Steric Effects on the Formation of Isomeric Electron Donor–Acceptor Complexes

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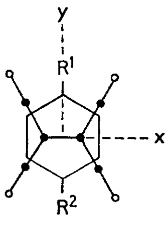
Summary Relative charge-transfer band areas for complexes of tetracyanoethylene (TCNE) with substituted benzenes show that isomeric structures in which the TCNE double bond is perpendicular to the axis through the *para* substituents are progressively favoured with increasing size of the substituent groups.

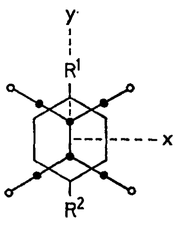
MULTIPLE intermolecular charge-transfer absorption bands have been reported for a variety of organic molecular complexes.[1] The appearance of two bands in complexes of chloranil with substituted benzenes was first explained by Orgel[2] as due to the removal of degeneracy of the e_{1g} benzene orbitals upon substitution. According to the Mulliken maximum overlap principle[3] interactions of TCNE with substituted benzenes result in structures (I) and (II).

As discussed by several authors,[4] the occurrence of two charge-transfer bands is readily explained in terms of these two isomeric structures. In the X-configuration an electronic transition to the lowest unoccupied TCNE orbital from the formerly degenerate e_{1g} orbital having a longitudinal node (y-axis) is allowed, while a transition from the orbital with a transverse node (x-axis) is forbidden. In the Y-configuration the situation is reversed. For a series of related donors the relative integrated intensities of the two bands should provide a measure of the importance of the different conformations.



(I)

X-configuration



(II)

Y-configuration

R^1 and R^2 = H, Me, Bu^t

We have examined in detail the absorption spectra of TCNE complexes with benzene, toluene, *p*-xylene, t-butyl-, and *p*-di-t-butylbenzene dissolved in chloroform. Spectral measurements were carried out on a Cary 14 spectrophotometer at 298 ± 0·2K using matched 1 cm quartz cells with pure solvent as the reference.

TABLE

Band parameters for the charge-transfer spectra of TCNE with alkylbenzene donors

	Experimental				Calculated						
Donor	[TCNE] (M)	[D] (M)	ν_{max} (cm^{-1}) $\times 10^{-3}$	A_{max}	$(\nu_{max})_1$ (cm^{-1}) $\times 10^{-3}$	$(\Delta\nu_{\frac{1}{2}})_1$[a] $\times 10^{-3}$	$(A_{max})_1$	$(\nu_{max})_2$ (cm^{-1}) $\times 10^{-3}$	$(\Delta\nu_{\frac{1}{2}})_2$[a] $\times 10^{-3}$	$(A_{max})_2$	$\left(\frac{\text{area 1}}{\text{area 2}}\right)$
Benzene	0·0025	0·38	25·6	0·705	—	—	—	25·6	5·57	0·707	—
Toluene	0·0030	0·22	24·1	0·845	22·4	4·19	0·580	25·4	4·94	0·562	0·86
p-Xylene	0·0070	0·063	23·5 (21·5)[b]	0·836 (0·810)[b]	20·4	4·10	0·694	24·5	5·09	0·726	0·77
t-Butylbenzene	0·0050	0·25	23·8	0·639	22·1	4·28	0·368	24·9	5·39	0·439	0·67
p-Di-t-butylbenzene ..	0·013	0·46	23·4 (19·5)[c]	0·512 (0·315)[c]	19·2	3·97	0·220	23·5	5·88	0·472	0·32

[a] Half band width; [b] two distinct maxima observed; [c] shoulder on low energy side of principal band.

Compared to the benzene–TCNE complex, mono-substituted derivatives give considerably broader charge-transfer absorption curves suggestive of two strongly overlapping bands. In the case of *p*-xylene two distinct charge-transfer maxima occur, and with *p*-di-t-butylbenzene a pronounced shoulder appears on the low energy side of the band maximum. The overlapping asymmetric bands were resolved by an iterative least-squares technique in which the individual band shapes were approximated by skewed Gaussian functions.[5] Both experimental and resolved bands for TCNE with *p*-xylene and *p*-di-t-butylbenzene are shown in the Figure.

Following decomposition of the combination curves, individual band areas were computed from the relationship given by Fraser and Suzuki.[5] Experimental as well as calculated band parameters are listed in the Table.

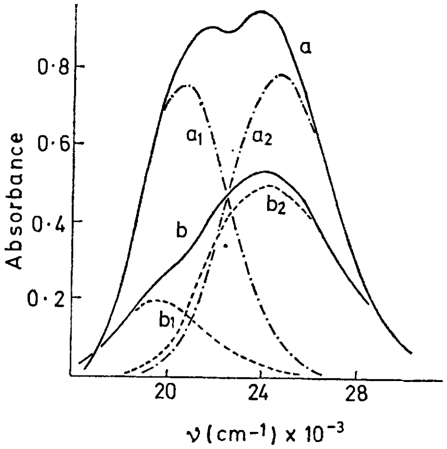


FIGURE. *Experimental (solid lines) and resolved (broken lines) absorption bands for molecular complexes of* TCNE *with* p-*xylene and* p-*di-t-butylbenzene in chloroform at* 298 K. *Curve a:* TCNE (0·007 M), p-*xylene* (0·072 M) *Curve b:* TCNE (0·013 M), p-*di-t-butylbenzene* (0·46 M).

The charge-transfer spectra for each of the substituted benzenes can be resolved into two asymmetric bands; a low energy band (1) occuring when the components are in the Y-configuration and a high energy band (2) due to the X-configuration. Calculated half-widths fall in the usual range of 4—6 × 10^3 cm^{-1} with band 2 invariably broader than band 1. Ratios of band areas (area 1 : area 2) are all less than unity and decrease with an increase in the number and size of the alkyl substituents. Thus, with more bulky R^1 and R^2 groups the Y-configuration becomes increasingly less important compared to the X-conformer. For the TCNE–*p*-xylene complex Hanna and his co-workers[6] have calculated the X-isomer to be about 3·3 kJ mol^{-1} more stable than the Y-structure. An even greater difference would be expected for complexes of the t-butyl compound. From a consideration of the bond lengths and angles of the TCNE molecule[7] it appears that the major repulsive forces responsible for the preferred orientation must occur between the four cyano carbon atoms and the R^1 and R^2 groups since the nitrogen atoms are farther from R^1 in the Y-configuration than in the X-structure. However, the weak intermolecular forces will allow considerable relative motion of donor and acceptor molecules which will cause substantial mixing of the two transitions. Still, these results indicate less steric hindrance for those geometrical orientations which approach the X-configuration.

A comparison of concentrations and measured intensities given in the Table for complexes of the methyl and corresponding t-butyl derivatives shows that the latter give a significantly lower intensity in each case. This is especially true for *p*-di-t-butylbenzene. These lower intensities are undoubtedly due to large steric effects of the t-butyl groups hindering the approach of a TCNE molecule thereby reducing the concentration of complex at equilibrium as well as the oscillator strengths of the intermolecular transitions.

The effects of changes in solvent and temperature on the preferred orientation were also investigated. Relative band areas (area 1 : area 2) for the *p*-di-t-butylbenzene–TCNE complex in carbon tetrachloride, chloroform, methylene chloride, and 1,2-dichloroethane at 298 K are 0·58, 0·32, 0·28, and 0·28 respectively. Preliminary studies of the *p*-xylene–TCNE complex at temperatures between 283 and 323 K indicate a smaller area ratio at lower temperatures. This trend is consistent with the expectation that the more stable X-conformer will be even more dominant at lower thermal energies. Thus, the effects of large *para*-substituted R groups in favouring the X-isomer are augmented still further by increased solvent polarity and lower temperatures.

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[1] For an excellent summary see R. Foster, 'Organic Charge-Transfer Complexes', Academic Press, London, 1969, p. 67–72.

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