

The Degree of Charge-transfer in the Ground States of π - π Molecular Complexes

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THE ground state of a 1:1 complex between an electron donor (D) and an electron acceptor (A) has been expressed¹ by the equation

$$\psi_N = a\psi(D,A) + b\psi(D^+-A^-) \quad (1)$$

where $\psi(D,A)$ is the no-bond component and $\psi(D^+-A^-)$ is the charge transfer structure in which an electron has been donated from D to A. Part of the observed dipole moment of many π -donor, π -acceptor systems [D = mesitylene, durene, hexamethylbenzene, naphthalene, *etc.*; A = 1,3,5-trinitrobenzene, chloranil, tetracyanoethene, *etc.*],

in which both D and A individually lack dipole moments, is induced in the donor by the acceptor. If the no-bond and charge-transfer structures have dipole moments $\mu_{D,A}$ and $\mu_{D^+A^-}$ respectively, the dipole moment of the complex can be written as

$$\begin{aligned} \mu_N = & a^2\mu_{D,A} + b^2\mu_{D^+A^-} \\ & + 2ab \int \psi(D,A) \hat{\mu} \psi(D^+-A^-) d\tau \end{aligned} \quad (2)$$

where $\hat{\mu}$ is the dipole moment operator.

At present it is generally believed that the contribution of the induced moment $\mu_{D,A}$ to the dipole moment of the complex is small² and Briegleb *et al.*^{3,4} have neglected this term in estimating the extent of charge-transfer in the ground states of a number of π - π complexes.

We have estimated the dipole moments of no-bond structures by assuming geometric models of the complexes in which the donor and acceptor molecules are parallel with their symmetry centres superimposed at a distance of about 3.5 Å. The electrostatic field E_n at the centre of the n^{th} bond in the donor was calculated through consideration of the charge distribution over the acceptor. Electrostatic bond polarizability tensors α_n for all bonds were assumed and the total dipole moment $\mu_{D,A}$ induced in the donor molecule was calculated as

$$\mu_{D,A} = \sum_n \alpha_n E_n \quad (3)$$

The polarization energy of the complex was estimated (ignoring polarization of the acceptor by the donor) as

$$U = \frac{1}{2} \sum_n \alpha_n E_n^2 \quad (4)$$

The induced moments, directed from D to A, amount to more than half the experimental^{3,4} moments of the complexes. Thus we believe the degree of charge-transfer in these complexes, $\frac{b^2}{a^2 + b^2}$, reported by Briegleb⁵ should be reduced

by a factor of at least two. If the energy of the pure D^+-A^- state² is less than or in the order of 100 kcal.mole⁻¹, the charge-transfer contribution to the binding energy will be less than 50%. Using equation (4) we find that the polarization interactions alone account for almost 50% of ΔH_N^0 .³⁻⁵

The electrostatic model outlined can be applied to the hexafluorobenzene complexes of aromatic hydrocarbons whose nature is of current interest.⁶⁻¹³ Apparent dipole moments have been found¹² for hexafluorobenzene in benzene and mesitylene *via* the refractivity method. Using the technique of dielectric relaxation (which is not subject to uncertainties due to atomic polarization) we have confirmed that these moments are non-zero, and have detected a dipole moment for the hexamethylbenzene-hexafluorobenzene complex in carbon tetrachloride. Since no u.v. spectroscopic evidence for charge-transfer has been found^{6,8,12} we infer that the dipole moments of these complexes in their ground states are due to polarization interactions between the components and not to charge-transfer.

We conclude that the extent of charge-transfer in the ground states of π - π donor-acceptor complexes is considerably less than previously reported on the basis of dipole moment measurements and that the stabilization of the ground states of such complexes is determined to a greater extent by Van der Waals' interactions in the no-bond structure than by charge-transfer.

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