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ELECTRONIC STRUCTURES AND CHARGE-TRANSFER SPECTRA OF *TRIS*[2.2.2]PARAXYLYLENE AND RELATED COMPOUNDS

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Abstract—Electronic spectra of *tris*[2.2.2]paraxylylene (3°-PX) and some related compounds were measured in order to investigate the electronic interaction (pπ-pπ and pσ-pσ type) between "normal" (undistorted) benzene rings 3°-PX showed a large hypochromic effect, i.e., its oscillator strength was observed to be 0·61 times of that of the corresponding linear polyparaxylylene. Charge-transfer (CT) spectra between these compounds and some electron acceptors were also studied. MO calculations (the VI/1, CNDO/2 and CI methods) were carried out in order to elucidate the electronic structure of 3°-PX and also the CT interactions between tetracyanoethylene and 3°-PX, benzene, toluene or *p*-xylene.

The electronic interaction between two conjugated molecules, especially for CT complexes,[1] or between two conjugated moieties within one molecule, particularly for cyclophanes have been investigated;† but, the interaction of three conjugated systems have only been studied for trypticene[3] or barrelene.[4] All these compounds as well as janusene[5] have a pσ-pσ type electronic interaction between π orbitals in addition to a common pπ-pπ type interaction. *Tris*[2.2.2]paraxylylene (abbreviated as 3°-PX)[6] and tetrakis[2.2.2.2]paraxylylene (4°-PX)[7] prepared by the authors seem appropriate to investigate the interaction between three or four "normal" benzene rings.‡ In this article we wish to report the electronic interaction in 3°-PX and the CT interactions between 3°-PX and several electron acceptors. The electronic and CT spectra of *p*-xylene and 4,4′-dimethylbibenzyl were measured to compare with those of 3°-PX.

The authors also treated these interactions with calculations by means of the variable integrals method 1 (VI/1)[8] or the CNDO/2 method[9] with the configuration interaction(CI) method. In the VI/1 calculations for 3°-PX the effects due to methylene bridges were considered as small perturbations of the orbital energies of the MO's.

EXPERIMENTAL

Materials. 3°-PX,[6] 4°-PX[7] and 4,4′-dimethylbibenzyl were prepared by the modified Wurtz reactions of *p*-xylylene chloride with a sodium-tetraphenylethylene complex as described elsewhere,[8] separated through a silica gel column and purified by repeated recrystalizations from n-hexane or a n-hexane-benzene mixture. Commercially available tetracyanoethylene (TCNE) was recrystalized from chloroform and sublimed in vacuo (mp 199·5°, lit [10] 200° in a sealed tube). Commercially available chloranil and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were recrystalized from chloroform (mp 292–292·5° and 211–212°, lit.[10] 290° and 213°, respectively). Commercially available spectrograde cyclohexane, n-heptane and methylene chloride were used without further purification.

Measurement of electronic and charge-transfer spectra. The electronic spectra were measured by using a Hitachi EPS-3T recording spectrophotometer. The CT spectra were measured immediately after the mixing of the two components dissolved in an appropriate solvent and kept at *ca* 25°. The concentration of 3°-PX or 4,4′-dimethylbibenzyl was adjusted to be from $1{\cdot}33 \times 10^{-2}$ to $24{\cdot}9 \times 10^{-2}$ M, and from $1{\cdot}19 \times 10^{-2}$ to $74{\cdot}3 \times 10^{-2}$ M, respectively, while the concentration of TCNE was taken to be *ca* $0{\cdot}1 \times 10^{-2}$ M. Equilibrium constants and molar extinction coefficients of the TCNE complexes were estimated by means of the Benesi-Hildebrand's equation.[11]

CALCULATIONS

Calculation procedure for 3°-PX. In our calculations 3°-PX was treated to be composed of mutually interacting three "normal" benzene rings. Calculations were carried out by use of the VI/1 method

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†In general, see ref. 2a, especially for [2.2]paracyclophane, see ref. 2b-d.

‡Our preliminary experiments of NMR spectra of these paraxylylenes suggested that benzene rings were statistically facing each other (perpendicular to a hypothetical molecular plane) i.e , 3°-PX had a D_3 and 4°-PX had a D_4 symmetry, respectively. And since several electronic spectra of mono-substituted 3°-PX or 4°-PX derivatives displayed that these absorptions consisted of the superposition of the components, each benzene ring was considered to be undistorted.

which treated π-electrons only. The details of this method were described elsewhere.[8] As previously mentioned for polyparaxylylenes and/or janusene, two types of electronic interactions ($p\pi$-$p\pi$ and $p\sigma$-$p\sigma$) of π orbitals should be considered. Thus for 3°-PX, resonance integrals and electron repulsion integrals were evaluated with the similar equations described in the original VI/1 method,[8] respectively. Namely, a parameter, k, was newly added to the original parametrization in a resonance integral, which was put equal to 0·92442.* The transition energies were calculated by means of the CI method restricted to the 36 singly excited configurations. For the present calculation, we assumed that 3°-PX had a D_{3h} symmetry and that for each benzene C—C bond length was 1·397 Å and C—C—C bond angle was 120°.

Calculation Procedure for benzene, toluene, p-*xylene and TCNE.* These four compounds were calculated by means of the CNDO/2 method according to the Del Bene and Jaffe's parametrizations.[7] On calculating these compounds the reasonable assumption was made for their symmetry being D_{6h} for benzene, Cs for toluene, C_{2v} for *p*-xylene and D_{2h} for TCNE. For benzene, toluene and *p*-xylene, C—C (benzene ring), C—C (single bond) and C—H bond lengths were taken to be 1·40, 1·52 and 1·08 Å, respectively, and bond angles in a benzene ring and a methyl group (∠CCH) were taken to be 120° and 109·5°, respectively. The geometry of TCNE was assumed to be the same as Wold's.[12] The transition energies were calculated by means of the CI method restricted to the 30 singly excited configurations.

Stabilization energies and transition energies of CT-complexes with TCNE. The stabilization energies due to the CT interaction between benzene, toluene, *p*-xylene or 3°-PX and TCNE and the transition energies of the CT-complexes thus formed were calculated by means of the CI method, where the ground, the CT and the locally excited (LE) configurations were taken into consideration. A wave function of a CT-complex was usually written as a linear combination of these configurations. But in the present calculations the back CT configurations (the charge transfer from TCNE to aromatics) and the LE configurations in TCNE were neglected.† For the CT-complex between benzene, toluene or *p*-xylene and TCNE, two CT configurations and four lowest LE configurations in donors were taken into consideration, where the CT configurations corresponded to one-electron transfer configurations from the two highest π-type occupied orbitals of TCNE, while for the CT-complex between 3°-PX and TCNE six CT configurations and the lowest six LE configurations were considered.

The energies of the CT configurations were evaluated as follows,

$$E^{CT}_{i\rightarrow 1} = I(i) - A(1) - C_{i1} \qquad (1)$$

where I(i) was the ionization potential of the i th MO of donors, A(1) was the electron affinity of the 1 th MO of TCNE, and C_{i1} was the Coulomb interaction between these two MO's. The Coulomb interaction was calculated according to the point-charge approximation.

The off-diagonal elements were taken to be proportional to the overlap integrals between the two related MO's as shown in equation (2),[13,14]

$$< \Psi_0|H|\Psi^{CT}_{i\rightarrow 1} > = -\kappa \cdot S_{i1} \qquad (2)$$

where κ was a constant and Ψ_0 was the wave function of the ground configurations etc.

Geometries of a CT-complex were so taken as one of the benzene planes of the donor molecule and TCNE plane to be parallel and to keep axial symmetry (mostly C_{2v}) on varying intermolecular distance, R, from 3·2 to 3·6 Å‡ (Fig 2) where at each

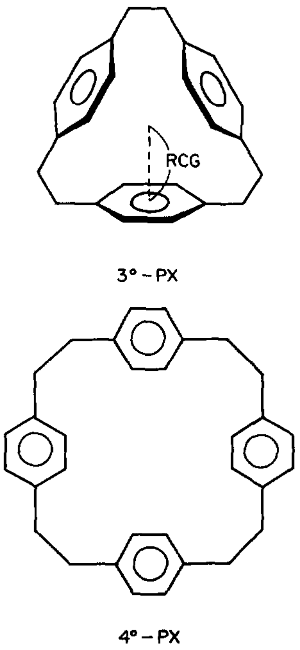

Fig 1. *Tris*[2.2.2]paraxylylene (3°-PX) and tetrakis-[2.2.2.2]paraxylylene (4°-PX). In 3°-PX, RCG means a radius of an inscribed circle of three benzene rings.

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*This value was taken so that the calculated lowest singlet transition energy of benzene should be 4·88 eV, see ref. 8.

†In the present cases, the overlap integrals between the ground configurations and the back CT configurations seemed to be very small because of the shapes of the MO's in question. See ref. 13.

‡In crystalline states of the TCNE complexes with aromatic compounds without Me substituent, these distances were observed to be 3·2–3·3 Å, see ref. 1*a* p. 234.

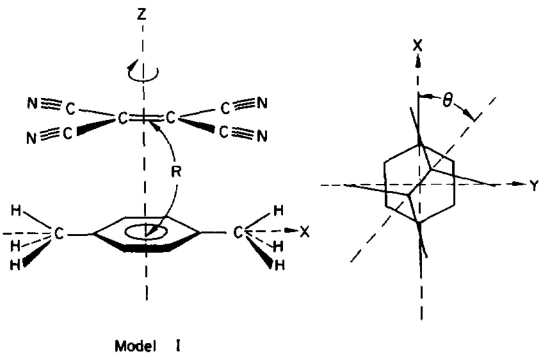

Fig 2. Assumed geometries of the *p*-xylene-TCNE complex. (model I).

fixed distance, TCNE was treated to rotate around the axis by 10° from 0° to 180°. In the cases of toluene and *p*-xylene two conformations about the substituents were considered as shown in Fig 2. The Model I corresponded to a geometry where one hydrogen of the methyl group on the plane of symmetry of the donor placed toward TCNE, while the model II corresponded to the reverse geometry.

All calculations in this work were carried out by using the FACOM 230 60 computer at the Data Processing Center of Kyoto University.

RESULTS AND DISCUSSION

Electronic structure of 3°-*PX*. Calculated singlet-singlet transition energies of the mutually interacting three benzene rings in 3°-PX are shown in Fig 3. According to the present calculation, a splitting of the original lowest excited state ($^1B_{2u}$) of each benzene ring into two via the transannular electronic interaction was not large on varying RCG (a radius of an inscribed circle of the three benzene rings). However the next higher excited states arisen from the penultimate excited state of benzene ($^1B_{1u}$) showed a large splitting. The difference in the directions of the transition moments might be responsible for this difference in the splitting.

Ionization potentials and singlet-singlet transition energies of benzene, toluene and *p*-xylene calculated by means of the CNDO/2 method are shown in Table 1 and 2, respectively. Ionization potentials were calculated by the Koopman's theorem and corrected so as the first ionization potential of benzene to be 9·40 eV. Results of the calculation suggested that "the methyl effects" were larger for the ionization potentials than for the transition energies, i.e., the Me substituents affected the orbital energies of the MO's more directly. Thus a tentative conclusion was drawn that "the methyl effect" was regarded to be a small modification of the calculation of the orbital energy. Such modification was extended to other π-type orbitals and applied to the MO's of benzene and the three interacting benzenes in order to calculate the transition energies of *p*-xylene and 3°-PX. The unperturbed MO's of 3°-PX were obtained by the above calculation at RCG = 2·5 Å (*cf* Fig 3), where the calculated energy difference between the lowest allowed transition of the system of three interacting benzenes and the lowest allowed transition of the system of three interacting benzenes and the lowest transition of benzene itself was in accord with the observed energy difference in the lowest transitions of 3°-PX and *p*-xylene.

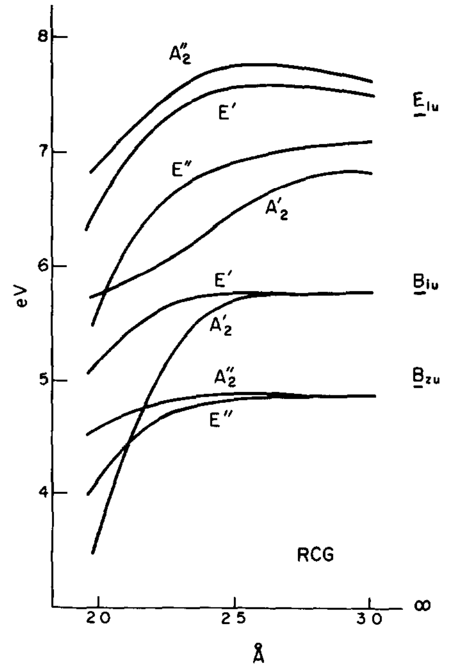

Fig 3. Singly excited states of mutually interacting three benzene rings

Table 1. Ionization potentials (eV)

	Benzene	Toluene	*p*-Xylene	3°-PX[c]
Calc.[a]	9·40	9·03	8·70	8·14
		9·37	9·35	8·94
				9·27
				9·50
Obs.[b]	9·40	8·9	8·71	
		9·13	9·21	

[a] Calculated by assuming $I_p = -\epsilon_i - 1{\cdot}367$ eV, where ϵ_i is the i th orbital energy.

[b] By photoelectronspectroscopic study, A. D. Baker, D. P May and D. W. Turner, J. Chem. Soc., (B) 22 (1968).

[c] Calculated by assuming $I_p = -\epsilon_i - 0{\cdot}944\,\text{eV} - \Delta$, where ϵ_i is the ith orbital energy and Δ is estimated as a perturbation, loc. cit.

Results of these CI calculations are shown in Table 3. Oscillator strengths of the lowest allowed

Table 2. The singlet-singlet transition energies of benzene, toluene and *p*-xylene

Calc.		Obs.		Calc.		Obs		Calc.		Obs.	
eV	(f)	eV	(ε)	eV	(f)	eV	(ε)	eV	(f)	eV	(ε)
4·71	(0·0)	4·75[a]	(160)	4·63	(0·004)	4·62[a]	(230)	4·53	(0·016)	4·52[a]	(620)
5·04	(0·0)	6·11[b]	(7400)	4·95	(0·006)	6 02[b]	(7000)	4·84	(0·022)	5·74[b]	(7500)
6·75	(1·85)	6·40[b]	(55000)	6·65	(0·886)			6·53	(0·786)		
				6·67	(0·972)			6·63	(1 01)		

[a] *Organic Electronic Spectral Data* (Edited by M. J. Kamlet), Volume I 1946–1952, Interscience, New York (1960)

[b] E S. Stern and C. J. Timmons, *Electronic Absorption Spectroscopy in Organic Chemistry*. (3rd Edition), London (1970)

Table 3. The calculated singlet-singlet transition energies of *p*-xylene and 3°-PX

p-Xylene		3°-PX	
eV	(f)	eV	(f)
4·593	(0·0193)	4·496	(0·0)
		4·538	(0·0413)
5·460	(0·0184)	5·223	(0·0)
		5·432	(0·0648)
7·100	(1·17)	6·307	(0·0)
		6·803	(0·0)
7·113	(1·20)	7·249	(2·85)
		7·439	(0·851)

Table 4. Absorption maxima of the CT spectra measured in methylene chloride

Acceptor Donor	TCNE (eV)	 (eV)	Chloranil (eV)	DDQ[a] (eV)
p-xylene	2·95	2·65	3·02	2·38
4,4′-dimethylbibenzyl	2·95	2·65	—[b]	2·37
3°-PX	2·70		2·76	2·26
4°-PX	2·90	2·58	2·88	2·27

[a] 2,3-Dichloro-5,6-dicyano-p-benzoquinone

[b] Superposed

transitions for *p*-xylene and 3°-PX were calculated to be 0·0193 and 0·0412, respectively, while the observed values were 0·006 and 0·011, respectively.* Observed oscillator strengths of these lowest transitions of linear *p*-xylene analogues were approximately proportional to the numbers of the benzene rings in a molecule, i.e., 0·006 for *p*-xylene, 0·012 for 4,4′-dimethylbibenzyl and 0·019 for (bis-*p*-xylyl)-*p*-xylene. Since 3°-PX has three benzene rings in a molecule, the oscillator strength of 3°-PX should be compared with three times of that of *p*-xylene by assuming the similar linearity. On this ground, the ratio of the calculated oscillator strength of 3°-PX to three times of that of *p*-xylene (0·0412: 0·0579) was 0·710, in good agreement with the observed ratio, 0·61(0·011: 0·018). Such a large hypochromic effect was not observed in [m,m]paracyclophanes (m ≧ 4) which were considered to have undistorted benzene rings.[15]

Charge-transfer spectra. Absorption maxima of CT spectra of the complexes of *p*-xylene, 4,4′-dimethylbibenzyl, 3°-PX or 4°-PX with TCNE, chloranil or DDQ measured in methylene chloride are shown in Table 4,† and equilibrium constants and molar extinction coefficients of the TCNE complexes in the same solvent are shown in Table 5. Table 4 shows qualitatively that the absorption maximum of a CT complex with a cyclic poly-*p*-xylylene (3°-PX or 4°-PX) locates in longer wavelength region than that of a CT complex with a linear poly-*p*-xylylene (*p*-xylene or 4,4′-dimethylbibenzyl). To be noted for the TCNE complexes with 3°-PX was that its equilibrium constant was much larger than the TCNE complexes with other donors. Another characteristic of this complex was that it showed a single broad detectable absorption maximum, while the TCNE

Table 5 Equilibrium constants (K's) and molar extinction coefficients (ε's) of the TCNE complexes[a]

Donor	λ mμ	K l/mol	ε l/mol · cm
p-Xylene[b]	415	0·489	2650
4,4′-Dimethyl-	420	0·35	3000
bibenzyl	474	0·22	4300
3°-PX	460	2·5	2000
4°-PX	428	(K · ε = 2300)[c]	
	480	(K · ε = 2200)[c]	

[a] Measured in methylene chloride at room temperature (ca. 25°).

[b] At 22°, R. E. Merrifield and W. D. Phillips, J. Am Chem. Soc, **80**, 2778 (1968), see ref. 14 (b), p. 184.

[c] Only products of K and ε were obtained.

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*These values were estimated by the equation, $f = 4{\cdot}32 \times 10^{-9} X \epsilon_{max} X \Delta\nu_{1/2}$.

†The CT spectrum of the TCNE complex with (bis-*p*-xylyl)-*p*-xylene was also measured, but its absorption maxima were very similar to that of *p*-xylene.

complexes with other donors showed two distinguishable absorption maxima, though superposed considerably. The latter characteristics in the shape of the CT spectra were often been observed for the CT spectra of the TCNE complexes with benzene derivatives. One possible interpretation for these characteristics was that two maxima were attributed to the two electronic CT configurations from the two highest occupied MO's of the donors to the one lowest unoccupied MO of TCNE.[1a] An alternative interpretation[16,*] was that two maxima were attributed to the two geometrically different orientation of the donor and the acceptor of different energies originated from the single electronic CT configuration.[1a] Calculated results of the CT complexes are shown in Table 6, where an electron affinity of TCNE was taken to be 2·10 eV,† which was obtained by means of the present CNDO/2 calculation, and the constant, κ, in Eq (2) was assumed to be equal to 25 eV.[13,14] Since the calculated stabilization energies, ΔE_{ST}, due to the CT interaction displayed only minor change on varying the angle θ, the two lowest transition energies, $h\nu_{CT_1}$ and $h\nu_{CT_2}$, were approximated to the average values of rotational isomers (θ, from 0 to 180°) at $R = 3{\cdot}4$ Å in the present calculation. The calculated stabilization energies and the rotational barriers of the TCNE complexes with benzene, toluene and *p*-xylene increased in the order. Each of the three complexes had two CT transition energies of similar magnitude, and the difference in the two CT transition energies also increased in the order (*ca* 0·1, 0·3 and 0·7 eV, respectively). And this difference varied with changing the distance, R. From these calculations the lowest energy differences were estimated to be 0·05 eV for benzene, 0·16 eV

Table 6. Calculated stabilization energies due to the CT interaction and the two lowest transition energies of the TCNE complexes at R = 3·4 Å

	Benzene	Toluene		*p*-Xylene		3°-PX
		model I	model II	model I	model II	
ΔE_{ST} max (kcal/mol)	−2·39	−2·44	−2·41	−2·54	−2·42	−2·92
θ(°)	30 (90)	50	90	50	90	0
barrier (kcal/mol)	0·04	0·31	0·15	0·56	0·21	0·50
$h\nu_{CT_1}$(eV)[b]	3·79	3·48	3·49	3·17	3·19	3·04
$h\nu_{CT_2}$(eV)[c]	3·89	3·82	3·81	3·80	3·79	3·80

[a] θ means that the stabilization energy is maximum at this degree. See Fig 2.

[b] An average value about the first lowest transition energies is shown.

[c] An average value about the second lowest transition energies is shown.

Table 7. Comparison of the calculated CT transition energies with the observed CT transition energies of TCNE complexes[a]

	Benzene	Toluene	*p*-Xylene[b]	4,4′ Dimethyl-[b] bibenzyl	3°-PX
Calc. (av.)[c]	3·84	3 65	3·49	—	3·42
gas phase[d]	3·67	3·35	3·12	—	—
n-heptane solution	3·29[d]	3·10[d]	2·91[d]	2·86	2·88
methylene chloride solution	3·19	3·02	2·80	2·80	2·70
Δ[e]	0·65	0·63	0·69	—	0·72

[a] Energies in eV. Calculations were carried out at R = 3·4 Å.

[b] Observed value is average one of two maxima.

[c] An average value of the two lowest transition energies is shown.

[d] M. Kroll, *J. Am. Chem. Soc.* **90**, 1097 (1968).

[e] Difference between calculated and observed (in methylene chloride) value.

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*For toluene- or *p*-xylene-TCNE complex, the present calculations showed that there was one rotationally most stable isomer for model I or model II, respectively, but the rotational barriers were considerably small as shown later. And for the transition probability of two CT transitions at each most stable configuration, both transitions was allowed for model I, although only one was permitted for model II

†Electron affinity of TCNE was estimated to be 2·2 eV from CT spectra of the complexes with electron donors, see ref. 1*a* p. 387.

for toluene, 0·44 eV for *p*-xylene and 0·60 eV for 3°-PX. These results suggested that the two maxima of CT spectra were difficult to distinguish for benzene and toluene. Observed widths of the absorptions at half maximum intensity of the CT spectra also supported this suggestion, i.e., 6200 cm^{-1} (0·77 eV) for benzene, 6700 cm^{-1} (0·83 eV) for toluene and 8900 cm^{-1} (1·1 eV) for *p*-xylene.

Comparison of the calculated CT transition energies with the observed absorption maxima of the CT spectra in gas phase and in solutions are shown in Table 7. On investigation of Table 6 and 7 a conclusion may be drawn that the transition energy of the TCNE complexes with toluene or *p*-xylene is in better agreements with the corresponding observed energy by taking the average value of the two transition energies than taking the lowest value. Table 7 shows that the differences between the calculated and observed transition energies are nearly constant for the donors used. (0·63–0·72 eV higher than in methylene chloride). According to the present calculation for the TCNE complex with 3°-PX, double maxima should be observed because of the considerably large difference between two calculated transition energies (it amounted to be at least 0·60 eV), in a contrast to the observed absorption shape of single broad maximum (the width of the absorption at half maximum intensity is observed to be 8200 cm^{-1} or 1·0 eV). Observed free energy difference between the TCNE complex with 3°-PX and that with *p*-xylene estimated from K values listed in Table 5 was *ca* 1 kcal/mol, while the calculated difference was *ca* 0·5 kcal/mol.

Eventually we should better note that the observed CT spectra of the TCNE complexes with the donors presented here consist with two CT transitions, in which mainly two for simple aromatics (six for 3°-PX) CT configurations are mixed in each other.

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