ELECTRON DONOR-ACCEPTOR CYCLOPHANES-I

(preliminary results)

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Introduction

Mulliken[1] predicted the importance not only of intermolecular distance but also of mutual orientation for charge-transfer (CT) interaction between an electron donor (D) and acceptor (A). Others[2,3] have elaborated his theory since, but detailed experimental proof of the stereochemical requirements for CT is still lacking, since the geometry of CT complexes in solution is largely unknown, and furthermore since for any given D/A pair only a limited number (often only one or none) of crystalline complexes is available.

We have therefore undertaken the synthesis of cyclophanes containing an electron donor-acceptor pair in a known mutual orientation, which can be varied in a predictable way by structural modification of the molecule.

Results and discussion

The cyclophanes Ia, b and c were synthesized. These were chosen because the intermolecular complex between a closely related electron-acceptor (II) and electron-donor (III) displays a distinct CT absorption band (λ_{max} = 435 nm in CH_2Cl_2) not masked[4] by the individual absorptions of II and III.
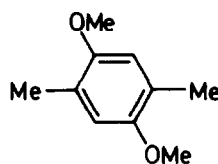
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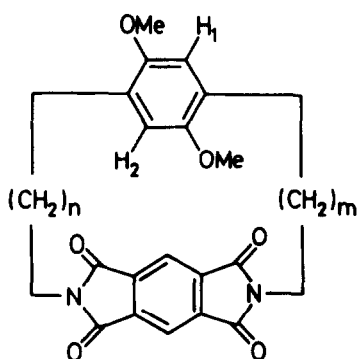
I   a   n=m=5
    b   n=m=6
    c   n=4 m=8
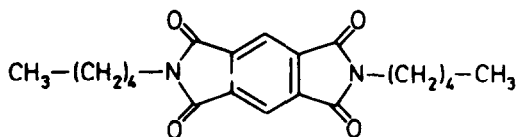
The mutual orientation of D and A in both Ia and Ib is such that their centers
are superimposed, while the interplanar distance in Ia is smaller than in Ib.
In Ic however, the centers of D and A are no longer superimposed as is also
indicated by PMR data. While in Ia and Ib, H_1 and H_2 are isochronous with δ =
6.20 ppm for Ia and δ = 6.21 ppm for Ib, they are anisochronous in Ic with
δ_{H_1} = 6.04 ppm and δ_{H_2} = 6.34 ppm (all in $CDCl_3$ relative to TMS).
Cyclophanes Ia, b and c display longwavelength absorption (cf. Fig. 1) attrib-
utable to intramolecular CT interaction as shown by the applicability of
Beer's law. For Ia (m = n = 5) and Ib (m = n = 6) this CT absorption is very
weak, being weakest for the compound (Ia) where the D-A distance is shortest.

Fig 1

	λ_{max}	ε_{max}
····· I a	410	37
── I b	415	65
─── I c	450	200

in CH_2Cl_2 at 20°
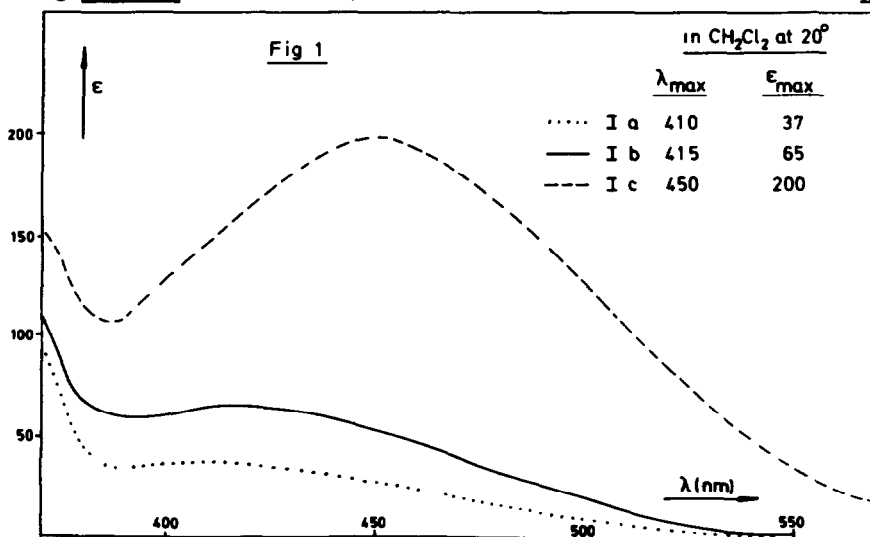
Thus we conclude that a short D-A distance is not a sufficient requirement for an intense CT transition in the complex studied. Our results indicate that an intense CT transition in this complex can not occur when the centers of D and A are superimposed. On the other hand a shift of the donor towards one of the imide rings in the acceptor as present in Ic, strongly enhances CT intensity. The Mulliken theory[1,5] of CT implies that an intense transition from the ground state to the first CT state will only occur when there is significant resonance interaction between the no-bond state $[\psi(D,A)]$ and the first dative state $[\psi(D^+A^-)]$. This interaction is mainly governed[2,3] by the overlap between the highest occupied molecular orbital (HOMO) of D and the lowest unoccupied molecular orbital (LUMO) of A. The orbital coefficients of HOMO and LUMO as calculated by the HMO method[6] are indicated below.

Full and open circles indicate positive and negative signs respectively

LUMO   HOMO
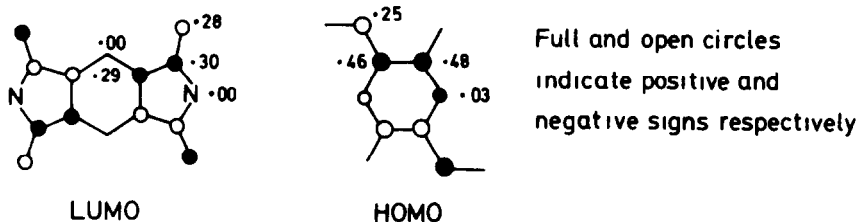
It is clear that in a centrosymmetrical (C_2) complex, with a twofold axis through the centers of D and A (such as Ia and Ib!), HOMO and LUMO belong to different symmetry classes (B and A resp.) of the C_2 point group, which makes their overlap zero regardless of the interplanar distance.

The relative intensities of the CT transitions in Ia, b and c thus fully agree with the Mulliken theory of CT, irrespective of questions[3] about the contribution of CT interaction to the ground state stabilization of molecular complexes. Even the small intensity difference between Ia and Ib can be logically explained: the longer polymethylene chains in Ib (m = n = 6), make this homologue somewhat more flexible than rigid Ia (m = n = 5), and consequently the greater deviations from strict C_2 symmetry enhance the CT-transition in Ib, despite the increased distance between D and A.

The syntheses of Ia, b, c and other electron donor-acceptor cyclophanes as well as the significance of their properties in relation to the corresponding

intermolecular complexes will be discussed in forthcoming papers.

References

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 c. G.R. Anderson, J. Amer. Chem. Soc. 92, 3552 (1970).

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3. B. Mayoh and C.K. Prout, J. Chem. Soc. Far. Trans. II 68, 1072 (1972).

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   The cyclophane containing a potential electron donor-acceptor pair repor-
   ted in this reference did not fullfil these requirements.

5. R.S. Mulliken and W.P. Person, "Molecular Complexes", Wiley, New York (1969).

6. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", John Wiley, New York (1961).
   Parameters given in this reference (p. 135) were used in the HMO calcula-
   tions. Other parameter-sets lead to somewhat different orbital coëfficients
   but do not change the symmetry of the HOMO and the LUMO.