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SOME OBSERVATIONS ON THE SECOND CHARGE-TRANSFER BAND OF THE TETRACYANOETHYLENE COMPLEXES WITH METHYL NAPHTHALENES

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Charge-transfer bands shift location with substitution in aromatic donors when a common acceptor is used. We applied perturbation theory to the shift in the first charge-transfer band of the tetracyanoethylene complexes with methyl naphthalenes (1). A similar evaluation of the second charge-transfer band for these complexes is therefore of interest. Such a treatment indicates that the electron transfer for the second band takes place between the penultimate occupied orbital of the donor and the lowest unfilled orbital of the acceptor. Furthermore the orientation of the molecules involved in the π-complex interaction differs if both the first and second absorption bands are allowed transitions.

Multiple charge-transfer absorption bands could arise from either n-π^* or π-π^* transitions in most of the substituted aromatics studied (2). However, only π-π^* transitions were possible in the polyaromatic hydrocarbon complexes with tetra-

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cyanoethylene and chloranil (3,4). On substitution, the location and intensity of these bands show only slight changes (5-7). Thus this band probably does not originate with the unpaired electrons on the substituents.

The limited range of the shifts and their correspondence to positions of substitution led to a perturbation treatment of the aromatic systems (1,8). Following the method of Orgel (8) on multiple charge-transfer bands in benzene derivatives, Voigt (6) found a less than ideal fit on methoxy substitution. This despite inclusion of solvent shift effects analogous to those of deMaine (9) A simple perturbation treatment of band broadening with the methyl benzenes gave quite reasonable results (5). The first charge-transfer band of the methyl benzenes and naphthalenes was used to evaluate the coulomb perturbation parameter (1).

In benzene a small perturbation of the degenerate E_{1g} orbitals gives occasional splitting but most frequently only broadening of the absorption band. The naphthalene case is more clear cut. An appreciable difference exists between the highest

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TABLE I

π-Complex Interactions with Tetracyanoethylene. Shifts of the Second Charge-transfer Band of Naphthalene on Methyl Substitution.

Substituent Position	$-\Delta E_{\pi 2}$[a] (e.v.)	$\sum_r c_{2r}^2$	Absorptivity Ratio[b]
0	(2.90)[c]	-	.97
1	.07	0	.94[d]
1,4	.09	0	.77
1,5	.10	0	.94
1,8	.05	0	.85
2	.18	.167	.95
1,2	.20	.167	.88
1,3	.21	.167	.92
1,6	.22	.167	.89
2,3	.37	.333	.99
2,6	.30	.333	.94
2,7	.37	.333	.99
2,3,5	.38	.333	1.02
2,3,6	.52	.500	.98

[a] Calculated from the gaussian maxima of ref. 1.

[b] The second charge-transfer optical density at the observed maximum divided by that of the first.

[c] Energy of unsubstituted parent molecule second charge-transfer band.

[d] The disappearance of first charge-transfer band and appearance of a new band (467 mμ) near the second charge-transfer absorption indicated reaction of 1-methylnaphthalene with tetracyanoethylene. The first charge-transfer band almost completely disappears after 2 hours.

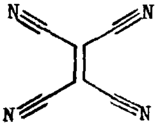
and penultimate occupied orbitals. This difference appears in the separation between the first and second charge-transfer bands of naphthalene with tetracyanoethylene (3,5) and with chloranil (5). The charge-transfer shifts on methyl substitution of naphthalene in tetracyanoethylene complexes are distinct. The first charge-transfer band is effected principally by substitution in the 1, 4, 5 and 8 positions while the second band shifts most (Table I) with substitution in the 2, 3, 6 and 7 positions. The atomic orbital coefficients of the Huckel molecular orbitals in naphthalene undergo parallel changes, as previously shown for the first charge-transfer band (1). The atomic orbital coefficients for the penultimate occupied orbital are zero and -0.408 in the 1 an 2 position. The coulomb perturbation term, the sum of the squares of the atomic orbital coefficients ($\sum_r c_{ir}^2$) at the positions of substitution (r) in the effected orbital (i), alone will suffice to describe the shift (Table I). The resonance perturbation terms require cross products between adjacent positions. Since the value at position 1 is zero, only the 2-3 interaction can contribute. Both effects thus imply an energy shift, $\Delta E_{\pi 2}$, on substitution in the 2 or equivalent (3, 6 or 7) positions. However loss of symmetry of the donor in the naphthalene derivatives indicates that a small change in the values may occur even when substitution is at the 1 or equivalent (4, 5 or 8) positions. From the equation:

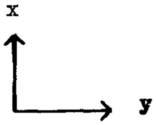
$$-\Delta E_{\pi i} = \sum_r c_{ir}^2 \, h\beta$$

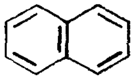
for the perturbation shift (1) and the resonance integral -

$\beta = -3.06$ e.v. (10) for tetracyanoethylene complexes, we have determined the perturbation coefficient h. The least squares value of -0.26 obtained from the data in Table I is within error of -0.21 determined by the same method for the first charge-transfer band (1).

The molecular orbital symmetry of the parent naphthalene molecule is appreciably different for the highest and penultimate orbitals. The highest occupied orbital has nodes at positions 9 and 10 and sign inversion between position 1 and 4 or 2 and 3, indicating a second set of nodes on the y axis. The penultimate orbital as indicated before has nodes at 1, 4, 5 and 8 positions and equal values without a sign change at 2, 3, 6 and 7 and of opposite sign at 9 and 10. The acceptor symmetry for the lowest unoccupied orbital inverts around the y axis. Selection rules in polyatomic species require inversion of sign along the axis of transition if the excitation is allowed (11). Thus the sign must reverse in the adjacent portions of the stacked donor and acceptor for a highly probable perpendicular transition. The first excitation band of naphthalene, with which the first charge-transfer band is associated (12), is polarized along the x axis. The symmetry requirements for the perpendicular







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charge-transfer transition therefore require an orientation of the tetracyanoethylene double bond above and to one side of the 9-10 bond of naphthalene. The symmetry of the molecular orbital involved in the second charge-transfer transition indicates that the tetracyanoethylene double bond would be perpendicular to the 9-10 bond and centered over one of the rings. Thus two conformations may be suggested for high transitional probability. The relatively equal intensities of these bands (Table I) and the lack of temperature dependence of this relative intensity in the naphthalene-tetracyanoethylene complex (3) indicate that while the bands are principal charge-transfer transitions, rotational conformers with equivalent heats of formation are required.

Although the description is compatible with two π-interaction conformers, a means of determining relative concentrations of the complex species and their oscillator strengths or x-ray structure analysis are needed to substantiate the existence of complex conformers.