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ELECTRON-DONOR-ACCEPTOR π-ORBITAL CORRELATIONS IN COFACIAL ISOMERS OF THE BENZENE-TETRACYANOETHYLENE SYSTEM

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Abstract: Anti correlation of highest bonding with lowest antibonding π-orbitals of the benzene - TCNE complex in cofacial isomers of C_{2v} symmetry leads to ground state stabilisation associated with EDA complex behaviour in each case.

Electron-donor-acceptor systems are classified according to the sequence of events leading to the production of excited donor-acceptor complexes. Thus exciplexes have unbound ground states and are generated by the association of one electronically-excited component (donor or acceptor) with the other[1]. Electron-donor-acceptor (EDA) complexes on the other hand may be excited directly by absorption in the long wave charge transfer band associated[2] with a transition from the stable ground state $^1(DA)$.

It has recently been proposed[3] that these different types of behaviour reflect different correlations of highest bonding (ϕ_D,ϕ_A) and lowest antibonding (ϕ_D*, ϕ_A*) orbitals of donor and acceptor. Specifically anticorrelation (ACMO) of donor-acceptor orbitals of the same symmetry, represented by the combinations $\phi_D \pm \phi_A^*$, $\phi_D^* \pm \phi_A$, produces intermolecular orbitals (IMO) described by the functions:

$$\psi_A = (1 + \lambda^2)^{-\frac{1}{2}}(\phi_A + \lambda\phi_D^*); \quad \psi_D^* = (1 + \lambda^2)^{-\frac{1}{2}}(\lambda\phi_A - \phi_D^*)$$

$$\psi_D = (1 + \mu^2)^{-\frac{1}{2}}(\phi_D + \mu\phi_A^*); \quad \psi_A^* = (1 + \mu^2)^{-\frac{1}{2}}(\mu\phi_D - \phi_A^*)$$

These are of predominantly donor (ψ_D, ψ_D^*) or acceptor (ψ_A, ψ_A^*) character ($\lambda<1>\mu$) in which case the totally-symmetric singly-excited configurations $\psi_D\psi_A{}^2\psi_A^*$ and $\psi_D{}^2\psi_A\psi_D^*$ correspond respectively to the zeroth-order charge transfer (CT) states $|D^+A^-\rangle$ and $|D^-A^+\rangle$. The complex ground state is accordingly stabilised a) in zeroth-order by the energy lowering of occupied IMO in the electronic configuration $\psi_D{}^2\psi_A{}^2$ and b) by first-order configuration interaction (CI) of the zeroth-order ground state $^1|DA\rangle$ with the zeroth-order CT states as in EDA complexes. On the other hand syn correlation (SCMO), described by the combinations $\phi_D \pm \phi_A$, $\phi_D^* \pm \phi_A^*$, leads to the IMO functions

$$\psi_D = (1 + \lambda^2)^{-\frac{1}{2}}(\phi_D + \lambda\phi_A); \quad \psi_A = (1 + \lambda^2)^{-\frac{1}{2}}(\lambda\phi_D - \phi_A)$$

$$\psi_A^* = (1 + \mu^2)^{-\frac{1}{2}}(\mu\phi_D^* + \phi_A^*); \quad \psi_D^* = (1 + \mu^2)^{-\frac{1}{2}}(\phi_D^* - \mu\phi_A^*)$$

where the respective stabilisation and destabilisation of ψ_D and ψ_A results in no zeroth-order binding of unexcited donor and acceptor. Moreover since the occupied (ψ_D, ψ_A) and unoccupied (ψ_D^*, ψ_A^*) IMO now belong to different symmetry species, zeroth-order excited states are non-totally symmetric and do not exhibit CI with the zeroth-order ground state;

this is characteristic of exciplex behaviour.

Since these conclusions[3] were based on a general treatment of an unspecified donor-acceptor pair it is of interest to examine a particular system with identifiable symmetry elements with a view to predicting (or interpreting)its behaviour. The benzene-tetracyanoethylene (TCNE) system is selected here as a model for TCNE complexes with benzene derivatives where the appearance of two CT absorption bands is believed to originate[4] in transitions from two rotational cofacial isomers of the complex ground state[5].

The benzene-TCNE conformers chosen for examination are those of highest cofacial symmetry (C_{2V}) proposed by Holder and Thompson[4] and shown in Figure 1. Mayoh and Prout[6] conclude that the K isomer exhibits greater donor-acceptor orbital overlap and is the more stable. Since the highest bonding (ϕ_2,ϕ_3) and lowest antibonding (ϕ_4*,ϕ_5*) π-orbitals of benzene are double degenerate, their correlations with the corresponding orbitals (θ_4, θ_5, θ_6*, θ_7*) of TCNE is regarded as a minimal requirement. Gray et al.[7] have shown however that θ_4 and θ_7* in the simple HMO approximation are respectively degenerate with θ_3 and θ_8* which must also be considered[8]. The symmetry species of these orbitals in C_{2V} for conformers K and L are as follows:-

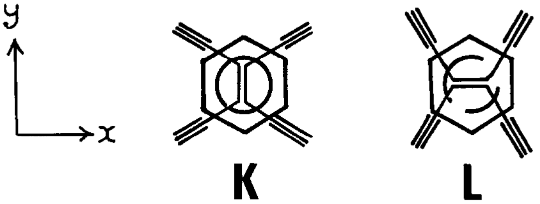

Figure 1

$$\theta_3 = \theta_4 < \phi_2 = \phi_3 < \theta_5 < \theta_6^* < \theta_4^* = \phi_5^* < \theta_7^* = \theta_8^*$$

K	b_1	a_2	b_2	b_1	a_1	b_2	a_1	a_2	b_1	a_2
L	b_2	a_2	b_2	b_1	a_1	b_1	a_1	a_2	b_2	a_2

where the indicated energy ordering[7] of simple HMOs is appropriate to the role of TCNE as electron acceptor.

We proceed on the assumption that either θ_4 and θ_7*, or θ_3 and θ_8*, correlate with the donor orbitals ϕ_i. In the former case linear combinations of donor and acceptor orbitals belonging to the same symmetry species reflect anticorrelation throughout and provide IMO of the following origin and transformation properties:-

IMO	K	L	IMO*	K	L
ψ_D'	$b_2(\phi_2 + \theta_6^*)$	$b_1(\phi_3 + \theta_6^*)$	ψ_A^*	$b_2(\phi_2 - \theta_6^*)$	$b_1(\phi_3 - \theta_6^*)$
ψ_D	$b_1(\phi_3 + \theta_7^*)$	$b_2(\phi_2 + \theta_7^*)$	$\psi_A^{*\prime}$	$b_1(\phi_3 - \theta_7^*)$	$b_2(\phi_2 - \theta_7^*)$
ψ_A'	$a_2(\theta_4 + \phi_4^*)$	$a_2(\theta_4 + \phi_4^*)$	ψ_D^*	$a_2(\theta_4 - \phi_4^*)$	$a_2(\theta_4 - \phi_4^*)$
ψ_A	$a_1(\theta_5 + \phi_5^*)$	$a_1(\theta_5 + \phi_5^*)$	$\psi_D^{*\prime}$	$a_1(\theta_5 - \phi_5^*)$	$a_1(\theta_5 - \phi_5^*)$

Here unprimed functions refer to highest bonding (ψ_D,ψ_A) and lowest antibonding (ψ_D^*, ψ_A^*) IMO whereas primed symbols describe IMO of lower (ψ_D', ψ_A') or higher ($\psi_D^{*\prime}$, $\psi_A^{*\prime}$) energy in the general sequence

$$\psi_A' < \psi_D' < \psi_D < A < \psi_A^* < \psi_D^* < \psi_D^{*\prime} < \psi_A^{*\prime}$$

The zeroth-order ground state configuration $(\psi_A')^2(\psi_D')^2(\psi_D)^2(\psi_A)^2$ of each isomer is accordingly stabilised by exchange interaction.

Sixteen singly-excited configurations of the complex, produced by electron promotion $\psi_i \longrightarrow \psi_j^*$, are identified as zeroth-order locally-excited (LE) states designated $|D^*A\rangle$ or $|DA^*\rangle$, or charge-transfer (CT) states represented by $|D^+A^-\rangle$and $|D^-A^+\rangle$. For the K isomer these are conveniently described by the matrix:-

ψ_i ψ_j^*	$\psi_A^*(b_2)$	$\psi_A^{*\prime}(b_1)$	$\psi_D^*(a_2)$	$\psi_D^{*\prime}(a_1)$
$\psi_D'(b_2)$	$\|D'^+A^-\rangle$	$\|D'^+A'^-\rangle$	$\|D'^*A\rangle$	$\|D'^{*\prime}A\rangle$
ψ_D (b_1)	$\|D^+ A^-\rangle$	$\|D^+ A'^-\rangle$	$\|D^* A\rangle$	$\|D^{*\prime} A\rangle$
$\psi_A'(a_2)$	$\|D A'^*\rangle$	$\|D A'^{*\prime}\rangle$	$\|D^-A'^+\rangle$	$\|D'^-A'^+\rangle$
ψ_A (a_1)	$\|D A^*\rangle$	$\|D A^{*\prime}\rangle$	$\|D^-A^+\rangle$	$\|D'^-A^+\rangle$

where for example $|D'^+A^-\rangle$ and $|DA^{*\prime}\rangle$ refer to higher energy zeroth-order states of CT and LE character. For the L isomer the transformation properties of $\psi_D'(b_1)$ and $\psi_D(b_2)$,ψ_A^*(b and $\psi_A^{*\prime}(b_2)$ are reversed but the symmetry species of zeroth-order states are unchanged. The following points are noted:-

1. Zeroth-order states on the leading diagonal transform as A_1 for both isomers and (in the singlet manifold) exhibit CI with the zeroth-order ground state to provide first-order states of charge resonance (CR) character described by the functions:-

$$^1\psi_i(A_1) = a_i|DA\rangle + b_i|D'^+A^-\rangle + c_i|D^+A'^-\rangle + d_i|D^-A'^+\rangle + e_i|D'^-A^+\rangle \quad (i = 0, 1\text{-}4)$$

This further stabilises the ground state $^1\psi_0(A_1)$ in each case and both conformers K and L are expected to exhibit EDA complex behaviour as previously suggested[4].

2. The lowest zeroth-order CT states $|D^+A^-\rangle$ and $|D^-A^+\rangle$ transform as A_2 with the result that the lowest-energy first-order state

$$^1\psi_1(A_2) = p_1|D^+A^-\rangle + q_1|D^-A^+\rangle + r_1|D'^+A'^-\rangle + s_1|D'^-A'^+\rangle$$

produced by radical-ion recombination is neither radiatively coupled[9] to, nor adiabatically correlated with[3], the $^1\psi_0(A_1)$ ground state. If therefore $^1\psi_1(A_2)$ lies below the acceptor triplet state $^3A^*$, the only possible (geminate) charge neutralisation sequence represented by

$$D^+ + A^- \longrightarrow {}^{1,3}\psi_1(A_2) \longrightarrow {}^1\psi_0(A_1) \longrightarrow D + A$$

is restricted by the non-radiative relaxation probability of the states $^{1,3}\psi_1(A_2)$.

3. Since the first-order excited states $^1\psi_j(B_1)$ and $^1\psi_k(B_2)$ are of purely exciton origin, the CT band is assigned to the transition $^1\psi_0(A_1) \longrightarrow {}^1\psi_1(A_1)$. Insofar as the orbital descriptions of the states $^1\psi_i(A_1, K)$ and $^1\psi_i(A_1, L)$ for the different isomers are indistinguishable, they may be degenerate in the absence of steric hindrance in this case both isomers should have identical CT absorption spectra consistent with the appearance of a single CT band. Alkylation of the donor molecule however is expected to introduce a donor-acceptor orientation-dependent steric hindrance with concomitant reduction in orbital overlap; in this case the states $^1\psi_i(A_1, K)$ and $^1\psi_i(A_1, L)$ are non-degenerate and the CT bands of both isomers are spectroscopically distinguishable[4].

Donor orbital correlations with acceptor orbitals θ_3 and θ^*_8 leave ψ_D', ψ_A, ψ_A^* and $\psi_D^{*'}$ unchanged, but the origins of the remaining IMO now reflect syn correlation as follows:-

	ψ_A'	ψ_D	$\psi_A^{*'}$	ψ_D^*
K	$b_1(\theta_3 + \phi_3)$	$b_1(\theta_3 - \phi_3)$	$a_2(\phi_5^* + \theta_8^*)$	$a_2(\phi_5^* - \theta_8^*)$
L	$b_2(\theta_3 + \phi_2)$	$b_2(\theta_3 - \phi 2)$	$a_2(\phi_5^* + \theta_8^*)$	$a_2(\phi_5^* - \theta_8^*)$

This reduces the zeroth-order binding energy since ψ_D is destabilised, the number of totally-symmetric zeroth-order CT states, and hence the CI stabilisation of the ground state, now described by the function

$$^1\psi_0'(A_1) = f_0|DA\rangle + g_0|D'^+A^-\rangle + h_0|D'^-A^+\rangle$$

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9. No vector of the electric dipole moment operator transforms as A_2.

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