

## Donor-Acceptor Cyclophanes with Biradical-Ionic Ground States

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Certain donor-acceptor (DA) cyclophanes are proposed which should be characterized by a biradical-ionic ground state  $D^{+q}A^{-q}$  with an electron transfer  $q > 1/2$  from the donor D to the acceptor A.

### INTRODUCTION

In donor-acceptor cyclophanes DA one expects an electron transfer from the donor D to the acceptor A already in the ground state, *i.e.*  $DA \rightarrow D^+A^-$ , if the DA distance and the difference between the ionization energy  $I_D$  of D and the electron affinity  $E_A$  of A are small enough. We shall use the term *biradical-ionic*<sup>1,2</sup> (*bi*) for a state which can be symbolized as  $D^{+q}A^{-q}$  with  $q > 1/2$ . Whereas *bi* ground states have been evidenced for many crystalline DA complexes<sup>3</sup> or solutions of strong donors and acceptors in highly polar solvents,<sup>4-6</sup> this does not apply to DA cyclophanes. Even for the cyclophanes *1a* and *1b* (cf. Figure 1) with the D/A pair TMPD (N,N,N',N'-tetramethyl-*p*-phenylenediamin)/*p*-benzoquinone a *bi* ground state could be excluded due to spectroscopic investigations.<sup>7</sup>

Clearly a *bi* ground state should become more likely for cyclophanes with D/A combinations characterized by smaller  $I_D - E_A$  values. Within a simple configuration interaction scheme we could derive<sup>2</sup> the following approximate criterion for the occurrence of a *bi* ground state of a DA system:

$$V^{\text{eff}} = I_D - E_A - \gamma - \delta < 0. \quad (1)$$

Eq. (1) is valid only if the overlap between the basis functions in D and those in A is small enough,<sup>8</sup> which is the case in cyclophanes where mean DA separations  $\geq 263$  pm (value for superphane<sup>9</sup>) are encountered.  $V^{\text{eff}}$  is a measure of the effective DA strength which does not only depend on  $I_D - E_A$  but also on the Coulomb repulsion  $\gamma$  between two electrons confined to D and A and the stabilization  $\delta$  due to the solvent as well. A small  $V^{\text{eff}}$  demands: (*i*) a small  $I_D - E_A$  difference which can be attained by

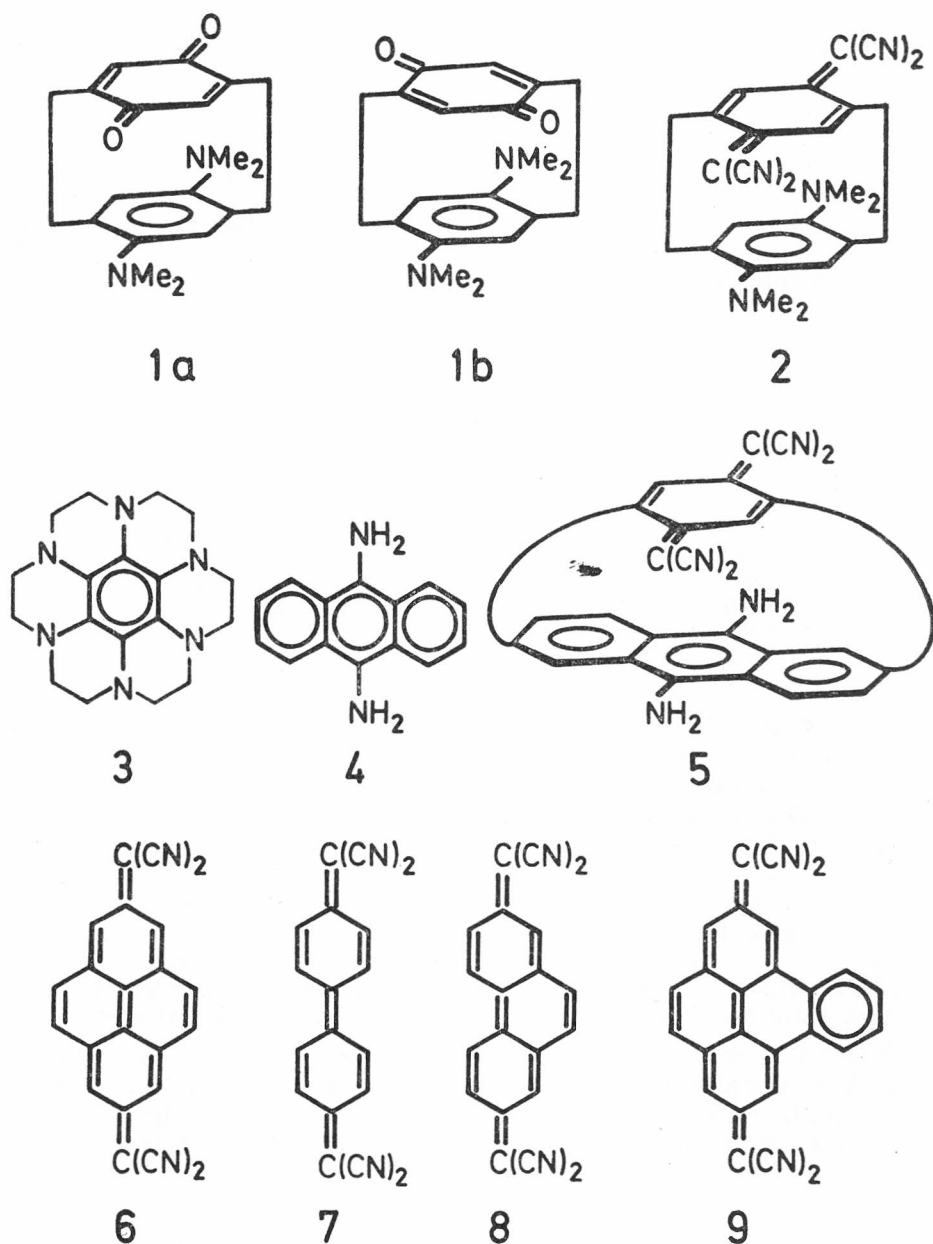


Figure 1. Survey of compounds under study.

choosing the appropriate D/A pair, (ii) a large  $\gamma$  thus demanding a small DA separation, and (iii) a large  $\delta$ . In highly polar solvents, *e.g.* acetonitrile,  $\delta$  is estimated<sup>2</sup> to be in the order of 0.5 eV in systems like 1 but will be smaller if more extended donors and acceptors are chosen. The parameter

$\gamma$  can be calculated simply by a Hückel procedure<sup>2,10</sup> as well as  $I_D$  and  $E_A$  if experimental values are unknown.

## RESULTS AND DISCUSSION

Applying criterion (1) it becomes evident why *1a* and *1b* do not exhibit *bi* ground states since  $I_D - E_A = 4.9$  eV<sup>11</sup> and  $\gamma = 3.8$  (*1a*) or 3.7 eV (*1b*) so that  $V^{\text{eff}} \geq 0.6$  eV. Replacing *p*-benzoquinone by the better acceptor TCNQ (7,7,8,8-tetracyanoquinodimethane) yields  $I_D - E_A = 3.9$  eV<sup>11</sup> and  $\gamma = 3.4$  eV so that  $V^{\text{eff}} \cong 0$  and a *bi* ground state for the yet unknown cyclophane *2* would be predicted. However, we could show<sup>2</sup> that the effective  $I_D$  of TMPD in such a phane is considerably enhanced since the conjugation between the NMe<sub>2</sub> groups and the benzene ring is reduced due to steric hindrance caused by the methylene bridges. Therefore a *bi* ground state for *2* will most probably not be realized. Obviously one has to look for stronger D/A pairs since significantly larger  $\gamma$  values are unlikely. Although  $I_D$  ( $E_A$ ) can be lowered (increased) by introducing electron donating (withdrawing) substituents, this is usually not feasible in cyclophanes due to the bridges connecting donor and acceptor.

The search for organic metals lead to the preparation of new donors, most of them are sulphur and selenium heterocycles, but they do not exhibit significantly better donor strength than TMPD. Breslow<sup>12</sup> suggested *3* as a potential strong donor and indeed we calculate  $I_D \cong 6.5$  eV.<sup>13</sup> Whereas *3* will surely present some obstacles in its synthesis, 9,10-diaminoanthracene *4* is known<sup>14</sup> and should present a comparable strong donor with  $I_D \cong 6.3$  eV. For a DA cyclophane *5* with the D/A pair *4*/TCNQ and a (mean) DA separation of 300 pm we calculate  $I_D - E_A - \gamma = 0.3$  eV, see Table I. Therefore  $V^{\text{eff}} \leq 0$  and consequently this system should be characterized by a *bi* ground state. For larger DA distances  $\gamma$  will be smaller and hence the occurrence of a *bi* ground state becomes less likely.

TABLE I

Calculated  $E_A$ ,  $I_D - E_A$ ,  $\gamma$ , and  $I_D - E_A - \gamma$  Values for the DA Systems Containing *4* as Donor and TCNQ or *6* — *9* as Acceptor. The DA Separation was Fixed as 300 pm and D and A are Arranged as in *5* (cf. Figure 1). All Values are Given in Units of eV.

A	$E_A$	$I_D - E_A$	$\gamma$	$I_D - E_A - \gamma$
TCNQ	2.8 <sup>a</sup>	3.5	3.2	0.3
<i>6</i>	3.4	2.9	2.8	0.0
<i>7</i>	3.2	3.1	2.9	0.2
<i>8</i>	3.3	3.0	2.9	0.0
<i>9</i>	3.4	2.9	2.8	0.1

<sup>a</sup> Agrees with the experimental value.<sup>9</sup>

In order to obtain acceptors which are superior to TCNQ it was suggested<sup>15</sup> to extend the conjugated framework. Examples for some large acceptors are displayed in Figure 1. So far only *6* (TCNP)<sup>16</sup> and a bridged analog of *7* (TCNDQ)<sup>17</sup> have been synthesized. According to our calculations the electron affinities  $E_A$  of *6* — *9* are indeed higher by 0.4 — 0.6 eV than that of TCNQ, see Table I. The lowest virtual orbital of *9* is loca-

lized by 98.5% in the phenanthrene subunit and agrees closely with that of 8. Thus 9 can be considered as a model for 8 with respect to the acceptor property. This is further corroborated by the similar  $E_A$  values.

The enhanced  $E_A$  values lead to a decrease of  $I_D - E_A$  which is, however, counterbalanced for the most part by a decrease of  $\gamma$  (and possibly also by that of  $\delta$ ) due to the extension of the conjugated system. Consequently the resulting  $V^{\text{eff}}$  values are not significantly smaller than that obtained for the system 5. A mutual orientation of D and A different from that assumed in 5 results in a slightly smaller  $\gamma$  value, however, the reduction is never greater than 0.1 eV with all studied compounds. The replacement of the donor 4 by TMPD would increase  $V^{\text{eff}}$  by at least 0.8 eV. Therefore a *bi* ground state will be realized most probably only with 4 as donor and TCNQ or 6—9 as acceptor and if D and A can be brought into close enough contact, say 300 to 320 pm.

In all these systems the highest occupied orbital of the donor and the lowest virtual orbital of the acceptor belong to the same irreducible representation of the point group of the whole DA system (unless A is rotated by 90° with respect to the orientation given in 5). Thus one would expect a singlet ground state which could be symbolized as  ${}^1\Psi = a {}^1\Psi(D,A) + b {}^1\Psi(D^+ - A^-)$  with  $b^2 > a^2$ .  ${}^1\Psi(D,A)$  and  ${}^1\Psi(D^+ - A^-)$  stand for the no-bond and the dative singlet functions using Mulliken's notion.<sup>5</sup> However, a precise prediction of the electronic structure of the *bi* ground state could only be given by using highly sophisticated theoretical approaches which are hardly feasible with the extended systems studied here.<sup>18</sup>

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#### SAŽETAK

#### Donor-akceptorski ciklofani s biradikalsko-ionskim osnovnim stanjima

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U donorsko-akceptorskih ciklofana (DA) dolazi do transfera elektrona s donora D na akceptor A, pa se osnovno stanje takvih molekularnih sustava označuje s  $D^+A^-$ . Da bi se to ostvarilo, mora udaljenost između fragmenata D i A varirati u određenim granicama, a razlika između ionizacijskog potencijala  $I_D$  i elektronskog afiniteta  $E_A$  mora biti mala. U ovom radu predloženo je da se sustavi  $D^{+q}A^{-q}$  ( $q > 1/2$ ) nazovu biradikalsko-ionskima. Potanko su razmotreni uvjeti za realizaciju biradikalsko-ionskih osnovnih stanja DA-ciklofana.