ϕ_9	−0.339	$-0.1354\chi_1+0.2922\chi_2-0.1370\chi_3+0.2306\chi_4-0.1370\chi_5+0.2292\chi_6-0.3683\chi_7-0.3672\chi_8-0.3672\chi_9+0.3566\chi_{\mathrm{N}_1}+0.3558\chi_{\mathrm{N}_2}+0.3558\chi_{\mathrm{N}_3}$
ϕ_{10}	1.209	$-0.3895\chi_1+0.1198\chi_2+0.1926\chi_3-0.2354\chi_4+0.1939\chi_5+0.1191\chi_6+0.5463\chi_7-0.2728\chi_8-0.2746\chi_9-0.4007\chi_{\mathrm{N}_1}+0.2004\chi_{\mathrm{N}_2}+0.2018\chi_{\mathrm{N}_3}$
ϕ_{11}	1.216	$-0.0007\chi_1-0.2043\chi_2+0.3366\chi_3-0.0004\chi_4-0.3359\chi_5+0.2047\chi_6+0.0010\chi_7-0.4740\chi_8+0.4731\chi_9-0.0008\chi_{\mathrm{N}_1}+0.3480\chi_{\mathrm{N}_2}-0.3473\chi_{\mathrm{N}_3}$
ϕ_{12}	2.807	$-0.3834\chi_1+0.3410\chi_2-0.3844\chi_3+0.3415\chi_4-0.3844\chi_5+0.3410\chi_6+0.2274\chi_7+0.2291\chi_8+0.2911\chi_9-0.1304\chi_{\mathrm{N}_1}-0.1316\chi_{\mathrm{N}_2}-0.1316\chi_{\mathrm{N}_3}$

a) χ_n is the AO of the n-th carbon atom. The numbering of the atoms is shown in the figure next to Table 2.



where $^3\Psi_{j\to k}=|\theta_1\theta_1\cdots\phi_1\phi_1\cdots\phi_j\phi_k|$, ϕ_j and ϕ_k being the j-th (occupied) and k-th (vacant) SCF MO's of TRCNB, respectively.

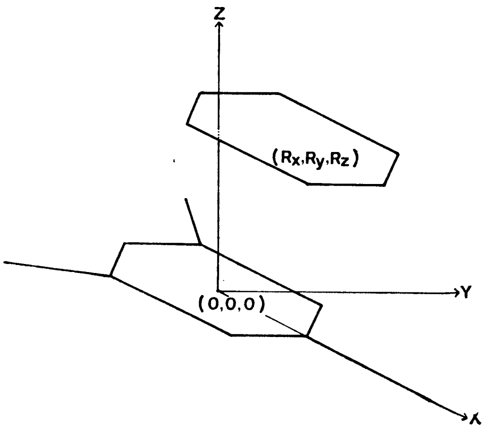


Fig. 1. Models assumed for the TRCNB-benzene complex.

Model	R_x (Å)	R_y (Å)	R_z (Å)
1	0.0	0.0	3.4
2	0.695	0.0	3.4
3	1.274	0.602	3.4
4	1.39	0.0	3.4
5*	0.0	0.0	3.4

* One of the benzene rings is rotated about the z axis by 30° from the other.

The geometrical structure of this complex is not yet known. Therefore, the actual calculation was made with five tentative geometrical models shown in Fig. 1. The separation between the two benzene rings was fixed to 3.4 Å. The off-diagonal elements of the total electronic Hamiltonian representing the interactions between the zero-order CT triplet states and the zero-order LE triplet states were taken to be $\beta=-kS_{ij}$, where the parameter k was assumed to be 10[17] and the overlap integral $S_{ij}=\int\theta_i(1)\phi_j(1)\mathrm{d}\tau$ was calculated by the use of the SCF MO's. The energies of the zero-order triplet states were determined by the procedures described in the previous paper.[12] The result on the TRCNB–HMB complex is shown in Table 1.

Results and Discussion

Electronic Absorption Spectra. The donors used in the present study show absorption bands in the wavelength region shorter than 280 nm.[18] The acceptor, TRCNB, exhibits the longest wavelength band at 300 nm. Methanol solutions containing TRCNB as an electron acceptor and HMB or durene as an electron donor exhibit a weak CT band in the 300—360 nm region. TRCNB in mesitylene also shows a CT band at 290 nm. The CT band of the TRCNB–HMB complex, as an example, is shown in Fig. 2. No CT band could be observed with TRCNB in toluene.

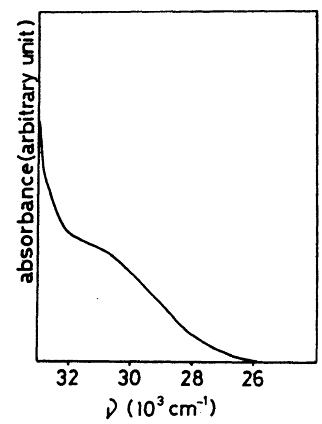


Fig. 2. The electronic absorption spectrum of the methanol solution of the TRCNB-HMB complex.

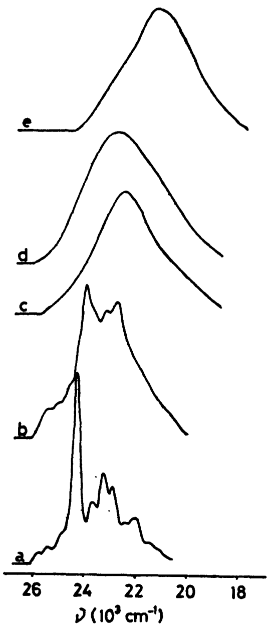


Fig. 3. Phosphorescence spectra of TRCNB and its Complexes in EP at 77 K. (a) TRCNB (b) TRCNB–toluene (c) TRCNB–mesitylene (d) TRCNB–durene (e) TRCNB–HMB.

It is expected to appear around 270 nm and may be covered with the strong absorptions of the component molecules.

The Phosphorescence Spectra. The phosphorescence spectra of the TRCNB complexes were measured by use of a Toshiba UV-D2 filter so that the excitation was effected only in the CT bands. The observed phosphorescence spectra are shown in Fig. 3, together with that of TRCNB. Their peak positions are shown in Table 3, together with the phosphorescence lifetimes. The characteristics of the phosphorescences of the TRCNB complexes are as follows: (1) the vibrational structures appearing in the phosphorescence spectrum of TRCNB disappear or become obscure in the spectra of the CT complexes; (2) the phosphorescence spectra shift to the longer wavelengths for the complexes than for the acceptor; (3) the phosphorescence lifetimes are slightly shorter for the complexes than for the acceptor. These characteristics are similar to those observed for the TCNB complexes⁴⁾ and suggest that the lowest excited states of the complexes under consideration have the CT character to some extent.

Table 3. Phosphorescence maxima ($\nu_{\max}$) and lifetimes (τ) observed for TRCNB and its complexes with methyl substituted benzenes

	$\nu_{\max}$ (10^3 cm^{-1})	τ (s)
TRCNB	25.8	7.0
TRCNB–Toluene	24.0	7.0
TRCNB–Mesitylene	22.8	6.7
TRCNB–Durene	23.0	5.5
TRNCB–HMB	21.5	5.0

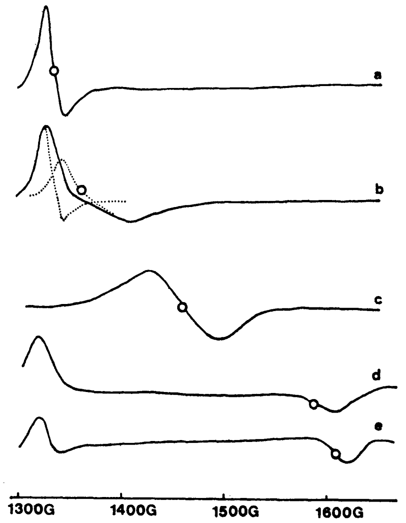


Fig. 4. ESR spectra ($\Delta m=\pm 2$) observed with the ternary solutions containing TRCNB and various donors in EP at 77 K. (a) TRCNB (b) TRCNB–toluene (c) TRCNB–mesitylene (d) TRCNB–durene (e) TRCNB–HMB. Open circles denote the position of $H_{\min}$ The signal due to the TRCNB was not observed for curve (c) because of the high concentration of mesitylene. The signals due to the complex and the TRCNB are close to each other in curve (b). The $H_{\min}$ value in this case was obtained with the curve corrected for the contribution from the TRCNB.

The ESR Spectra. In order to discuss the character of the lowest triplet state quantitatively, we measured ESR spectra for TRCNB and its complexes. ESR spectra due to the $\Delta m=\pm 2$ transitions of the lowest triplet states were observed for the EP solutions of the CT complexes and of the acceptor itself by steady irradiation with the 500 W mercury lamp through a UV-D25 filter. The observed spectra are shown in Fig. 4. The lowest possible resonance fields ($H_{\min}$) were determined as the midpoint between the maximum and minimun of each of the observed derivative curves. From the $H_{\min}$ value, the zero-field splitting constant, D^*, was evaluated by the following equation:¹⁹⁾

$$D^* = \left\{\frac{3}{4}(h\nu)^2 - 3(g\beta H_{\min})^2\right\}^{1/2}$$

where $D^*=(D^2+3E^2)^{1/2}$. D, E, ν, g, and β have their conventional meanings. The g value was assumed

Table 4. The observed D^* values and the CT characters

Donor	TRCNB		TCNB[a]	
	D^* ($\mathrm{cm^{-1}}$)	CT(%)	D^* ($\mathrm{cm^{-1}}$)	CT(%)
Toluene	0.1478	9	0.1189	11
Mesitylene	0.1237	25	0.0844	42
Durene	0.0698	65	0.0502	72
HMB	0.0557	76	0.0231	95
	0.1567[b]		0.1317[b]	

a) Ref. 4). b) Values for the acceptors.

to be 2.003 and 2.000 for the acceptor and the complexes, respectively.[5] From the D^* values obtained for the complexes we evaluated the degree of CT, x(%), in the lowest triplet state for the molecular complexes by the following equation.[5]

$$D^* = xD_{\mathrm{CT}}^* + (1-x)D_{\mathrm{A}}^*$$

Here D_{A}^* is the observed valueof TRCNB itself (0.1567 $\mathrm{cm^{-1}}$) and D_{CT}^* is the theoretical value of the zero-order CT triplet state. By considering the electron spin dipolar interaction, D_{CT}^* was calculated to be 0.0243, 0.0228, 0.0229, and 0.0250 $\mathrm{cm^{-1}}$ for the zero-order CT triplet states represented by $\Phi_{\mathrm{CT_1}}$, $\Phi_{\mathrm{CT_2}}$, $\Phi_{\mathrm{CT_3}}$, and $\Phi_{\mathrm{CT_4}}$, respectively. Since they are close to one another, the average value, 0.0238 $\mathrm{cm^{-1}}$ was used as D_{CT}^*. The D^* and x values are given in Table 4, together with those for the TCNB complexes.

The results show that the CT character of the lowest triplet state increases for the TRCNB complexes with the decreasing I_{p} of the donor. This tendency was also found for the TCNB and dicyanobenzene complexes. Table 4 shows that the lowest triplet state is mainly contributed by the CT structure in the TRCNB complexes with HMB and durene, whereas by the LE structure in those with mesitylene and toluene.

T-T Absorptions of the TRCNB Complexes with Methyl Substituted Benzenes. The T-T absorption spectra observed for the TRCNB complexes with HMB, durene, mesitylene, and toluene are shown in Fig. 5. The spectrum of each complex apparently consists of four bands, bands A and B in 10000—15000 $\mathrm{cm^{-1}}$, and bands C and D in $>$20000 $\mathrm{cm^{-1}}$.[20] Neither TRCNB

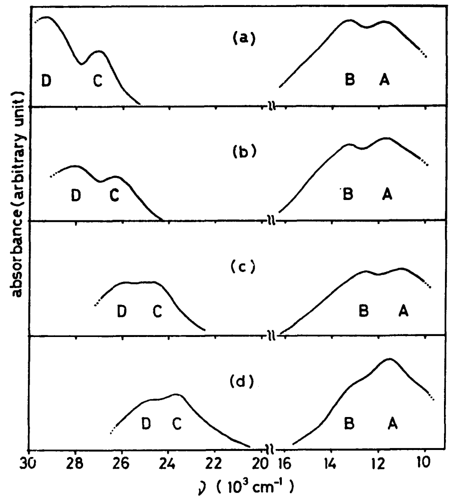


Fig. 5. T-T absorption spectra observed with the TRCNB complexes with (a) toluene (b) mesitylene (c) durene (d) HMB.

Table 5. T-T absorption maxima (in 10^3 $\mathrm{cm^{-1}}$) observed for the TRCNB complexes with methyl substituted benzenes

Donor	Band A	Band B	Band C	Band D
Toluene	11.8	13.3	27.0	29.4
Mesitylene	11.6	13.2	26.3	28.0
Durene	10.9	12.5	24.7	26.0
HMB	11.6	13.2	23.8	25.0

Table 6. Observed and calculated transition energies (10^3 $\mathrm{cm^{-1}}$) and oscillator strengths (in parentheses) for the TRCNB–HMB complex

	Calcd					Obsd[a]
	1	2	3	4	5	
$T_2 \leftarrow T_1$	2.6 (0.004)	3.0 (0.003)	2.2	2.6 (0.003)	2.6	
$T_3 \leftarrow T_1$	4.5 (0.004)	3.9 (0.004)	2.3	2.7 (0.001)	4.5	
$T_4 \leftarrow T_1$	4.5 (0.001)	3.9 (0.001)	2.3	2.7 (0.000)	4.5	
$T_5 \leftarrow T_1$	10.6 (0.330)	8.9 (0.220)	5.6	6.4 (0.150)	10.6	11.6 (S)
$T_6 \leftarrow T_1$	13.5 (0.000)	12.5 (0.090)	10.5	11.0 (0.110)	13.5	13.2 (M)
$T_7 \leftarrow T_1$	19.7 (0.075)	19.8 (0.030)	19.4	19.4 (0.020)	19.7	
$T_8 \leftarrow T_1$	22.7 (0.170)	22.0 (0.280)	20.5	20.9 (0.240)	22.7	23.8 (M)
$T_9 \leftarrow T_1$	24.9 (0.100)	23.4 (0.050)	20.5	21.4 (0.090)	24.9	25.0 (M)

a) S and M in parentheses mean strong and medium intensities, respectively.

Table 7. Wave functions calculated for the TRCNB–HMB complex (model 2)

$$^3\psi_1=0.5963\,^3\Phi_{\mathrm{CT}_1}+0.3399\,^3\Phi_{\mathrm{CT}_2}-0.1784\,^3\Phi_{\mathrm{CT}_3}+0.3089\,^3\Phi_{\mathrm{CT}_4}+0.6179\,^3\Phi_{\mathrm{LE}_1}-0.1395\,^3\Phi_{\mathrm{LE}_2}$$
$$^3\psi_2=-0.4179\,^3\Phi_{\mathrm{CT}_1}-0.2363\,^3\Phi_{\mathrm{CT}_2}-0.4085\,^3\Phi_{\mathrm{CT}_3}+0.7066\,^3\Phi_{\mathrm{CT}_4}+0.1261\,^3\Phi_{\mathrm{LE}_1}+0.2988\,^3\Phi_{\mathrm{LE}_2}$$
$$^3\psi_3=0.8618\,^3\Phi_{\mathrm{CT}_3}+0.4981\,^3\Phi_{\mathrm{CT}_4}$$
$$^3\psi_4=-0.4929\,^3\Phi_{\mathrm{CT}_1}+0.8648\,^3\Phi_{\mathrm{CT}_2}$$
$$^3\psi_5=-0.3446\,^3\Phi_{\mathrm{CT}_1}-0.1965\,^3\Phi_{\mathrm{CT}_2}+0.2224\,^3\Phi_{\mathrm{CT}_3}-0.3850\,^3\Phi_{\mathrm{CT}_4}+0.7579\,^3\Phi_{\mathrm{LE}_1}+0.2618\,^3\Phi_{\mathrm{LE}_2}$$
$$^3\psi_6=0.3288\,^3\Phi_{\mathrm{CT}_1}+0.1874\,^3\Phi_{\mathrm{CT}_2}+0.1090\,^3\Phi_{\mathrm{CT}_6}-0.1670\,^3\Phi_{\mathrm{LE}_1}+0.8975\,^3\Phi_{\mathrm{LE}_2}$$
$$^3\psi_7=0.2820\,^3\Phi_{\mathrm{CT}_5}-0.4882\,^3\Phi_{\mathrm{CT}_6}+0.8193\,^3\Phi_{\mathrm{LE}_3}$$
$$^3\psi_8=0.8659\,^3\Phi_{\mathrm{CT}_5}+0.5002\,^3\Phi_{\mathrm{CT}_6}$$
$$^3\psi_9=-0.4078\,^3\Phi_{\mathrm{CT}_5}+0.7061\,^3\Phi_{\mathrm{CT}_6}+0.5712\,^3\Phi_{\mathrm{LE}_3}$$

nor the donors show any T-T absorption in these wave number regions. The observed absorption bands for the respective complexes decay at the same rate as the corresponding phosphorescences. Therefore, we can safely assign them to the T-T absorption bands of the complexes. The observed band positions are given in Table 5.

Assignment of the T-T Absorptions. We interpreted the observed absorption spectra considering the calculated transition energies and oscillator strengths, the TRCNB–HMB complex being taken as an example. The observed and the calculated transition energies for this complex are shown in Table 6. The calculations were made with five geometrical models shown in Fig. 1. In Table 6 are also shown the calculated oscillator strengths for three of the models.

The calculated band positions and intensities vary considerably with the choice of models. Model 1 (face-to-face model) is rather favorable from the comparison between the observed and calculated transition energies, but the calculated intensities for this model can not explain even qualitatively the observed ones; particularly the intensity predicted for band B is too weak. The transition energies calculated for models 3 and 4 become too low compared with the observed data (particularly for band A). As a whole, the overall feature of the observed spectrum (the appearance of the two pairs of bands with comparable intensities) seems to be reproduced by model 2.[21)]

The wave functions calculated for model 2 are given in Table 7.[22)] Since the lowest four zero-order CT triplet states (3.0 eV) and the lowest zero-order LE triplet state (3.2 eV) are close to each other in the TRCNB–HMB complex, they mix with each other efficiently and give rise to the five states, T_1—T_5. The bands corresponding to the transitions from T_1 to T_2—T_4 are expected to be too weak to be observed. A fairly strong band due to the transition between T_1 and T_5 is expected to appear in the lowest energy region. Therefore, we assign band A in the near-infrared region to the $T_5 \leftarrow T_1$ transition. As is clearly seen in Table 6, bands B, C, and D can reasonably be assigned to the transitions from T_1 to T_6, T_8, and T_9, respectively.[23)]

From the wave functions given in Table 7, it is found that T_1 is mainly contributed by the zero-order CT triplet states, while the main components of T_5 and T_6 are $^3\Phi_{\mathrm{LE}_1}$ and $^3\Phi_{\mathrm{LE}_2}$, respectively. Therefore, bands A and B are assigned to the LE←CT transitions.

The $T_8 \leftarrow T_1$ and $T_9 \leftarrow T_1$ transitions may be interpreted as due to the local excitations within the TRCNB anion. The T_8 and T_9 states arise mainly from the interaction between the $^3\Phi_{\mathrm{CT}_5}$ and $^3\Phi_{\mathrm{CT}_6}$ structures. This means that the $T_8 \leftarrow T_1$ and $T_9 \leftarrow T_1$ transitions correspond to the strong absorption of the TRCNB anion appearing at 18500 cm^{-1}.[24)] The shifts to the higher frequencies (5300 and 6500 cm^{-1}) caused by the complex formation may partly be due to the stabilization of the lowest zero-order triplet state.

Effect of Electron Donors. The calculated (model 2) and observed triplet levels are shown in Fig. 6, in which the triplet-state energies of the complexes are plotted against the ionization potentials of the donors,

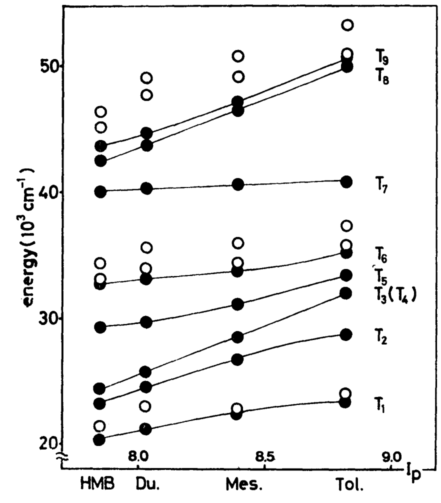


Fig. 6. The triplet state energy diagrams calculated (model 2) and observed for the TRCNB complexes. ○: observed, ●: calculated.

Table 8. CT characters (%) estimated for the triplet states of the TRCNB complexes (model 2)

Donor	T_1[a)]	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9
Toluene	25 (9)	42	100	100	76	76	4	100	96
Mesitylene	37 (25)	72	100	100	57	34	8	100	92
Durene	53 (65)	86	100	100	42	21	19	100	80
HMB	60 (76)	89	100	100	36	16	32	100	67

a) The values in parentheses are estimated from the ESR spectra.

I_p. The calculated energy levels, though they are commonly about 0.25 eV smaller for the T_5, T_6, T_8, and T_9 states of all the complexes than the observed values, can well explain the observed energy dependences upon I_p.

The calculated contributions of the zero-order CT triplet states to the $T_1 \sim T_9$ states of the complexes are given in Table 8. The character of T_1 is mainly of the CT triplet for the complexes with HMB and durene and mainly of the LE triplet for those with mesitylene and toluene. A similar tendency was found for the TCNB complexes with these methyl substituted benzenes. The contributions of the zero-order CT triplet states to T_1 are 60, 53, 37, and 25% for the TRCNB complexes with HMB, durene, mesitylene, and toluene, respectively. This estimation is semi-quantitatively consistent with the results of the ESR study. The CT characters of the T_5 state are 36, 42, 57, and 76% for the TRCNB complexes with HMB, durene, mesitylene, and toluene. Consequently, it is confirmed that the character of band A is of the LE←CT transition for the TRCNB–HMB and TRCNB–durene complexes, and of the CT←LE transition for the TRCNB–mesitylene and TRCNB–toluene complexes.

Band B is comparatively insensitive to the electron donors. The calculation shows that the energies of the upper and lower states of this band, T_1 and T_6, change almost in parallel with each other by changing the electron donor from toluene to HMB. This is a reason why band B does not shift remarkably from donor to donor.

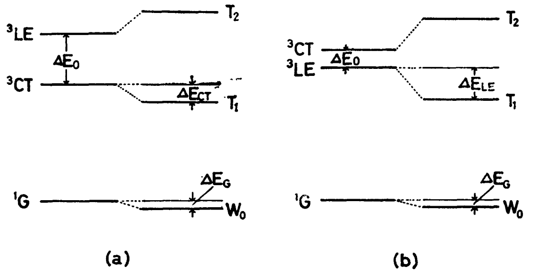
Bands C and D shift toward the higher frequencies with the increasing I_P of the donor. The upper states of these bands, T_8 and T_9, are mainly of the CT character and their energies increase more steeply than that of the T_1 state.

Comparison among Polycyanobenzene Complexes. Table 9 shows the observed values of $\Delta\nu_p = \nu_{00}^A - \nu_{max}^C$, x, and τ_C/τ_A for the phthalonitrile (PN), TRCNB, TCNB complexes with various donors. Here ν_{00}^A and ν_{max}^C are the phosphorescence 0-0 band frequency of the acceptor and the phosphorescence maximum frequency of the complex, respectively, x is the CT character of the phosphorescent state of the complex obtained from the ESR spectrum, and τ_A and τ_C are the phosphorescence lifetimes obtained for the acceptor and the complex, respectively.

Table 9. $\Delta\nu_p$, x, and τ_C/τ_A for various polycyanobenzene complexes

$\Delta\nu_p$(10^3 cm^{-1})	PN[a]	TRCNB	TCNB[b]
HMB	3.6	4.5	4.4
Durene	2.8	2.8	3.2
Mesitylene	2.8	3.0	2.9
Toluene		1.8	2.1
x(%)	PN[a]	TRCNB	TCNB[b]
HMB	48	76	95
Durene		65	72
Mesitylene	10	25	42
Toluene		9	11
τ_C/τ_A	PN[a]	TRCNB	TCNB[b]
HMB	0.89	0.71	0.44
Durene	0.84	0.79	0.60
Mesitylene	0.95	0.96	1.0
Toluene		1.0	1.0

a) Taken from Ref. 6. b) Taken from Ref 4.



(a) (b)

Fig. 7. Schematic energy diagrams of the lower triplet states of the HMB complexes with (a) TCNB or TRCNB; (b) PN.

As clearly seen in Table 9, $\Delta\nu_p$ and x increase, while τ_C/τ_A decreases, for a fixed acceptor with the decreasing I_p of the donor. This holds for all the complexes under consideration. On the other hand, for a fixed donor, $\Delta\nu_p$ is the largest for the TRCNB complex. For example, taking HMB as donor, $\Delta\nu_p$ is 4500, 4400, and 3600 cm^{-1} for the TRCNB, TCNB, and PN complexes, respectively. The phosphorescent states are mainly of the CT character for the TCNB and TRCNB complexes and of the LE character for the PN complex. As is seen in Fig. 7, $\Delta\nu_p$ is expressed as follows;

$$\Delta\nu_p = \Delta E_0 + \Delta E_{CT} - \Delta E_G$$

for the TCNB and TRCNB complexes

$$\Delta\nu_p = \Delta E_{LE} - \Delta E_G \qquad \text{for the PN complex.}$$

The energy difference between the zero-order CT and LE triplet states, ΔE_0, is estimated to be 2480 and 1600 cm^{-1} for the TCNB and TRCNB complexes, respectively. The stabilization energy of the ground configuration, ΔE_G, is estimated to be 240—480 cm^{-1} for the TCNB complex,[17] and is expected to be smaller for the TRCNB and PN complexes. Thus, the stabilization energy of the lowest zero-order CT or LE triplet state (ΔE_{CT} or ΔE_{LE}, respectively), is expected to be the greatest for the PN complex and the smallest for the TCNB complex. This is reasonable in view of the fact that the ΔE_0 value is the greatest for the TCNB complex and the smallest for the PN complex (160 cm^{-1}).

According to Table 9, the x values for a fixed donor decrease in the following order of acceptors; TCNB> TRCNB>PN. This is consistent with the expectation that the electron affinities of the acceptors decrease in the same order.

Finally let us consider the relation between the phosphorescence lifetime of a complex and the CT character in its lowest triplet state.[4] The τ_C/τ_A values are plotted *versus* x in Fig. 8. The figure shows that τ_C/τ_A decreases with the increasing x, and the decrease becomes appreciable, in particular, in the region of $x>50\%$. This may suggest that such phosphorescence quenching processes as ion-pair formation and ioniza-

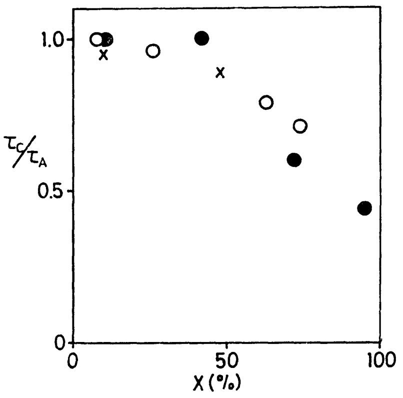


Fig. 8. Plots of τ_C/τ_A *versus* x for the complexes.
●: TCNB complexes, ○: TRCNB complexes, ×: PN complexes.

tion become important in that region of x.

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20) We could observe no T-T absorption band for the complexes in the region below 10000 cm^{-1}.

21) The overlap integral between the highest occupied orbital of the donor and the lowest vacant one of the acceptor, and consequently the stabilization energy of the ground state, is larger for models 2, 3, and 4 than for model 1. Thus, the former models favor the formation of a stable complex.

22) The calculated energy levels have a general tendency to be about 2000 cm^{-1} lower than the observed ones. This tendency was also seen to some extent in the TCNB complexes.[12] These discrepancies may originate from the underestimation of the interaction term. As the interaction is expected to increase in the excited state, the constant k should be taken to be greater than 10.

23) We did not assign band C to the $T_7 \leftarrow T_1$ transition. The $T_7 \leftarrow T_1$ transition is predicted to show a red shift with the increasing I_p of the donor, while as shown in Fig. 6, band C shifts to the higher frequencies with the increasing I_p.

24) Private communication from Dr. T. Shida, The Institute of Physical and Chemical Research.