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On the Existence of Biradical-Ionic States of Donor-Acceptor Cyclophanes. A Simple MO-Theoretical Study*

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The longest wavelength absorption in the UV-VIS spectra of donor-acceptor cyclophanes corresponds to an excitation from the donor D to the acceptor A with the transfer of one electron, i. e. $DA \xrightarrow{h\nu} D^{+}A^{-}$. The size of the electron transfer should become larger with increasing donor-acceptor strength already in the ground state. One expects a biradical-ionic ground state $D^{+q}\ A^{-q}$ with a large q, say $q > 1/2$, for certain donor-acceptor combinations with a small enough difference between the ionization energy I_D of the donor and the electron affinity E_A of the acceptor. In this work we investigate the ground state and the lowest excited singlet and triplet states of donor-acceptor cyclophanes within a semi-empirical four-orbital configuration interaction model. The dependence of energies and size of the electron transfer in these states on molecular parameters of donor and acceptor and on their mutual geometrical arrangement is elucidated. Our model leads to the simple approximate condition $V^{\text{eff}} \leqq 0$ for the occurrence of a biradical-ionic ground state. V^{eff} is a measure of the effective donor-acceptor strength which does not only depend on the difference $I_D - E_A$ but also on the Coulombic repulsion between an electron in D and one in A and on the stabilizing effect of the solvent. The symmetries of the frontier orbitals, i. e. the highest occupied molecular orbital of the donor and the lowest unoccupied molecular orbital of the acceptor, determine whether the biradical-ionic ground state will be a triplet or a singlet. According to our simple model a triplet biradical-ionic ground state should occur if the frontier orbitals belong to different representations of the point-group of the phane. The transition from an ordinary ground state without an appreciable electron transfer from D to A into the biradical-ionic ground state is discontinuous. This transition is, however, continuous if the frontier orbitals belong to the same representation, although the magnitude of the electron transfer q changes significantly only in a narrow range of V^{eff} whose width is determined by the size of the transanular and through-bond interaction between the frontier orbitals. Finally we discuss how to choose donor and acceptor in a cyclophane in order to fulfill the condition for a biradical-ionic ground state.

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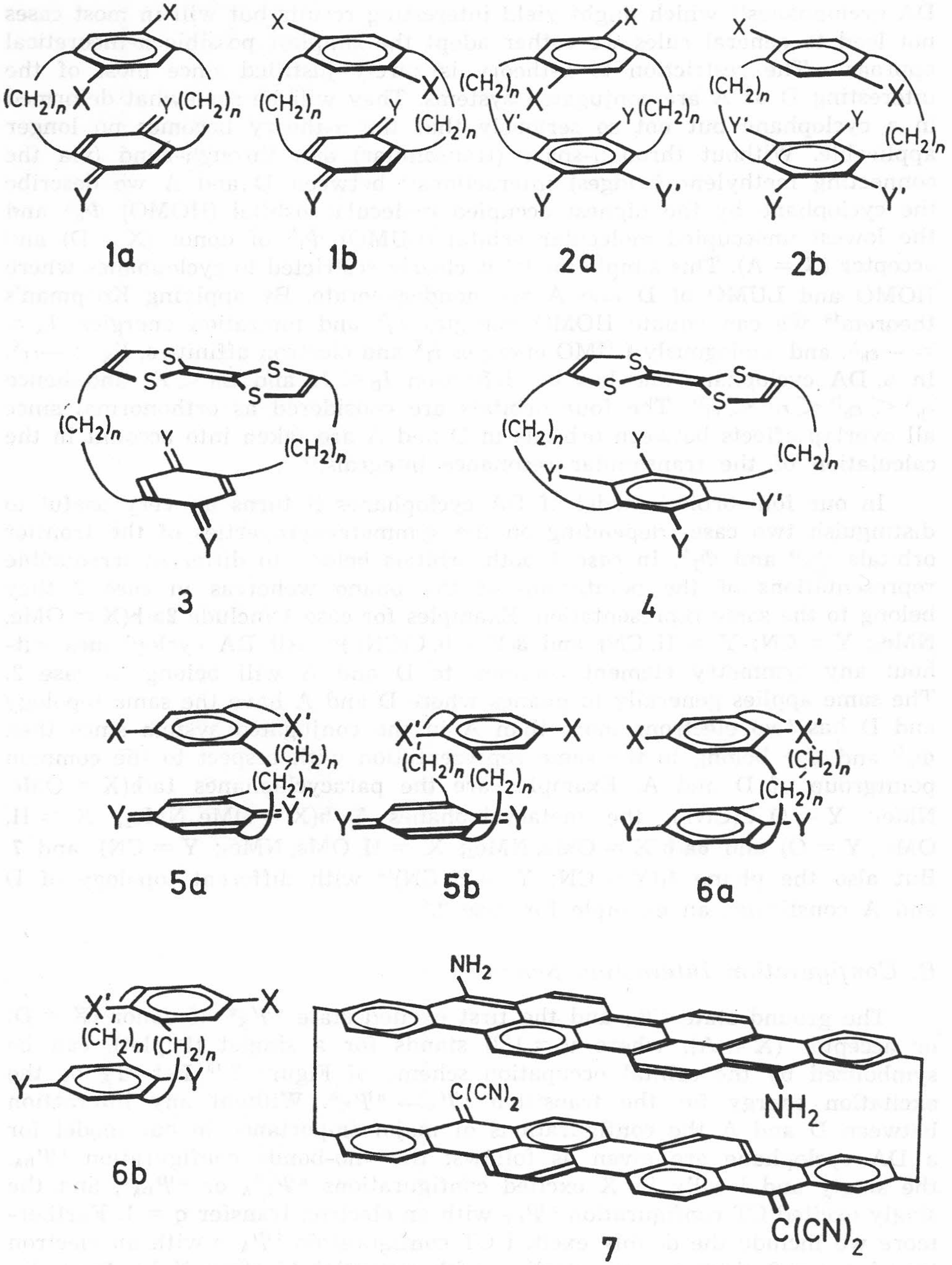
I. INTRODUCTION

In donor-acceptor cyclophanes DA with a sufficiently small distance between the donor D and the acceptor A one might expect an electron transfer from D to A already in the ground state, i. e. $DA \rightarrow D^+A^-$, if the difference between the ionization energy I_D of D and the electron affinity E_A of A is small enough. Depending on the kind of coupling between the two unpaired electrons we should get a singlet or a triplet ground state but not two independent doublet states for D and A since the close spatial proximity of D and A prevents a break-down of the Pauli principle. There should be a continuous transition with decreasing $I_D - E_A$ from a ground state without any appreciable electron transfer from D to A to one with a complete transfer of one electron. We shall use the term *biradical-ionic*[1,2] (*bi*) for a state which can be symbolized as $D^{+q} A^{-q}$ with $q > 1/2$. This defines a somewhat arbitrary borderline between ordinary and *bi* cyclophanes DA. Such a *bi* ground state was evidenced for some crystalline complexes of the strong donor *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and chloranil or 7,7,8,8-tetracyanoquinodimethane (TCNQ) as acceptors.[2-4] The presence of a *bi* ground state in a crystal depends strongly on the magnitude of the Madelung energy.[5] In solutions of TMPD and some quinones in highly polar solvents one observes uv-vis absorption spectra which resemble those of the Wurster's blue radical cation and the semiquinone radical anions.[3,6,7] However, it seems difficult to decide experimentally on the nature of the ionic species, whether there are mainly contact ion pairs $(D^+A^-)_{solv}$ or solvent separated ion pairs $D^+_{solv} + A^-_{solv}$.[8] On the other hand, ionic species are not observed in polar solvents for the D/A pair tetrathiofulvalene (TTF)-TCNQ.[9] In less polar solvents the spectra show a characteristic long wavelength absorption which is absent in the corresponding spectra of D and A alone. According to Mulliken's theory[3,6] this absorption corresponds to an excitation $DA \xrightarrow{h\nu} D^+A^-$ and is called a charge-transfer (CT) band.

Staab et al.[10-12] synthesized the cyclophanes (see Figure 1) **1a/b**($X = NMe_2$, $Y = O$, $n = 2$) and **1a/b**($X = OMe$, $Y = C(CN)_2$, $n = 2, 3$) with the D/A pairs TMPD/*p*-benzoquinone and 1,4-dimethoxybenzene/TCNQ. Spectroscopic investigations exclude paramagnetic ground states and according to the orientation and solvent dependence the longest wavelength absorption corresponds to an excitation from a less polar ground state into a more polar lowest excited singlet state. Obviously the stabilization of ionic states by environmental cooperative action of the solvent[6] is no longer as effective as with the aforementioned DA complexes, possibly since in the cyclophanes the formation of solvent separated ion pairs is impossible. Clearly a *bi* ground state should become more probable for cyclophanes with D/A combinations with sufficiently low $I_D - E_A$ values. But we can ask if this is the only parameter determining the size of the electron transfer *q*. Therefore, in this paper we will discuss the following questions: Which molecular parameters of D and A are important in order to obtain a *bi* ground state? Will this be a singlet or a triplet since it is well known[13] that both should be of comparable energy in biradicaloid molecules. Which role does the solvent play in DA cyclophanes? How does the character of the longest wavelength absorption change with decreasing

$I_D - E_A$? Does a *bi* ground state necessarily imply a lowest excited singlet state with only a small electron transfer q from D to A thus resulting in a reverse CT-transition[6] $D^+A^- \xrightarrow{h\nu} DA$?



1a 1b 2a 2b

3 4

5a 5b 6a

6b 7

Figure 1. Examples of donor-acceptor cyclophanes.

II. A. THEORY OF DA CYCLOPHANES

A. A Four-Orbital Model

Instead of performing more or less sophisticated calculations on selected DA cyclophanes[14] which might yield interesting results but will in most cases not lead to general rules we rather adopt the simplest possible π-theoretical approach. The restriction to π-theory is surely justified since most of the interesting D or A are conjugated systems. They will be somewhat deformed in a cyclophane but not so seriously that the π-theory becomes no longer applicable. Without through-space (transanular) and through-bond (via the connecting methylene bridges) interactions[15] between D and A we describe the cyclophane by the highest occupied molecular orbital (HOMO) Φ_h^X and the lowest unoccupied molecular orbital (LUMO) Φ_l^X of donor (X = D) and acceptor (X = A). This simple model is clearly restricted to cyclophanes where HOMO and LUMO of D and A are nondegenerate. By applying Koopman's theorem[16] we can equate HOMO energies ε_h^X and ionization energies, $I_X = -\varepsilon_h^X$, and analogously LUMO energies ε_l^X and electron affinities, $E_X = -\varepsilon_l^X$. In a DA cyclophane one has by definition $I_D < I_A$ and $E_D < E_A$ and hence $\varepsilon_h^A < \varepsilon_h^D < \varepsilon_l^A < \varepsilon_l^D$. The four orbitals are considered as orthonormal since all overlap effects between orbitals in D and A are taken into account in the calculation of the transanular resonance integrals.[17]

In our four-orbital model of DA cyclophanes it turns up very useful to distinguish two cases depending on the symmetry properties of the frontier orbitals Φ_h^D and Φ_l^A. In *case 1* both orbitals belong to different irreducible representations of the pointgroup of the phane wehereas in *case 2* they belong to the same representation. Examples for case 1 include **2a**/**b**(X = OMe, NMe$_2$; Y = CN; Y′ = H, CN) and **3**(Y = 0, C(CN)$_2$)[18]. All DA cyclophanes without any symmetry element common to D and A will belong to case 2. The same applies generally to phanes where D and A have the same topology and D has two electrons more than A in the conjugated system since then Φ_h^D and Φ_l^A belong to the same representation with respect to the common pointgroup of D and A. Examples are the paracyclophanes **1a**/**b**(X = OMe, NMe$_2$; Y = O, C(CN)$_2$), the metacyclophanes **5a**/**b**(X = OMe, NMe$_2$; X′ = H, OMe$_2$, Y = O) and **6a**/**b**(X = OMe, NMe$_2$; X′ = H, OMe, NMe$_2$; Y = CN), and **7**. But also the phane **4**((Y = CN; Y′ = H, CN)[18] with different topology of D and A constitutes an example for case 2.

B. Configuration Interaction Scheme

The ground state $^1\Psi_X$ and the first excited state $^u\Psi_X^*$ of donor (X = D) or acceptor (X = A), where u = 1(3) stands for a singlet (triplet), can be symbolized by the orbital occupation scheme of Figure 2.[19] Let ^uT_X be the excitation energy for the transition $^1\Psi_X \rightarrow {}^u\Psi_X^*$. Without any interaction between D and A the configurations of major importance in our model for a DA cyclophane are given as follows: the »no-bond« configuration $^1\Psi_{DA}$, the singly and locally in X excited configurations $^u\Psi_{D^*A}$ or $^u\Psi_{DA^*}$, and the singly excited CT configuration $^u\Psi_{CT}$ with an electron transfer $q = 1$. Furthermore we include the doubly excited CT configuratoin $^1\Psi_{A-2}$ with an electron transfer $q = 2$ since we are dealing with potential *bi* states.[13] In Appendix

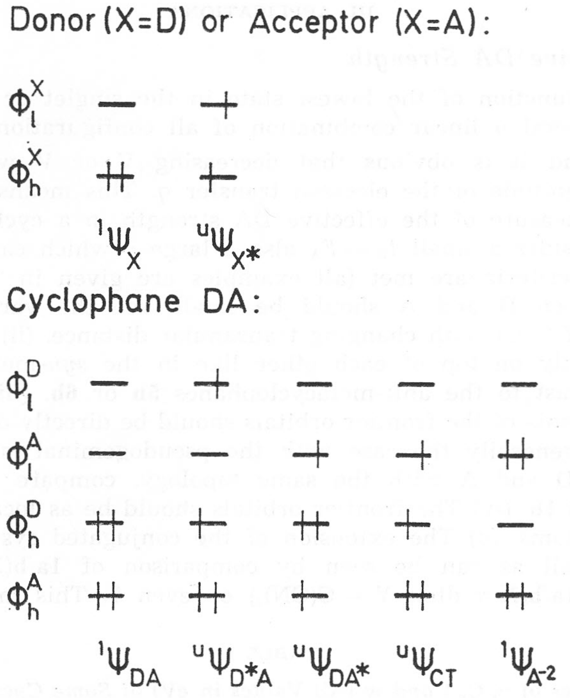


Figure 2. Orbital occupation schemes of the configurations of donor D or acceptor A and of the cyclophane DA.

I it is shown why we neglect other doubly excited configurations and that transanular and throughbond interaction lead to the following configuration interaction matrices, where the two configurations $^u\Psi_{D^*A}$ and $^u\Psi_{AD^*}$ have been replaced by a single locally excited (LE) configuration $^u\Psi_{LE}$ with an energy ^uT if we fix the zero of energy at the energy of $^1\Psi_{DA}$:

$$\text{singlet manifold:}\quad \begin{array}{cccc} ^1\Psi_{DA} & ^1\Psi_{LE} & ^1\Psi_{CT} & ^1\Psi_{A^{-2}} \\ \hline \end{array} \qquad \text{triplet manifold:}\quad \begin{array}{cc} ^3\Psi_{LE} & ^3\Psi_{CT} \end{array}$$

$$\begin{bmatrix} 0 & 0 & t & 0 \\ & ^1T & w & 0 \\ & & V & t \\ & & & \overline{V} \end{bmatrix} \qquad \begin{bmatrix} ^3T & V \\ & w \end{bmatrix} \tag{1}$$

Here $V = I_D - E_A - \gamma$ and $\overline{V} = 2\,V + C$ with the Coulomb repulsion γ between an electron in D and one in A. C ist twice the difference between the electron repulsion of two electrons in D or A and γ. $^1\Psi_{DA}$, $^1\Psi_{CT}$ and $^1\Psi_{A-2}$ are coupled by t depending on the transanular and through bond interaction between the frontier orbitals $\Phi_h{}^D$ and $\Phi_l{}^A$. Analogously w couples $^u\Psi_{LE}$ and $^u\Psi_{CT}$ and depends on the interaction between the orbitals $\Phi_h{}^D$ and $\Phi_h{}^A$ or $\Phi_l{}^D$ and $\Phi_l{}^A$.

III. APPLICATIONS

A. The Effective DA Strength

The wavefunction of the lowest state in the singlet or triplet manifold will be in general a linear combination of all configurations of appropriate multiplicity and it is obvious that decreasing V or $\overline{V}$ will result in an increasing magnitude of the electron transfer q. This means that V and not $I_\mathrm{D} — E_\mathrm{A}$ is a measure of the effective DA strength in a cyclophane. A small V demands besides a small $I_\mathrm{D} — E_\mathrm{A}$ also a large γ which can be achieved if the following criteria are met (all examples are given in Table I): (i) The distance between D and A should be small, see the variations in γ for **1a**($X = NMe_2$, $Y = O$) with changing transanular distance. (ii) D and A should be fixed directly on top of each other like in the *syn*-metacyclophanes **5a** or **6a** in contrast to the anti-metacyclophanes **5b** or **6b**. (iii) The numerical largest coefficients of the frontier orbitals should be directly one upon another. This will be generally the case with the pseudogeminal isomers of phanes consisting of D and A with the same topology, compare for example the isomers **1a** and **1b**. (iv) The frontier orbitals should be as localized as possible at only few atoms. (v) The extension of the conjugated system of D and A should be small as can be seen by comparison of **1a**/**b**($X = NMe_2$, OMe; $Y = O$) with **1a**/**b**(X = dto.; $Y = C(CN)_2$) or even **7**. This means that trying

TABLE I

Calculated Values of γ, C, t *and* w *(All Values in eV) of Some Cyclophanes of Figure 1 with a Transanular Distance* R *(in pm). Details Concerning the Calculations see Appendix II*

Cyclophane	Case	R	γ	C	$\|w\|$	$\|t\|$
1a ($X = NMe_2$, $Y = O$)	2	295[a]	3.59	3.49—5.73	0.	0.36(0.39)[c]
		320	3.42	3.85—6.08	0.	0.26[c]
		350	3.23	4.23—6.46	0.	0.15[c]
		400	2.95	4.78—7.02	0.	0.06[c]
1b ($X = NMe_2$, $Y = O$)	2	295	3.51	3.66—5.89	0.	0.13
1a ($X = NMe_2$, $Y = C(CN)_2$)	2	295	3.20	2.55—4.51	0.	0.36
1b ($X = NMe_2$, $Y = C(CN)_2$)	2	295	3.11	2.72—4.68	0.	0.13
1a ($X = OMe$, $Y = O$)	2	295	3.63	3.54—5.79	0.	0.32
1b ($X = OMe$, $Y = O$)	2	295	3.56	3.68—5.95	0.	0.10
1a ($X = OMe$, $Y = C(CN)_2$)	2	295	3.20	2.66—4.63	0.	0.22
1b ($X = OMe$, $Y = C(CN)_2$)	2	295	3.14	2.79—4.75	0.	0.06
2a ($X = OMe$, $Y = CN$, $Y' = H$)	1	295	3.32	3.04—5.10	0.35	0.
2b ($X = OMe$, $Y = CN$, $Y' = H$)	1	295	3.24	3.19—5.27	0.43	0.
2a ($X = OMe_2$, $Y = CN$, $Y' = H$)	1	295	3.32	2.93—4.97	0.32	0.
2b ($X = NMe_2$, $Y = CN$, $Y' = H$)	1	295	3.20	3.17—5.22	0.39	0.
3 ($Y = C(CN)_2$)[d]	1	295	3.13	2.00—3.87	0.22[c]	0.
4 ($Y = CN$, $Y' = H$)[d]	2	295	3.24	2.41—4.38	0.	0.13[c]
5a ($X = X' = NMe_2$, $Y = O$)	2	295	3.60	3.52—5.76	0.06	0.37
5b ($X = X' = NMe_2$, $Y = O$)[b]	2	295	3.24	4.24—6.47	0.08	0.15
6a ($X = X' = NMe_2$, $Y = CN$)	2	295	3.33	2.94—5.01	0.41	0.01
6b ($X = X' = NMe_2$, $Y = CN$)[b]	2	295	3.08	3.44—5.51	0.28	0.25
7	2	295	2.41	0.70—1.90	0.	0.48

[a] Mean transanular distance in [2.2]paracyclophanes, see: H. Vogler, G. Ege, and H. A. Staab, *Tetrahedron* **31** (1975) 2441—2443.. [b] Only one atom of D and A are directly one upon another. [c] Without through-bond interaction. [d] $|w|$ and $|t|$ are slightly underestimated, see Reference 36.

to decrease $I_D - E_A$ by the choice of larger conjugated D and A does not necessarily result in a greater effective DA strength. A further increase in q in the lowest singlet state can be achieved by a small C which demands a small distance between D and A (cf. criterion (i) above for a small γ) and an extended conjugated system of D and A as in **7**. This last condition is only helpful if one succeeds in finding systems where the corresponding decrease of γ (cf. criterion (v) above) is belanced by that of $I_D - E_A$.

B. Case 1 Cyclophanes

Here we have $t = 0$ and it follows immediately from (1) that ${}^1\Psi_{DA}$ and ${}^1\Psi_{A\text{-}2}$ constitute already states of the system. Another state ${}^u\Psi$ is obtained by interaction of ${}^u\Psi_{CT}$ and ${}^u\Psi_{LE}$ with an energy of ${}^uE = \{V + {}^uT - (({}^uT - V)^2 + 4w^2)^{1/2}\}/2$ and an electron transfer $q = \{1 + (V - {}^uE)^2/w^2\}^{-1}$. In Case 1 we need not to discuss ${}^1\Psi_{A\text{-}2}$ any further since this state will be higher in energy than ${}^1\Psi_{DA}$ and ${}^u\Psi$ for reasonable values $V > -C$. All energies of these states as a function of V are shown in Figure 3. If $V = w^2/{}^uT$ the states ${}^1\Psi_{DA}$ and ${}^u\Psi$ become degenerate and we have $q = \{1 + (w/{}^uT)^2\}^{-1}$ thus leading to the condition $V < w^2/{}^uT < {}^uT$ for a *bi* ground state with an electron transfer $q > 1/2$. This condition reduces to

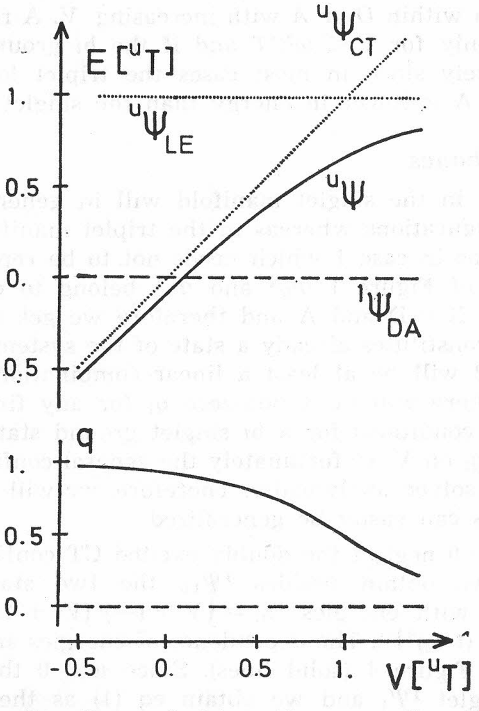


Figure 3. Energies of configurations and states and corresponding electron transfers q as a function of V for a case 1 cyclophane with $w = 0.32/{}^uT$.

$$V < w^2/{}^uT \quad \text{or} \quad I_D - E_A < \gamma + w^2/{}^uT \qquad (2)$$

if we consider that generally $w^2 < {}^{u}T^2$. The *bi* ground state will be a triplet if ${}^{3}T < {}^{1}T$.

In order to fulfill eq (2) $I_D - E_A$ and ${}^{u}T$ have to be small whereas γ and w^2 should be chosen as large as possible. It can be shown that $|w| < \sqrt{2}\,|\beta_{max}|$ where β_{max} is the numerically largest transanular resonance integral (we neglect the small contribution of the through-bond resonance integrals). For carboconjugated phanes with a transanular distance as in [2.2]paracyclophanes this estimate yields $|w| < 0.76$ eV. Heteroatoms like nitrogen or oxygen will reduce $|w|$ and our calculated values in Table I are usually at most half the maximum estimate. In most systems $w^2/{}^{u}T$ will be only about 0.1 eV and insted of eq (2) we obtain the approximate condition.

$$I_D - E_A < \gamma \tag{3}$$

for a *bi* ground state in case 1 cyclophanes. By the introduction of boron atoms into the conjugated systems of D and A larger $|w|$ values are likely.[21]

For $V > w^2/{}^{1}T$ the longest wavelength absorption corresponds to the excitation ${}^{1}\Psi_{DA} \rightarrow {}^{1}\Psi$ which is mainly a CT-transition if $V < {}^{1}T$ but turns to a local transition within *D* or *A* with increasing *V*. A reverse CT-transition will be observed only for $V < w^2/{}^{1}T$ and if the *bi* ground state is a singlet which seems unlikely since in most cases the triplet locally excited configuration of D and A is lower in energy than the singlet and hence ${}^{3}T < {}^{1}T$.

C. *Case 2 Cyclophanes*

Here all states in the singlet manifold will in general be linear combinations of all configurations whereas in the triplet manifold we end up with the same problem as in case 1 which needs not to be repeated. With all case 2 paracyclophanes of Figure 1 Φ_h^X and Φ_l^X belong to different irreducible representations for X = D and A and therefore we get $w = 0$ (see Table I). In that case ${}^{u}\Psi_{LE}$ constitutes already a state of the system. The lowest singlet state ${}^{1}\Psi_1$ in case 2 will be at least a linear combination of ${}^{1}\Psi_{DA}$ and ${}^{1}\Psi_{CT}$. In the state ${}^{1}\Psi_1$ there will be a non-zero q_1 for any finite value of V and in order to derive conditions for a *bi* singlet ground state we have to study the dependence of q_1 on V. Unfortunately the general configuration interaction problem cannot be solved analytically. Therefore, we will consider two special cases whose results can easily be generalized.

Let us put $w = 0$ neglect the doubly excited CT configuration ${}^{1}\Psi_{A^-2}$ (i. e. $C \rightarrow \infty$).[22] Then we obtain besides ${}^{1}\Psi_{LE}$ the two states ${}^{1}\Psi_i = a_i\,{}^{1}\Psi_{DA} + b_i\,{}^{1}\Psi_{CT}$ $(i = 1, 2)$ with energies ${}^{1}E_i = \{V + (-)^i (V^2 + 4t^2)^{1/2}\}/2$ and electron transfers $q_i = \{1 + (t/E_i)^2\}^{-1}$. The dependence of energies and electron transfers on V is shown in Figure 4 (solid lines). Since $w = 0$ the ground state will always be the singlet ${}^{1}\Psi_1$ and we obtain eq (1) as the condition for a *bi* ground state. For $V = {}^{1}T - (t^2/{}^{1}T) \cong {}^{1}T$ (cf. case 1) ${}^{1}\Psi_2$ and ${}^{1}\Psi_{LE}$ become degenerate. Therefore the longest wavelength absorption ${}^{1}\Psi_1 \rightarrow {}^{1}\Psi_2$ corresponds to a local excitation in D or A if $V > {}^{1}T$ and to a CT transition for not too small a $V < {}^{1}T$ since then $q_1 \cong 0$ and $q_2 \cong 1$. In the relatively small interval defined by $|V| < 2.7\,|t|$ q_1 and q_2 undergo drastic changes, e. g. $q_1 = 0.1$ if $V = 2.7\,|t|$ and 0.3 if $V = |t|$, and for $V = 0$ we have $q_1 = q_2$ and the smallest possible excitation energy ${}^{1}E_2 - {}^{1}E_1 = 2\,|t|$. Thus in this interval

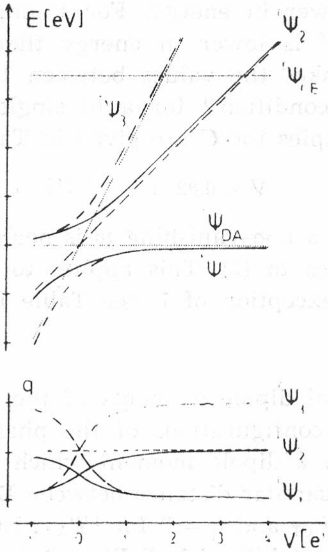


Figure 4. Energies of configurations and states and corresponding electron transfers q as a function of V for a case 2 cyclophane with $w = 0$, $t = 0.4$ eV, neglect of the configuration $^1\Psi_{\mathrm{A-2}}$ (———) or with C = 0 (— — —), respectively.

it is no longer appropriate to speak of neither a CT nor a reverse CT transition. The latter would occur only for $V < -|t|$.

Another analytically solvable special case is given by $w = C = 0$. Then besides $^1\Psi_{\mathrm{LE}}$ one has three states $^1\Psi_{\mathrm{i}} = a_{\mathrm{i}}\,{}^1\Psi_{\mathrm{DA}} + b_{\mathrm{i}}\,{}^1\Psi_{\mathrm{CT}} + c_{\mathrm{i}}\,\Psi_{\mathrm{A-2}}$ (i = 1—3) with energies $^1E_{\mathrm{i}} = V + (-)^{(\mathrm{i}+1)/2}(1 - \delta_{\mathrm{i}2})(V^2 + 2t^2)^{1/2}$ and electron transfers $q_{\mathrm{i}} = 1 + {}^1E_{\mathrm{i}}(V - {}^1E_{\mathrm{i}})\{2t^2 + {}^1E_{\mathrm{i}}(V - {}^1E_{\mathrm{i}})\} \times \{2t^4 + t^2\,{}^1E_{\mathrm{i}}(2V - {}^1E_{\mathrm{i}}) + {}^1E_{\mathrm{i}}^2({}^1E_{\mathrm{i}} - V)^2\}^{-1}$ where $q_2 = 1$ irrespective of V. The dependence of energies and electron transfers on V is shown in Figure 4 (dashed lines). The main difference to the special case just considered is the doubled extremal q for $^1\Psi_1$ and $\Psi^1{}_3$. For $V = 0$ it is $q_1 = q_2 = q_3 = 1$ and $^1E_{1,3} = \pm\sqrt{2}\,|t|$, $^1E_2 = 0$, and a *bi* ground state is already obtained for $V < 0.82\,|t|$. The characteristic of the longest wavelength absorption remains unchanged except for $V < 0$ where we now have a transition from a state with $1 < q_1 < 2$ to one with $q_2 = 1$. The lowest triplet state is for all V degenerate with $^1\Psi_2$.

In general one will have $w \neq 0$, e. g. with the metacyclophanes of Figure 1, which influences the second singlet (for finite C) and the lowest triplet especially in the region $V \cong {}^uT$ since now all states can no longer cross $^u\Psi_{\mathrm{LE}}$. Concerning the lowest singlet $^1\Psi_1$ a non-vanishing w leads to an effectice V^{eff} with $V - (w^2/{}^1T) < V^{\mathrm{eff}} < V$ as can easily be shown by applying the partitioning technique[23]. Thus there will be a change of V^{eff} with respect to V by at most 0.1 eV and this will not alter significantly the condition for a lowest *bi* singlet state. As we have seen the ground state will always be a singlet as long as $w = 0$ and even for non-vanishing w it is very unlikely that a triplet will be lower in energy. For example, it can be shown that for $V = 0$ the triplet ${}^3\Psi$ is lower in energy than the singlet ${}^1\Psi_1$ only if $w^2 > x^3 T\,|\,t\,|$ where x takes the values between 1 ($C \rightarrow \infty$) and $2^{1/2}$ ($C = 0$). Thus we can state the condition[24] for a *bi* singlet ground state in case 2 for any value of C (examples for C are given in Table I) as follows,

$$V < 0.82\,|\,t\,|\,e^{-0.26C/|t|} \tag{4}$$

where the small effect of a non-vanishing w is neglected. However, if $C/|\,t\,|$ is large condition (4) reduces to (3). This applies to all cyclophanes shown in Figure 1 with the only exception of **7**, see Table I.

D. *Effect of Solvent*

Apart from permanent dipole moments of the isolated D or A ${}^1\Psi_{DA}$ and ${}^u\Psi_{LE}$ describe non-polar configurations of the phane DA whereas ${}^u\Psi_{CT}$ and ${}^u\Psi_{A-2}$ are functions with a dipole moment which can be estimated roughly as $\mu = eqR$. R is the transanular distance between D and A and q the electron transfer, i. e. $q = 1$ for ${}^u\Psi_{CT}$ and $q = 2$ for ${}^1\Psi_{A-}$. In a medium with dielectricity constant ε a dipole is stabilized by[25] $W = (2\mu^2 r^{-3})\, f_\varepsilon$ where r is the radius of the cavity created by the phane in the medium, and $f_\varepsilon = (\varepsilon - 1)(2\varepsilon + 1)^{-1}$. For highly polar solvents, e. g. acetonitril, we have $f_\varepsilon \cong 0.5$ and r can be estimated[26] as the largest molecular radius including the van der Waals radii of all atoms. Then the energies of ${}^u\Psi_{CT}$ and ${}^1\Psi_{A-2}$ in the solvent are obtained by simple replacement of V and C by the effective parameters $V^{\text{eff}} = V - 2e^2 R^2 r^{-3} f_\varepsilon$ and $C^{\text{eff}} = C - 4e^2 R^2 r^{-3} f_\varepsilon$. With $f_\varepsilon = 0.5$ we obtain for cyclophanes of the kind **1a/b** or **2a/b** with n = 2.

$$V^{\text{eff}} \cong V - 0.5 \text{ eV}, \qquad C^{\text{eff}} \cong C - 0.9 \text{ eV} \tag{5}$$

or for **7** with its extended D and A

$$V^{\text{eff}} \cong V - 0.1 \text{ eV}, \qquad C^{\text{eff}} \cong C - 0.2 \text{ eV} \tag{6}$$

IV. SOME NUMERICAL EXAMPLES

A. *Examples for Case 1*

The excitation energy of the longest wavelength absorption in the UV-VIS spectra of DA cyclophanes is simply given by ${}^1E$ and we can calculate from ${}^1E$, ${}^1T$, and w a quasi »experimental« V and γ, i. e. $V = {}^1E + w^2 ({}^1T - {}^1E)^{-1}$ and $\gamma = I_D - E_A - V$. As is shown in Table II the γ so obtained for **2a/b**(X = OMe, Y = CN, Y′ = H, n = 2) are only slightly larger by about 0.2 eV than those given in Table I. This proves that our simple model yields a satisfactory description of such DA cyclophanes.

To our knowledge the cyclophane **3** (Y = C(CN)$_2$, n = 2, 3)[18] with the D/A pair TTF/TCNQ has not yet been synthesized. Experimentally one has[27] $I_D - E_A = 4$ eV and it is obvious by inspection of Table I that condition (3) is not fulfilled, even if we assume that our calculated γ might be too small by about 0.2 eV as in the afore-mentioned cyclophanes **2a/b**. The same applies

TABLE II

Quasi »Experimental« V and γ Values of Some Cyclophanes Obtained from Experimental Values for ^{1}T, ^{1}E = ^{1}E$_2$—^{1}E$_1$, I$_D$, *and* E$_A$

Cyclophane[a]	Case	^1T[b]	^1E	I_D	E_A	V	γ
1a (X = OMe, Y = O)	2		2.57[c]	7.92[g]	1.72[g]	2.5	3.7
1b (X = OMe, Y = O)	2		2.49[c]			2.5	3.7
1b (X = OMe, Y = C(CN)$_2$)	2		1.7[d]	7.92[g]	2.68[g]	1.7	3.5
1a (X = NMe$_2$, Y = O)	2		2.27[e]	6.7[h]	1.8[h]	2.2	2.7
1b (X = NMe$_2$, Y = O)	2		2.33[e]			2.3	2.6
2a (X = OMe, Y = CN, Y′ = H)	1	4.07	3.22[f]	7.92[g]	1.15[g]	3.4	3.4
2b (X = OMe, Y = CN, Y′ = H)	1	4.23	3.16[f]			3.4	3.4

[a] In all cyclophanes n = 2. [b] Obtained from ^1T_D = 4.24 eV and ^1T_A = 4.05 eV (see footnote f). [c] H. A. Staab, C. P. Herz, and H.-E. Henke, *Chem. Ber.* **110** (1977) 3351—3357, [d] See Reference 11 and: H. Tatemitsu, B. Natsume, M. Yoshida, Y. Sakata, and S. Misumi, *Tetrahedron Lett.* 1978, 3459—3462. [e] Reference 10. [f] H. A. Staab, and V. Taglieber, *Chem. Ber.* **110** (1977) 3366—3376. [g] Calculated from orbital energies as described in Appendix II. [h] Experimental values for TMPD D. G. Streets, W. E. Hall, and G. P. Ceasar, *Chem. Phys. Lett.* **17** (1972) 90—94 and *p*-benzoquinone (see Reference 30).

to condition (2) although $^3T \cong {}^3T_A \ll {}^1T \cong {}^1T_A$ = 3.1 eV[28]. According to eq (5) even the stabilization by a polar solvent will not lead to a *bi* triplet ground state. This explains to some extent the failure in observing ionic species in solutions of TTF and TCNQ in a polar solvent.[9] The CT band should be around 1400 nm, although possibly the deformations in such a phane, see for example a related system[29], might lead to a hypsochromic shift.

B. Examples for Case 2

Similar as in case 1 we can calculate an »experimental« V and γ from the longest wavelength absorption as long as $w = 0$ and $C \gg 0$, i. e. $V = ({}^1E^2 - 4t^2)^{1/2}$ and $\gamma = I_D - E_A - V$. This applies to all case 2 paracyclophanes of Figure 1 and similar as in our examples for case 1 the »experimental« γ of **1a**/**b** (X = OMe, Y = O, C (CN)$_2$; n = 2) in Table II are only sligthly higher than the corresponding ones in Table I. However, this does not apply to **1a**/**b** (X = NMe$_2$, Y = 0, n = 2) where the »experimental« γ are much smaller than expected. Obviously the ionization energy I_D of the donor TMPD in these phanes is increased by at least 0.9 eV since the conjugation between the NMe$_2$ groups and the benzene ring is reduced due to steric hindrance caused by the methylene bridges. These steric effects are absent in solutions of complexes of TMPD and quinones. For TMPD/*p*-benzoquinone $I_D - E_A$ = 4.9 eV (see Table II) and $\gamma \cong$ 3.6 eV if we take the value of **1a** (X = NMe$_2$, Y = O, n = 2) in Table I. Thus we get $V \cong$ 1.3 eV and even a very polar solvent will not lead to a $V^{\text{eff}} \cong 0$. Replacing *p*-benzoquinone by cloranil reduces $I_D - E_A$ by 0.6 eV[30] and we obtain with eq (5) $V^{\text{eff}} \cong$ 0.2 eV. Thus the experimental finding[3,6,7] of ionic species in solutions of TMPD/chloranil but not of TMPD/*p*-benzoquinone becomes plausible, more-over since another stabilization by the formation of solvent separated ion pairs might be of importance.

Finally let us take a look at the hitherto unknown cyclophane **7** which, according to our calculations, contains a donor even stronger than TMPD (I_D = 6.09 eV, I_{TMPD} = 6.7 eV, see Table II) and an acceptor ranging between *p*-benzoquinone and TCNQ (E_A = 2.45 eV, $E_{p\text{-benzoquinone}}$ and E_{TCNQ} see Reference

30). Taking the values for $|t|$, C, and γ from Table I together with a possible stabilization by a polar solvent (see eq (6)) condition (4) reads $V^{\text{eff}} < 0.1$—0.3 eV. However, our calculated V^{eff} is well over this limit.

SUMMARY AND CONCLUSIONS

In this paper we use a simple theoretical four-orbital configuration interaction model within π-theory for the study of DA cyclophanes in their ground and lowest excited states. Their energies and the size of the electron transfer from D to A depend only on four parameters, i. e. the effective DA strength $V = I_D - E_A - \gamma$, the electron repulsion term C, and the transanular and through-bond interactions t between the frontier orbitals and w between the HOMO's or LUMO's of D and A. A similar analysis using Mulliken's model[6] would need more parameters. It is possible to distinguish two cases with respect to the symmetry of the frontier orbitals, i. e. HOMO of D and LUMO of A. Both cases show quite different behaviour especially with respect to the ground state of the phane. Suppose the frontier orbitals belong to different irreducible representations of the pointgroup of the phane (Case 1), then there is a discontinuous transition at a certain value of V which is given by condition (2) from a »no-bond« ground state with no electron transfer q from D to A to a *bi* ground state with $q > 1/2$. Correspondingly the longest wavelength absorption changes from a CT to a reverse CT transition, although the latter will be not of much concern since the *bi* ground state should be most likely a triplet. On the other hand if the frontier orbitals belong to the same representation (Case 2) there is with decreasing V a continuous transition from the »no-bond« ground state to one with significant electron transfer from D to A and (4) constitutes the condition for a *bi* ground state, now being almost certainly a singlet quite in contrast to case 1. It is interesting to note that just for V values defining the borderline between an ordinary and a *bi* ground state the longest wavelength absorption is neither a CT nor a reverse CT transition since both states of interest have comparable electron transfer.

It follows from the conditions (2) and (4) that a small enough V is essential for the occurence of a *bi* ground state. In solvents with a high polarity V is replaced by V^{eff} being the lower with respect to V the smaller D and A are. In case 2 a slightly larger V is sufficient for condition (4) if very small C or C^{eff} and large $|t|$ can be achieved. Detailed rules how to choose D and A in order to obtain large γ and small C values have been given. To the authors knowledge hitherto no cyclophanes with a *bi* ground state have been prepared and we can ask if the search for such sompounds will be successful at all. In case 1 and even in case 2 if $C \gg 0$ the approximate condition (3) applies leading to $I_D - E_A \leqq 3.1$—3.6 eV or, for a cyclophane with small D and A in a polar solvent, $I_D - E_A \leqq 3.6$—4.1 eV according to eq (5) if we take the extremal γ values in Table I for para- or *syn*-metacyclophanes with n = 2. In case 2 a large $|t|$ and a small C would facilitate the fulfillment of condition (4) but only with small systems where the stabilization by the solvent is most effective. But the C values of the smaller cyclophanes are obviously already too large for an appreciable effect, see for example C values of **1**, **5a** and **6** in Table I. On the other hand C will be surely small in such extended systems like **7**. But what is gained by a small C we lose by the poor stabilization by a solvent (if there is any solubility at all, however, this problem would vanish once a *bi* ground state is present). It seems most likely that cyclophanes with a *bi* ground state should be characterized by a small D and A with $I_D - E_A \leqq 3.6$—4.1 eV and maximum γ. The extension of the present work with a systematic search for DA cyclophanes which might exhibit a *bi* ground state is now underway.

APPENDIX I

Derivation of the Configuration Interaction Matrices

The orbitals Φ_i^X ($i = h, l$; $X = D, A$) are eigenfunctions of the Hartree-Fock operator F^X, i.e. $F^X \Phi_i^X = \varepsilon_i^X \Phi_i^X$ with[31] $F^X = h^X + 2(\text{——} \,|\, \Phi_h^X \Phi_h^X) - (\text{—}\Phi_h^X \,|\, \text{——}\Phi_h^X)$ where $(\Phi_i \Phi_j \,|\, \Phi_k \Phi_l) = \langle \Phi_i(1) \Phi_j(1) \,|\, e^2 r_{12}^{-1} \,|\, \Phi_k(2) \Phi_l(2) \rangle$. It is $\varepsilon_h^X = \langle \Phi_h^X \,|\, h^X \,|\, \Phi_h^X \rangle + J_{hh}^{XX}$ and $\varepsilon_l^X = \langle \Phi_l^X \,|\, h^X \,|\, \Phi_l^X \rangle + 2 J_{hl}^{XX} - K_{hl}$ with $J_{ij}^{XX} = (\Phi_i^X \Phi_i^X \,|\, \Phi_j^Y \Phi_j^Y)$ and $K_{ij}^{XY} = (\Phi_i^X \Phi_j^Y \,|\, \Phi_i^X \Phi_j^Y)$. The total energy ${}^1E_X$ of X in its ground state ${}^1\Psi_X$ and the excitation energies ${}^uT_X$ for transitions from ${}^1\Psi_X$ into the lowest excited singlet ($u = 1$) and triplet ($u = 3$) states ${}^u\Psi_{X*}$ are given as follows, ${}^1E_X = 2\varepsilon_h^X - J_{hh}^{XX}$ and ${}^uT_X = \varepsilon_l^X - \varepsilon_h^X - J_{hl}^{XX} + 2\delta_{u1} K_{hl}^{XX}$. Since Φ_i^D and Φ_j^A are localized on different parts of the cyclophane we have $(\Phi_i^D \Phi_j^A \,|\, \text{——}) = 0$ within the ZDO approach. The mean distance between D and A is large and it is reasonable to introduce the following approximation for the Coulomb repulsion integrals $\gamma_{st}^{DA} = (\chi_s^D \chi_s^D \,|\, \chi_t^A \chi_t^A)$ between basis functions χ_s^D at atom s in D and χ_t^A at atom t in A: $\gamma_{st}^{DA} \to \gamma$ for all χ_s^D and χ_t^A. Thus we obtain $J_{ij}^{DA} = \gamma$ and the non-vanishing matrix elements ${}^uH_{i,j} = \langle ui \,|\, H \,|\, uj \rangle$ and ${}^uE_i = \langle ui \,|\, H \,|\, ui \rangle$ between the configurations $|ui\rangle = {}^1\Psi_{DA}$, ${}^u\Psi_{DA*}$ ${}^u\Psi_{D*A}$, ${}^u\Psi_{CT}$, and ${}^1\Psi_{A^{-2}}$ with respect to the Hamiltonian H of the cyclophane are given as follows:

$$ {}^1E_{DA} = {}^1E_D + {}^1E_A + 4\gamma := 0 \quad \text{(arbitrary fixed)} $$

$$ {}^uE_{CT} = {}^1E_{DA} + V $$

$$ {}^uE_{DA*} = {}^1E_{DA} + {}^uT_A \quad \text{and} \quad {}^uE_{D*A} = {}^1E_{DA} + {}^uT_D $$

$$ {}^1E_{A^{-2}} = {}^1E_{DA} + \overline{V} $$

$$ {}^1H_{DA,CT} = {}^1H_{CTA^{-2}} = t $$

$$ {}^uH_{D*A,TC} = w_l \quad \text{and} \quad {}^uH_{DA*,TC} = -w_h $$

where

$$ V = \varepsilon_l^A - \varepsilon_h^D - \gamma \quad \text{and} \quad \overline{V} = 2V + C $$

$$ C = J_{hh}^{DD} + J_{ll}^{AA} - 2 J_{hl}^{DA} \geqq 0 \quad \text{(see Reference 32)} $$

$$ t = 2^{1/2} \langle \Phi_h^D \,|\, \breve{\beta} \,|\, \Phi_l^A \rangle $$

$$ w_h = \langle \Phi_h^D \,|\, \breve{\beta} \,|\, \Phi_h^A \rangle \quad \text{and} \quad w_l = \langle \Phi_l^D \,|\, \breve{\beta} \,|\, \Phi_l^A \rangle $$

and the operator $\breve{\beta}$ contains the transanular and through-bond resonance integrals as described in Reference 17. In the four-orbital model there is another CT configuration with an excitation from A to D. However, this configuration can be disregarded here since it is much higher in energy than ${}^u\Psi_{CT}$ and can interact only with the locally excited configurations ${}^u\Psi_{DA*}$ and ${}^u\Psi_{D*A}$. The latter do not interact as well and we will construct two new orthogonal linear combinations $^u\Psi_{LE}$ and $^u\Psi_{LE}$, so that $^u\Psi_{LE}$, does no longer interact with $^u\Psi_{CT}$. We obtain $^u\Psi_{LE} = \{1 + (w_h/w_l)^2\}^{-1/2} \{^u\Psi_{DA*} — (w_h/w_l)\, ^u\Psi_{D*A}\}$ and $w = {}^uH_{CT,LE} = \{1 + (w_h/w_l)^2\}^{1/2} w_l$ if $w_l \neq 0$ or $^u\Psi_{LE} = {}^u\Psi_{DA*}$ and $w = {}^uH_{CT,LE} = — w_h$ if $w_l = 0$. The energy of $^u\Psi_{LE}$ is simply given by $^uE_{LE} = {}^1E_{DA} + {}^uT$ with $^uT = \{1 + (w_h/w_l)^2\}^{-1} \{^uT_D + (w_h/w_l)^2\, ^uT_A\}$ if $w_l \neq 0$ or $^uT = {}^uT_A$ if $w_l = 0$ and ^uT is bracketed by ^uT_D and ^uT_A.

Besides the configuration $^1\Psi_{A^{-2}}$ there can be constructed several other doubly excited singlet configurations within the four-orbital model (see Reference 33): $^1\Psi_{D**A}$, $^1\Psi_{DA**}$, $^1\Psi_{D^{-2}}$, $^1\Psi_{D*^+A^-}$, $^1\Psi_{D^-A*^+}$, $^1\Psi_{D^+A*^-}$, $^1\Psi_{D*^-A^+}$, and $^1\Psi_{D*A*(b)}$ with b = 1, 2. The first two configurations are locally in D or A excited and describe correlation effects in D or A which should be considered as taken into account implicitely in the parametrization. Furthermore their energy is quite high, e. g. $^1E_{D**A} \geqq {}^1T_D + {}^3T_D$. The configurations $^1\Psi_{D^{-2}}$, $^1\Psi_{D^-A*^+}$, and $^1\Psi_{D*^-A^+}$ correspond to an electron transfer A → D with an energy generally higher than those of the already disregarded singly excited configuration $^1\Psi_{D^-A^+}$ (for $^1\Psi_{D^-A*^+}$ this is strictly true if $\frac{1}{2}\,(^1T_A + {}^3T_A) > J^{AA}_{hh} — 2\, J^{AA}_{hl}$ which is most likely fulfilled; a similar condition holds for $^1\Psi_{D*^-A^+}$). Also the two configurations $^1\Psi_{D*A*(b)}$ will have no significant influence on the ground state and the lowest excited singlet state since their energy is bracketed by $(^3T_D + {}^3T_A)$ and $(^1T_D + {}^1T_A)$ and is V independent. However, the energies of $^1\Psi_{D*^+A^-}$ and $^1\Psi_{D^+A*^-}$ with an electron transfer D → A depend on V, i. e. $^1E_{D*^+A^-} = V + \frac{1}{2}\,(^1T_D + {}^3T_D) + (2\, J^{DD}_{hh} — J^{DD}_{hl})$ (for $^1E_{D^+A*^-}$ replace D by A), but will in most cases be higher than those of $^1\Psi_{CT}$ and $^1\Psi_{LE}$. Consequently they will lead to considerable rearrangements of higher excited states but not of the ground state and the lowest excited singlet state. Therefore it seems appropriate within our model to neglect all doubly excited singlet configurations except $^1\Psi_{A^{-2}}$ whose energy shows a $2\,V$ dependence. The same reasoning applies to the possible doubly excited triplet configurations (see Reference 34): $^3\Psi_{D*^+A^-}$, $^3\Psi_{D^-A*^+}$, $\Psi^3_{D^+A*^-}$, and $^3\Psi_{D*A*(c)}$ with $c = 1, 2, 3$.

APPENDIX II

Calculational Procedure

All calculated values in this work have been obtained applying the SC-HMO procedure of Kakitani et al.[33] with $\omega = 1$. The parameters for the methyl and the methylene group Me and the transanular[34] and through-bond resonance integrals were given in Reference 17. Furthermore the following parameters are used: $\alpha_{C(\equiv N)} = —7.43$ eV, $\alpha_{N(\equiv C)} = —8.46$ eV (both were determined so as to obtain a single regression line between reduction potentials and LUMO energies for nitriles and quinones, $\beta_{CS} = \beta_{CC}/2 = —1.475$ eV (chosen according to Reference 35), $\alpha_S = —8.9$ eV (was determined so as to reproduce the experimental ionization energy of TTF[27]).

With the chosen parametrization we obtain the following regression lines between experimental first reduction potential R_1 or electron afinities E and LUMO energies ε_1 and between experimental ionization energies I and HOMO energies ε_h (R_1 in V, all other values in eV, correlation coefficient k):

$$(R_1 \pm 0.125) = —(2.316 \pm 0.114)\, \varepsilon_1 — (13.410 \pm 0.592) \quad (k = 0.988)$$

$$(E \pm 0.124) = —(1.480 \pm 0.059)\, \varepsilon_1 — (6.210 \pm 0.286) \quad (k = 0.998)$$

$$(I \pm 0.123) = —(1.317 \pm 0.082)\, \varepsilon_h — (2.942 \pm 0.683) \quad (k = 0.988)$$

All experimental and calculated values are given in Table III.

TABLE III

Experimental First Reduction Potentials R_1*, Ionization Energies* I*, Electron Affinities* E*, and Calculated HOMO and LUMO Energies* ε_h *and* ε_l *of Some Conjugated Compounds* (R_1 *in* V, All Other Values in eV)

Compound	R_1[a]	I	E	—ε_h	—ε_1
p-benzoquinone	—0.810[b]		1.8[g]		5.430
duroquinone	—1.150[b]				5.302
2,5-dimethyl-1,4-benzoquinone	—0.970[b]				5.362
2,6-dimethyl-1,4-benzoquinone	—0.970[b]				5.362
cyanobenzene	—2.74[c]				4.607
1,2-dicyanobenzene	—2.12[c]				4.954
1,3-dicyanobenzene	—2.17[c]				4.727
1,4-dicyanobenzene	—1.97[c]				5.001
1,2,4,5-tetracyanobenzene	—1.02[c]				5.332
1,4-dicyano-2,5-dimethylbenzene	—2.011[b]				4.969
1,2,4,5-tetracyano-3,6-dimethylbenzene	—1.055[b]				5.319
2,3-dicyano-1,4-benzoquinone	+0.010[b]				5.780
benzene		9.24[d]	—1.14[g]	9.24	3.36
naphthalene		8.12[d]	—0.20[g]	8.45	4.15
anthracene		7.40[d]		7.91	
naphthacene		7.00[d]		7.56	
hexamethylbenzene		7.95[d]		8.42	
aniline		8.04[e]		8.25	
p-phenylenediamine		7.3[f]		7.69	
phenol		8.74[e]		8.78	
7,7,8,8-tetracyanoquinodimethane (TCNQ)			2.8[g]		6.05

[a] In acetonitrile vs. Ag/Ag$^+$. [b] T. Geiger, *Thesis (University of Heidelberg)*, 1978. [c] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.* 85 (1963) 683—693. [d] G. Briegleb and J. Czekalla, *Angew. Chem.* 72 (1960) 401—413. [e] I. Danihel and J. Kuthan, *Collect. Czech. Chem. Commun.* 44 (1979) 873—883. [f] D. G. Streets, W. E. Hall, and G. P. Ceasar, *Chem. Phys. Lett.* 17 (1972) 90—94. [g] J. M. Younkin, L. J. Smith, and R. N. Compton, *Theor. Chim. Acta* 41 (1976) 157—176.

The electron interaction integrals γ and $C = J_{hh}^{DD} + J_{ll}^{AA} - 2\gamma$ are calculated using the Hückel orbitals, the one-center repulsion integrals of Reference 36, and the Ohno-Klopman (OK) formula[37] for the two-center repulsion integrals. The Nishimoto-Mataga (NM) formula[38] would yield far too small γ values but we do not know which of the two formula is appropriate for the calculation of $J_{hh}^{DD} + J_{ll}^{AA}$. Therefore we give two extremal values for C obtained either with the OK formula for all integrals or the NM formula only for $J_{hh}^{DD} + J_{ll}^{AA}$.

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REFERENCES AND NOTES

TABLE III

Experimental First Reduction Potentials R_1, *Ionization Energies* I, *Electron Affinities* E, *and Calculated HOMO and LUMO Energies* ε_h *and* ε_l *of Some Conjugated Compounds* (R_1 *in* V, All Other Values in eV)

Compound	R_1^{a}	I	E	$-\varepsilon_h$	$-\varepsilon_l$
p-benzoquinone	-0.810^{b}		1.8^{g}		5.430
duroquinone	-1.150^{b}				5.302
2,5-dimethyl-1,4-benzoquinone	-0.970^{b}				5.362
2,6-dimethyl-1,4-benzoquinone	-0.970^{b}				5.362
cyanobenzene	-2.74^{c}				4.607
1,2-dicyanobenzene	-2.12^{c}				4.954
1,3-dicyanobenzene	-2.17^{c}				4.727
1,4-dicyanobenzene	-1.97^{c}				5.001
1,2,4,5-tetracyanobenzene	-1.02^{c}				5.332
1,4-dicyano-2,5-dimethylbenzene	-2.011^{b}				4.969
1,2,4,5-tetracyano-3,6-dimethylbenzene	-1.055^{b}				5.319
2,3-dicyano-1,4-benzoquinone	$+0.010^{b}$				5.780
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naphthalene		8.12^{d}	-0.20^{g}	8.45	4.15
anthracene		7.40^{d}		7.91	
naphthacene		7.00^{d}		7.56	
hexamethylbenzene		7.95^{d}		8.42	
aniline		8.04^{e}		8.25	
p-phenylenediamine		7.3^{f}		7.69	
phenol		8.74^{e}		8.78	
7,7,8,8-tetracyanoquinodimethane (TCNQ)			2.8^{g}		6.05

[a] In acetonitrile vs. Ag/Ag^{+}. [b] T. Geiger, *Thesis (University of Heidelberg)*, 1978. [c] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.* 85 (1963) 683—693. [d] G. Briegleb and J. Czekalla, *Angew. Chem.* 72 (1960) 401—413. [e] I. Danihel and J. Kuthan, *Collect. Czech. Chem. Commun.* 44 (1979) 873—883. [f] D. G. Streets, W. E. Hall, and G. P. Ceasar, *Chem. Phys. Lett.* 17 (1972) 90—94. [g] J. M. Younkin, L. J. Smith, and R. N. Compton, *Theor. Chim. Acta* 41 (1976) 157—176.

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SAŽETAK

O postojanju biradikal-ionskih stanja donor-akceptor ciklofana. Jednostavna MO-teorijska studija

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Apsorpcija najveće valne duljine u UV-VID spektrima donor-akceptor ciklofana odgovara pobuđenju od donora D prema akceptoru A s prijelazom jednog elektrona, tj. $DA \xrightarrow{h\nu} D^{+}A^{-}$. Veličina elektronskog prijelaza trebala bi postati veća s povećanjem donorsko-akceptorske moći već u osnovnom stanju. Za kombinacije donor-akceptor s dovoljnom malom razlikom između ionizacijske energije (I_D) donora i elektronskog afiniteta (E_A) akceptora očekuje se biradikal-ionsko osnovno stanje $D^{+q} A^{-q}$ s velikim q, npr. $q > 1/2$. U ovom radu istražuje se osnovno stanje i najniža pobuđena singletna i tripletna stanja donor-akceptor ciklofana unutar semiempirijskog modela konfiguracijskih interakcija s četiri orbitale. Procijenjena je ovisnost energija i veličina elektronskog prijelaza u tim stanjima o molekularnim parametrima donora i akceptora i o njihovu međusobnom geometrijskom rasporedu. Naš model dovodi do jednostavnog aproksimativnog uvjeta $V^{\text{eff}} \leqq 0$ za pojavu biradikal-ionskog osnovnog stanja. V^{eff} je mjera efektivne donorsko-akceptorske moći koja ne ovisi samo o razlici $I_D - E_A$ nego i o coulombskom odbijanju elektrona u D i elektrona u A te o stabilizirajućem efektu otapala. Simetrije graničnih orbitala, tj. najviše popunjene molekulske orbitale donora i najniže nepopunjene molekulske orbitale akceptora, određuju da li će biradikal-ionsko osnovno stanje biti tripletno ili singletno. Prema našemu jednostavnom modelu tripletno biradikal-ionsko osnovno stanje javit će se ako granične orbitale pripadaju različitim reprezentacijama točkine grupe fana. Prijelaz iz običnog osnovnog stanja u biradikal-ionsko osnovno stanje, bez znatnijeg elektronskog prijelaza iz D U A, jest diskontinuiran. Taj je prijelaz, međutim, kontinuiran ako granične orbitale pripadaju istoj reprezentaciji, iako se veličina elektronskog prijelaza q znatno mijenja samo u uskom intervalu V^{eff} čija je širina određena iznosom transanularne interakcije i interakcije kroz vezu između graničnih orbitala. Konačno, razmotrili smo kako odabrati donor i akceptor u ciklofanu u svrhu ispunjenja uvjeta za biradikal-ionsko osnovno stanje.