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THE SECOND CHARGE TRANSFER BANDS OF SOME MOLECULAR COMPLEXES[1]

Arnold Zweig
American Cyanamid Company
Stamford, Connecticut

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Orgel[2] first noted that the charge transfer spectra of polymethylbenzenes with p-chloranil showed some evidence of double absorption bands and that these bands may be due to the removal of the degeneracy of the highest filled orbitals of the ground state of the benzene π-electron system. A similar effect was noted by Merrifield and Phillips[3] in the tetracyanoethylene (TCNE) complexes of methylbenzenes. Since methyl groups exert a relatively weak perturbing effect on the benzene ring, more strongly interacting substituents could result in larger separation of the two charge transfer maxima.

In the LCAO approximation, the degenerate highest filled molecular π-orbitals of benzene, ψ_2 and ψ_3 are made up of linear combinations of the atomic p-orbitals in the following manner[4].

$$\psi_2 = \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$
$$\psi_3 = 1/2\ (\phi_2 + \phi_3 - \phi_5 - \phi_6).$$

While ψ_2 uses all of the atomic orbitals about the benzene ring, ψ_3 does not use ϕ_1 and ϕ_4. If the benzene ring is substituted by an

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[1] Cumulative Influence of Conjugated Substituents on the π-System Properties of Aromatic Hydrocarbons, VI. Paper V, A. Zweig, W. G. Hodgson, W. H. Jura, and D. L. Maricle, Tetrahedron Letters No.26,1821(1963).

[2] L. E. Orgel, J. Chem. Phys., 23, 1352 (1955).

[3] R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc. 80, 2778 (1958).

[4] F. A. Cotton, Chemical Applications of Group Theory, Interscience Publishers, New York, N. Y., p. 128. (1963)

electron donating group at position 1, or by two electron donating groups at positions 1 and 4, orbital Ψ_2 will have its energy raised but orbital Ψ_3 will be unaffected.

Dewar and Lepley[5] showed that linear plots are obtained when the energy of charge transfer maxima are plotted against the parameter x in the Hückel equation $\epsilon = \alpha - x\beta$, where ϵ is the energy of the highest filled donor molecular orbital, and α and β are the coulomb and resonance integrals, respectively. If charge transfer transitions occur from other than the highest filled donor orbitals then mono- and para-di-substituted benzenes acting as electron donors should have absorption maxima associated with the Ψ_3 energy level. This level should be of nearly constant energy regardless of the substituents on positions 1 and 4.

To examine this effect, we chose TCNE as our standard acceptor molecule. The first charge transfer maxima of benzene with TCNE in methylene chloride occurs at 385 mμ, a wavelength which is considerably longer than that of the strong absorption bands of TCNE or of the simply substituted benzenes. This consequence of the high electron affinity of TCNE makes the assignment of the positions of its charge transfer maxima reliable and accurate. Hückel M.O. calculations also indicate that TCNE does not have a second low energy unfilled molecular orbital. Charge transfer to a second acceptor level could also be responsible for the

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[5] M. J. S. Dewar and A. R. Lepley, J. Am. Chem. Soc., **83**, 4560 (1961).

occurence of charge transfer absorption bands. This possibility apparently has not been previously considered although such transitions might occur, for example, where quinones are employed as acceptors.

Donor substituents on the benzene nucleus which we have examined include methoxy, hydroxy, dimethylamino, methylthio, and methyl. Benzene compounds mono- and p-di-substituted with these substituents form charge transfer complexes with TCNE which have two distinct well-separated absorption maxima. In Table I we report these maxima for 12 such benzene derivatives, with methylene chloride employed as the solvent. The first charge transfer maximum (λ CT-1) of these complexes varies with the substitients from 485mμ to 850mμ (9000 cm.$^{-1}$). The second absorption maximum (λ CT-2) occurs in the range 355-405mμ (3500 cm.$^{-1}$), eight having maxima between 380 and 400mμ (1400 cm.$^{-1}$). The second charge transfer maxima of all these complexes were of lesser intensity than the first maxima of the same complexes. This indicated that these are not n-π transitions as the latter should absorb more intensely than the first maxima, which are in these cases, π-π transitions[6]. Charge transfer from non-bonding electrons, on sulfur and oxygen also would not be expected to be energetically as close as these maxima are.

We also report in Table I, the intensities of each second transfer maximum relative to its first charge transfer maximum. These spectra were run at several concentrations, and in no case was a significant change in the intensity ratio observed.

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[6] R. S. Mulliken and W. B. Person, Ann. Rev. Phys. Chem., **13**, 107 (1962).

TABLE I

FIRST AND SECOND CHARGE TRANSFER MAXIMA OF SUBSTITUTED BENZENES WITH TETRACYANOETHYLENE IN CH_2Cl_2

Compound	λ_{CT-1} (mμ)	λ_{CT-2} (mμ)	A_{CT-2}/A_{CT-1}
Phenol	485	390	0.30
Anisole	507	387	0.70
Thioanisole	573	380	0.30
p-Dimethylaminothioanisole	850	400	0.93
p-Dimethylaminoanisole	755	365	0.87
Dithiohydroquinonedimethylether	675	400	0.73
Thiohydroquinonedimethylether	650	355	0.53
p-(Methylthio)phenol	625	405, 360	0.50, 1.05
Hydroquinone	580 (475sh)	375	0.67, (1.1)
Hydroquinonedimethylether	621	380	0.50
p-Methylanisole	563	395	0.60
p-Methylthioanisole	610	390	0.36

A further consideration in the examination of charge transfer maxima of the strong π-electron acceptor, TCNE, with strong electron donors, is the possibility of the charge transfer being complete, or almost so, in the ground state. This tendency is greatly enhanced in polar solvents, where strong absorption maxima are frequently seen which are due to the ion radical species $D^{\dot{+}}$ and $TCNE^{\dot{-}}$[7].

The characteristic $TCNE^{\dot{-}}$ absorption maxima centered near 430 mμ which contains much vibrational fine structure[8] was completely absent in these spectra, indicating that the second maxima of these complexes are not due to ion-radicals. We conclude, therefore, that the charge transfer absorption bands of these donors with TCNE in the 355-405 mμ region are due to an electronic transition from the antisymmetric second highest filled m.o. of the donor to the lowest unfilled m.o. of the acceptor. The inconstancy of the position of the second band may be due in part to mixing of the orbitals, which causes the donor substituent to affect the energies of all the orbitals, and in part may be due to the inaccuracy of the approximation which regards charge transfer absorption maxima as solely dependent on the relative energies of the orbitals[6].

As the first charge transfer band (CT-1) is highly allowed, and polarized perpendicular to the molecular plane, the highest filled molecular orbital (HFMO) of the donor must have the same symmetry as the lowest vacant molecular orbital (LVMO) of TCNE. Group theory and Hückel molecular orbital calculations on TCNE indicate that the LVMO

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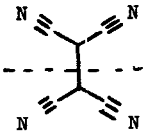
[7] R. Foster and T. J. Thompson, Trans. Faraday Soc., **58**, 860 (1962); **59**, 296 (1963).

[8] W. D. Phillips, J. C. Rowell, and S. I. Weissman, J. Chem. Phys., **33**, 326 (1960); O. W. Webster, W. Mahler, and R. E. Benson, J. Am. Chem. Soc., **84**, 3678 (1962).

has a nodal plane passing through the center bond (Fig. 1). In the



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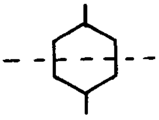

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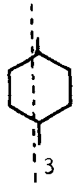

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5

configuration of the complex involving ψ_2 of the benzene derivative and TCNE where CT-1 is most highly allowed (Fig. 4) a CT-2 band involving the LVMO of TCNE and the benzene's second HFMO, ψ_3 (with a nodal plane as shown in Fig. 3) would be strongly forbidden. However, in an alternative configuration (Fig. 5) for the complex, the CT-2 transition becomes highly allowed and the CT-1 transition forbidden. Thus the two bands may be attributed to a mixture of two configurational isomeric charge transfer complexes, and the relative intensities may reflect not only oscillator strengths, but also relative stabilities of the CT complex conformers[9].

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[9] I wish to thank a referee for pointing out this possibility.