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### A R T I C L E S

# Charge Separation in Ground-State 1,2,4,5-Tetra-Substituted Benzene Derivatives

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***Abstract:*** The conditions required for a formal biradical to exist in a zwitterionic form in the ground state are discussed following the recent experimental observation[1] of zwitterionic structure in the ground state of a quinoid molecule (di-*tert*-butyl derivative of 2,5-diamino-1,4-benzoquinonediimine, I). A unique characteristic of molecules of this class is the fact that they may be considered as being formed by the union of two radicals, each having an odd number of $\pi$ electrons. In the case of I, one fragment carries the two amino group having 7 $\pi$ electrons; it acts as the electron donor. The other fragment carries the two oxygen atoms (carrying 5 $\pi$ electrons) and acts as an electron acceptor. A model that predicts the properties of these systems is presented, based on previous work on non-Kekule hydrocarbons[2,3] and on the electron donating and attracting properties of the donor and acceptor groups, respectively. The zwitterion is formed by an electron transfer leading to two subunits carrying 6 $\pi$ electrons each and may become more stable than the triplet biradical even in the gas phase (i.e., in the absence of an external field) if the ionization potential of the donor is small (of the order of 3−4 eV). In some cases solvation in a polar solvent is required to make the zwitterionic form the lowest energy species on the ground-state surface. The 'spacer' between the donor and acceptor groups (which need not be necessarily derived from an aromatic structure) can be varied and influences the overall dipole moment that is calculated in some cases to be quite large (over 20 D in the gas phase).
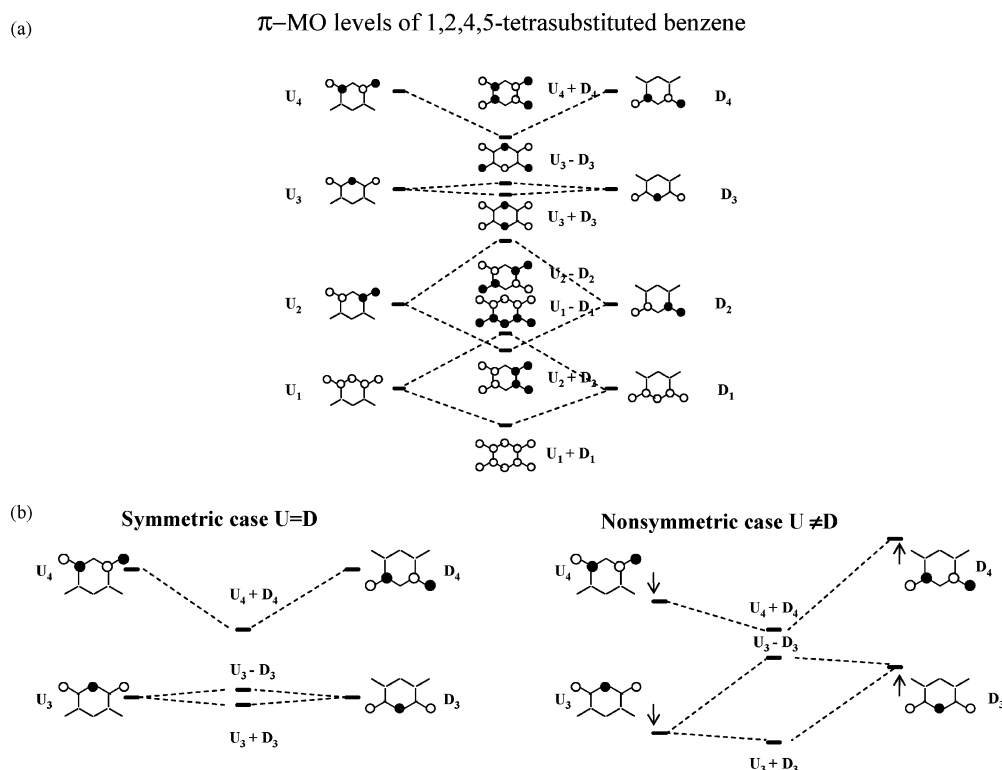
## I. Introduction

The recent experimental observation[1] of zwitterionic structure in a quinoid molecule (di-*tert*-butyl derivative of 2,5-diamino-1,4-benzoquinonediimine, I, see Figure 1 for structure), is an unprecedented synthetic accomplishment that attracted considerable theoretical interest.[4−6] In this paper, we show that the properties of these molecules can be understood in terms of a model used by Borden and Davidson to predict the properties of non-Kekulé hydrocarbons.[2,3] Several quantum chemical calculations on the model molecule Ia were shown to reproduce the salient properties of this molecule, especially the large dipole moment. Sawicka et al.[4] used second-order Moeller−Plesset theory with a large basis set to show that the zwitterionic isomer of the quinoid species is indeed the lowest energy isomer in the gas phase. All canonical tautomers were found to lie at higher energies, and to be separated from the zwitterion isomer by a relatively high barrier. Le et al.[5] using HF, CASSCF, and DFT methods showed that the molecule can be considered as consisting of two separately subunits in which the $\pi$ electrons are delocalized: a positively charged N−C−C(H)−C−N
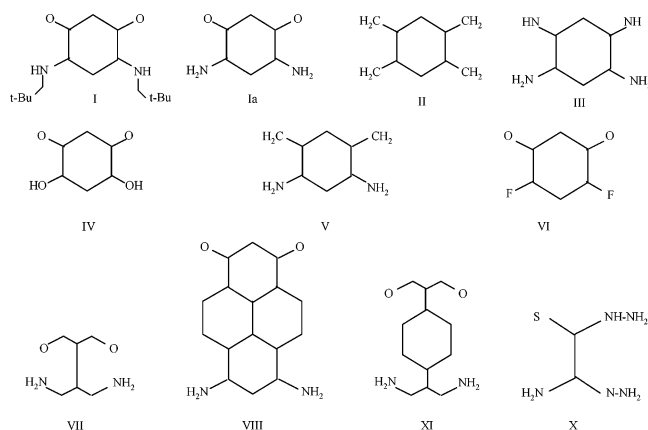


**Figure 1.** Structures of molecules discussed in the paper. Only the sigma structure of the ring is shown, as the detailed pi structure varies between different molecules. The detailed structure is further discussed in Sections II, VI, and VII.

subunit, connected by two single C−C bonds to a negatively charged O−C−C(H)−C−O subunit. The division into two separated subunits containing 6 $\pi$ electrons each was confirmed by Braunstein et al.[6] using DFT calculations; the calculated dipole moment of I was found to be 10.0 D, in very good agreement with the measured value (9.7 D in dichloromethane). The authors pointed out the similarity to other heterocyclic molecules having a zwitterionic ground state.[7,8] The DFT calculation showed that the lowest triplet state was considerably

(1) Siri, O.; Braunstein, P. *Chem. Commun.* **2002**, 208.
(2) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.
(3) Borden, W. T.; *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195.
(4) Sawicka, A.; Skurski, P.; Simons, J. *Chem. Phys. Lett.* **2002**, *362*, 527.
(5) Le, H. T.; Nam, P. C.; Dao, Y. L.; Veszpremi, T.; Nguyen, M. T. *Mol. Phys.* **2003**, *101*, 2347; Delaere, D.; Nam, P. C.; Nguyen, M. T. *Chem. Phys. Lett.* **2003**, *382*, 349.
(6) Braunstein, P.; Siri, O.; Taquet, J.-P.; Rohmer, M.-M.; Benard, M.; Welter, R. *J. Am. Chem. Soc.* **2003**, *125*, 12 246.

(a)

π–MO levels of 1,2,4,5-tetrasubstituted benzene



(b)

**Symmetric case U=D**                    **Nonsymmetric case U ≠D**



**Figure 2.** Construction of the $\pi$ MOs of TMB and substituted analogues from two pentadienyl radicals. (a) The seven lowest energy $\pi$ orbitals of TMB (two identical radicals). (b) The three highest occupied $\pi$ MOs. Left: in the symmetric case, as in (a). Right: Two radicals having different substituents.

higher in energy than the singlet zwitterion and had also a delocalized $\pi$ character.

However, none of these papers presented a physical model that can predict whether a given molecule that is formally a biradical will assume a zwitterionic ground state character or not. I is formally derived from an aromatic structure, but the question whether an aromatic framework is necessary (or relevant) was not addressed, although an antiaromatic character was considered due to the fact that it carries 12 electrons.[6,8] In this work, we propose a simple model that underlines the essential features of the system and accounts for the observed effects. Several systems in which the union of two radicals leads to zwitterionic species are considered, and it is shown that charge separation in the ground state molecule is expected when the ionization potential of the donor radical is low enough and the electron affinity of the acceptor relatively high. The model, which allows the prediction of several ground-state charge separated systems, is backed up by ab initio calculations.

## II. MO Analysis of 1,2,4,5-Tetra-Substituted Benzenes

I is related to 1,2,4,5-tetramethylenebenzene (TMB) (II) and thus belongs to a class of aromatic molecules known as non-Kekule hydrocarbons, molecules for which no classical Kekule structures can be written.[3,9] TMB and similar systems (such as the much more extensively studied 1,3 benzo-quinodimethane, Schlenk's biradical,) have a biradical ground state.[2,10,11] This 10 $\pi$-electrons system was shown to have a singlet ground state in apparent violation of Hund's rule.[11] We use this system as a convenient starting point for the analysis of the electronic struc-ture of molecule I and its analogues—based on the earlier classi-fication of Borden.[3] Three types of $\pi$ MOs can be distinguished in a non-Kekule hydrocarbons:[2,9] Bonding MOs (BMOs), non-bonding ones (NBMOs) and antibonding (ABMOs). NBMOs

are characterized by the absence of electron overlap between neighboring atoms. Substituents that add an even number ($2k$) of electrons to the $\pi$-system modify the basic $\pi$-electron distribution of the parent benzene ring. The degeneracy of the two HOMOs of benzene is removed, and $k$ more orbitals are occupied. As previously discussed,[2,3] the two highest lying occupied MOs are typically nonbonding; two configurations contribute approximately equally to the ground-state wave function, and the system has a biradical character.

It is instructive to express the electronic structure of TMB in terms of the correlation diagram shown in Figure 2. The molecular orbitals of the system are constructed from the MOs of two pentadienyl radicals, containing 5 $\pi$ electrons each. The $\pi$ orbitals are added to the sigma electronic frame of TMB which provides the basic binding scheme for the six-membered ring. We label the 'up-side' radical as U and the 'down-side' one as D; the four lowest-lying MOs of these radicals are termed $U_1$ through $U_4$ and $D_1$ thorough $D_4$, respectively. In terms of the binding of the $CH_2$ radicals to the ring, orbitals 1 and 2 are bonding, 3 nonbonding and 4 is antibonding. The shapes and relative energies of the lowest $\pi$ orbitals of the combined molecule are depicted. The lowest four are bonding (with respect to the four substituents), the two next ones (formed by the in-phase and out-of-phase combinations of $U_3$ and $D_3$) are NBMOs and the seventh is an ABMO.

(7) Beer, L.; Oakley, R. T.; Mingie, J. R.; Preuss, K. E.; Taylor, N. J. *J. Am. Chem. Soc.* **2000**, *122*, 7602; Beer, L.; Brusso, J. L.; Cordes, A. W.; Haddon, R. C.; Itkis, M. E.; Kirschbaum, K.; McGregor, D. S.; Oakley, R. T.; Pinkertonm, A. A.; Reed, R. W. *J. Am. Chem. Soc.* **2002**, *124*, 9498.
(8) Hutchison, K.; Srdanov, G.; Hicks, R.; Yu, H.; Wudl, F.; Strassner, T.; Nendel, M.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 2989.
(9) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 24.
(10) Hrovat, D. A.; Murcko, M. A.; Lahti, P. M.; Borden, W. T. *J. Chem. Soc. Perkin Trans.* **1998**, *2*, 1037.
(11) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 6327.

The case of TMB, in which 10 $\pi$ electrons are fed into these orbitals was studied by Hrovat and Borden et al.,[11] who showed that the singlet state has a lower energy than the triplet (Hund's rule is violated). Anticipating the discussion of the electronic structure of I, we briefly summarize the salient properties of TMB as revealed by Figure 2a. The order of the seven MOs shown in the figure can be predicted based on the number of nodes which increases continuously from $U_1 + D_1$ to $U_4 + D_4$. The special properties of TMB are due to the two NBMOs, which may be chosen so that they are disjoint.[11] These combined orbitals $U_3 + D_3$ and $U_3 - D_3$ are not degenerate by symmetry, but have almost the same energies, as there is no $\pi$ electron density on the atoms connecting the two fragments in both orbitals. The electronic structure of the 10 $\pi$ electrons TMB, formally an aromatic molecule, in fact decomposes to two separated 5 $\pi$ electron units. Indeed, calculation shows that the C1$-$C2 and C4$-$C5 bonds are relatively long in the ground state of TMB$-$an antiquinoid structure. As shown by Borden et al.[11] the $S_0$ state of this system can be constructed as the out-of-phase combinations of two closed shell configurations $|(D_1 + U_1)^2(D_2 + U_2)^2(D_1 - U_1)^2(D_2 - U_2)^2(D_3 + U_3)^2> - |(D_1 + U_1)^2(D_2 + U_2)^2(D_1 - U_1)^2(D_2 - U_2)^2(D_3 - U_3)^2 >$ (abbreviated as $|...(D_3 + U_3)^2> - |...(D_3 - U_3)^2>$). The configuration of the lowest triplet state is an open shell one $|...(D_3 + U_3)^1(D_3 - U_3)^1(\alpha\beta + \beta\alpha)>$.

We now extend the model to the dianion of TMB which carries 12 $\pi$ electrons, same as molecule I. If the energy of the ABMO is higher than that of both NBMOs, all lowest six orbitals, including the two NBMOs are doubly occupied and a singlet state is expected to be the ground state$-$in this case represented by a single closed shell configuration as $|...(D_3 + U_3)^2(D_3 - U_3)^2 >$. By these arguments, this 12 $\pi$-electrons dianion is expected to have a singlet ground state, with the lowest triplet lying at a relatively high energy. The VB description of dianion of TMB is very similar to neutral TMB$-$two separated pentadienyl units carrying 6 $\pi$ electrons each. The molecule has no aromatic or antiaromatic character: it will have an anti-quinoid structure$-$elongated C1$-$C2 and C4$-$C5 bonds as in TMB.

Let us consider now the case in which the two bonded fragments are nonequivalent; for instance, assume that the MOs of the U radical have a lower energy than those of the D radical. Figure 2b shows how this affects the two NBMOs: the energy of $D_3 + U_3$ is lowered, it has mostly $U_3$ character and that of $D_3 - U_3$ is increased. Assuming that the energy of the ABMO is not changed (compared to TMB dianion) it may be close to that of the out-of-phase NBMO. In this case a triplet state may have a lower energy than the singlet and become the ground electronic state. Thus, if the energy ordering is $\epsilon(D_3 + U_3) < \epsilon(D_3 - U_3) \approx \epsilon(D_4 + U_4)$, two configurations are expected to have similar energies:

A singlet: $c_1\{(D_1 + U_1)^2(D_2 + U_2)^2(D_1 - U_1)^2(D_2 - U_2)^2(D_3 + U_3)^2(D_3 - U_3)^2\} - c_2\{(D_1 + U_1)^2(D_2 + U_2)^2(D_1 - U_1)^2(D_2 - U_2)^2(D_3 + U_3)^2(D_4 + U_4)^2\}$

And a triplet: $(D_1 + U_1)^2(D_2 + U_2)^2(D_1 - U_1)^2(D_2 - U_2)^2(D_3 + U_3)^2(D_3 - U_3)^1(D_4 + U_4)^1$

## III. Heteroatoms Added$-$Which is More Stable, Biradical or Zwitterion? A Basic Model

Replacing the two 'upper' $CH_2$ groups by oxygen atoms, and the two 'lower' ones by $NH_2$ moieties, leads to a nonsymmetric case as described above: the MOs of the oxygen-substituted biradical have lower energies than those of the amino-substituted one (due to of the difference in electronegativity). In addition, a nonsymmetric electron distribution is obtained: there are now 5 $\pi$ electrons in the 'upper' part and 7 in the 'lower' one.

Accepting the partition of Ia to two $\pi$-electron systems an excess of negative charge appears on the nitrogen side and a deficiency on the oxygen side. The unbalanced charge distribution creates a metastable situation which may be relieved by transferring an electron to the oxygen side, thereby creating a zwitterionic state. A simple electrostatic model brings to light the essential physics of the system. Consider two weakly coupled neutral radicals A and D. The energy required to transfer an electron from D to A in a vacuum is

$$\Delta E = -E_{coul} + IP_B - EA_A \tag{1}$$

where $R$ is the distance between the two species, $-E_{coul} = e^2/R$ is the Coulomb attraction between the opposite charges, $IP_D$ is the ionization potential of species D and $EA_A$ is the electron affinity of A. If $\Delta E$ is negative the system will have a zwitterionic singlet ground state.

Assuming that the energy of the triplet state is equal to that of the two separated radicals, the zwitterion form will be isoenergetic with the triplet form if the Coulomb attraction will compensate for the energy invested in ionizing the donor minus the energy gained by attaching the electron to the acceptor:

$$E_{coul} = IP_B - EA_A$$

A rough numerical estimate may be made assuming that the two systems are separated by 6 Bohr radii ($r_B$) as in Ia, and that the about 0.7 of an elementary charge unit is transferred (to obtain the measured dipole moment of 9.7 D): the Coulomb attraction energy is (in atomic units) $E = (0.7e)^2/6r_B = 1/12H \approx 2.2$ eV. Since the electron affinity of radicals is small ($\sim$1 eV), this value means that a zwitterion will be of lower energy than the biradical only if the ionization potential of the donor is quite small, of the order of 3$-$4 eV. This prediction severely restricts the possible suitable donor candidates, and is borne out by more detailed calculations.
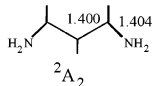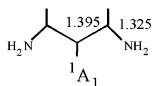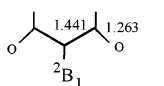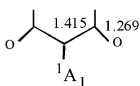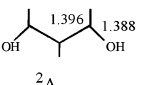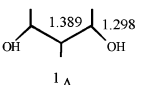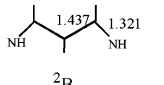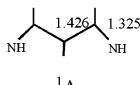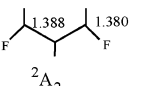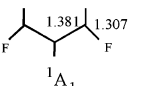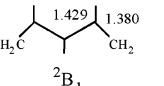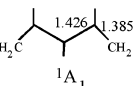
## IV. Computational Details

All calculations were performed using the CASSCF method[12] with a full $\pi$ active space, except VII and IX. In all cases, a complete vibrational analysis was performed at the optimized geometry to verify that it represented a local minimum on the potential surface. To include the effects of additional electron correlation, CASSCF-MP2 calculations were performed at the optimized points. The solvent effect was simulated by a crude electrostatic model for a dipole in a polarizable medium, since we were interested in the gross features rather than fine details. The interaction was introduced as perturbation to the gas-phase Hamiltonian (SCRF[13]). The perturbation Hamiltonian was taken

(12) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.
(13) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. T. *J. Am. Chem. Soc.* **1991**, *113*, 4776.

**Table 1.** Properties of Some Donor and Acceptor Radicals

| Donors | | | Acceptors | | |
|---|---|---|---|---|---|
| Radical/cation | D | D$^+$ | Radical/anion | A | A$^-$ |



|  | D$_N$ | | | A$_O$ | |
|---|---|---|---|---|---|
|  | 1.400 / 1.404 (H$_2$N ... NH$_2$) | 1.395 / 1.325 (H$_2$N ... NH$_2$) |  | 1.441 / 1.263 (O ... O) | 1.415 / 1.269 (O ... O) |
| Ground state | $^2A_2$ | $^1A_1$ | Ground state | $^2B_1$ | $^1A_1$ |
| E (H) | -226.49043 | -226.34872 | E (H) | -265.02286 | -265.06390 |
| IP (eV) | 3.86 | | EA (eV) | 1.12 | |

|  | D$_O$ | | | A$_N$ | |
|---|---|---|---|---|---|
|  | 1.396 / 1.388 (OH ... OH) | 1.389 / 1.298 (OH ... OH) |  | 1.437 / 1.321 (NH ... NH) | 1.426 / 1.325 (NH ... NH) |
| Ground state | $^2A_2$ | $^1A_1$ | Ground state | $^2B_1$ | $^1A_1$ |
| E (H) | -266.13510 | -265.92228 | E (H) | -225.33928 | -225.34596 |
| IP (eV) | 5.52 | | EA (eV) | 0.18 | |

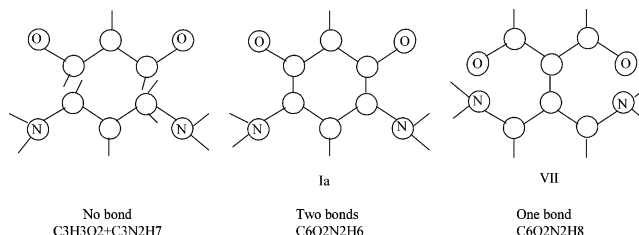|  | D$_F$ | | | A$_C$ | |
|---|---|---|---|---|---|
|  | 1.388 / 1.380 (F ... F) | 1.381 / 1.307 (F ... F) |  | 1.429 / 1.380 (H$_2$C ... CH$_2$) | 1.426 / 1.385 (H$_2$C ... CH$_2$) |
| Ground state | $^2A_2$ | $^1A_1$ | Ground state | $^2B_1$ | $^1A_1$ |
| E (H) | -314.86231 | -314.15526 | E (H) | -193.36037 | -193.32101 |
| IP (eV) | 7.97 | | EA (eV) | -1.07 | |

according to simple Kirkwood-Önsager [14,15] spherical cavity theory. The solute−solvent interaction is completely defined in this approximation by three parameters: solute dipole, dielectric constant of the solvent, and the cavity radius. Only two of these parameters are free as the solute dipole moment is estimated as the derivative of the energy expectation value according to reaction electric field. The solvent dielectric constants were taken from CRC Handbook and the Onsager radius was taken as 4.15 Å for I, III, and IV and 4.74 Å for VIII.

All computations were carried out using the GAMESS program suite.[16]

## V. Build-Up of Molecules from Two Radicals

The basic model suggests that the properties of the molecules may be predicted from those of the two radicals of which they are composed. Each radical is held together by a sigma-bonded structure, to which the $\pi$ electrons are added. According to the basic model, the exact nature of the bonding between the two subsystems is immaterial. They could be bound by a single bond, by a different linking group or not at all (Figure 3).

Table 1 lists the calculated energies of some radicals that may serve as donor or acceptor groups, as well as the ionization potentials of the donor groups, and the electron affinities of the acceptor groups. The quantity IP(D) − EA(A) is listed in Table 2 for some pairs. The donor with the lowest IP is D$_N$ and the acceptor with the largest electron affinity is A$_O$. This pair forms

(14) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 3511.
(15) Onsager, L. T. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
(16) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

**Figure 3.** Scheme showing the two separated D$_N$ and A$_O$ radicals and the structure of two possible linked structures having a zwitterionic ground state.

**Table 2.** IP(D)−EA(A) for Some Donor−Acceptor Pairs (CASSCF(12,10)/DZV). CASSCF-MP2 Results Are Shown in Parentheses

| pair | IP(D)−EA(A) (eV) | predicted ground state for 3Å separation |
|---|---|---|
| D$_N$−A$_O$ | 2.74 (1.97) | zwitterion GS |
| D$_N$−A$_N$ | 3.68 (3.07) | zwitterion GS |
| D$_O$−A$_O$ | 4.40 (4.11) | zwitterion/biradical GS |
| D$_N$−A$_C$ | 4.93 (4.44) | biradical GS |
| D$_F$−A$_O$ | 6.85 (5.88) | biradical GS |

Ia when bonded by two parallel CC bonds (two-bond D$_N$−A$_O$). A different bonding that can be envisioned is with one bond, (single-bond D$_N$−A$_O$, VII). (Figure 3).
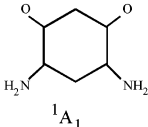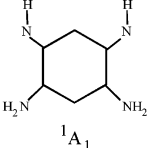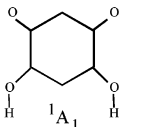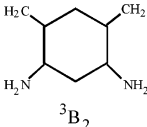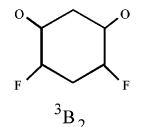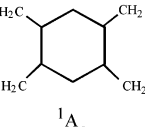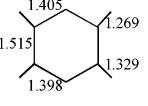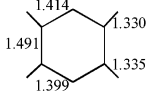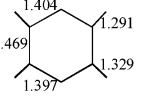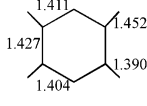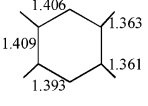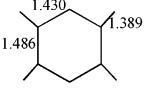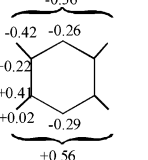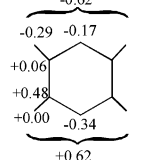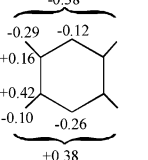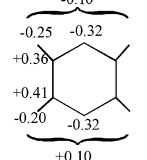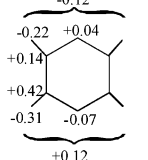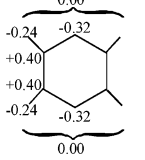
A model calculation was carried out also for the radical pair − D$_N$ and A$_O$ (or zwitterion pair D$_N^+$ and A$_O^-$) held at a coplanar configuration. At infinite separation, the triplet is favored by IP(D$_N$)−EA(A$_O$). The energies of the zwitterion and of the triplet radical pair at their respective optimum geometries are calculated to have about the same energy when their two components are separated by a normal van der Waals distance. Thus the Coulomb attraction term compensates in the case of

**Table 3.** Calculated Properties of S$_0$ of Some 12 $\pi$-electron Systems (CASSCF/DZV)[a]

| Molecule | Ia | III | IV | V | VI | II |
|---|---|---|---|---|---|---|
| Ground state | $^1A_1$ | $^1A_1$ | $^1A_1$ | $^3B_2$ | $^3B_2$ | $^1A_g$ |
| Leading configurations (coefficients) | I={2222220} II={2222202} $C_I$=0.87 $C_{II}$= -0.19 | I={2222220} II={2222202} $C_I$=0.92 $C_{II}$= -0.26 | I={2222220} II={2222202} $C_I$=0.82 $C_{II}$= -0.29 | I={2222220} II={2222202} $C_I$=0.72 $C_{II}$= -0.55 | I={2222220} II={2222202} $C_I$=0.43 $C_{II}$= -0.40 | I={222220} II={222202} $C_I$=0.65 $C_{II}$= -0.51 |
| $\mu$ (D) | 9.63 | 4.70 | 9.50 | 2.40 | 0.02 | 0 |

Geometry and charge structures shown for each molecule.

$^a$ The lowest energy electronic state ($^1A_1$ or $^3B_2$) of each species is also indicated (third row). The listed properties are from top to bottom: molecular structure ($C_{2v}$ symmetry, all molecules are planar); the symmetry of the ground electronic state; the leading configurations for the optimized singlet ground state ($\pi$ electrons only) and their calculated coefficients; the dipole moment (debye units); the geometry (Å units); the mulliken charge distribution (heavy atoms only). In the case of III and IV the calculated dipole moment depends of the conformation of the H atoms. The numbers shown refer to the conformation depicted.
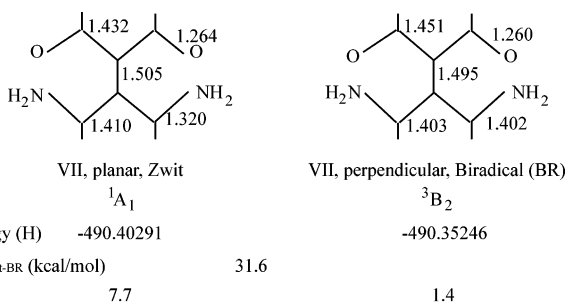


**Figure 4.** Structures, energies, and dipole moments of the lowest energy singlet and triplet states of VII calculated at the CASSCF(12/10)/DZV level.

**Table 4.** Energies (H) of Lowest Singlet and Triplet States (top line:CASSCF(12,10)DZV; Bottom Line: a Single Point Calculation at the Minimum of Each State Using MP2 Correction)

| molecule | $1^1A_1$ | $1^3B_2$ | $\Delta E$, kcal/mol | comments |
|---|---|---|---|---|
| Ia | −489.26796 | −489.25929 | 5.4 | |
|  | −490.12243 | −490.08870 | 21.2 | |
| II | −384.41899 | −384.41073 | 5.2 | 10e/10o |
|  | −385.13954 | −385.13231 | 4.5 | |
| III | −449.57455 | −449.57366 | 0.6 | |
|  | −450.41365 | −450.39190 | 13.6 | |
| IV | −528.81862 | −528.81441 | 2.6 | |
|  | −529.70255 | −529.70080 | 1.1 | |
| V | −417.55778 | −417.57531 | −11.0 | |
|  | −418.34718 | −418.35940 | −7.7 | |
| VI | −576.86596 | −576.89203 | −16.4 | |
|  | −577.68720 | −577.72189 | −21.8 | |

$D_N$ and $A_O$ for this factor. The properties of the single bonded $D_N$−$A_O$ molecule (VII) are displayed in Figure 4. The singly bonded molecule turns out to have a smaller dipole moment than Ia (the separation between the positive and negative parts is smaller) and a larger energy gap favoring the zwitterion state.

## VI. Properties of Ia and Some Related Compounds Constructed from Donor and Acceptor Radicals

To analyze the factors affecting the relative stability of the singlet and triplet, as well as the tendency to separate charges, we have calculated the properties of some analogues of Ia, in which the donor group NH$_2$ was replaced by the isoelectronic moieties OH and F, and the acceptor group O by the isoelectronic groups CH$_2$ and NH. The calculated dipole moments, geometries and charge distribution of the lowest singlet state of these 12-$\pi$ electron molecules that bear formal resemblance to Ia are summarized in Table 3 and the energies in Table 4,

along with the energies of T$_1$. The data for TMB (a 10-$\pi$ electron molecule) are shown for comparison.

Inspection of Table 3 reveals that molecules Ia, III, and IV have a singlet ground state with a relatively large dipole moment while V and VI have a triplet ground-state whose dipole moment is smaller. The energy differences between the lowest singlet and triplet states in a given molecule are not large at the CASSCF level except for V and VI. It is also seen that when the ground-state singlet is the zwitterion, a single configuration dominates the system, while if the triplet state is the ground state the lowest *singlet* has comparable contribution from two configurations. In the molecules having a triplet ground state the C1−C2 and C4−C5 bonds are significantly shorter than in the molecules having a singlet ground state.

These results are in agreement with the qualitative model of the previous Section. The data of Tables 3 and 4 indicate that
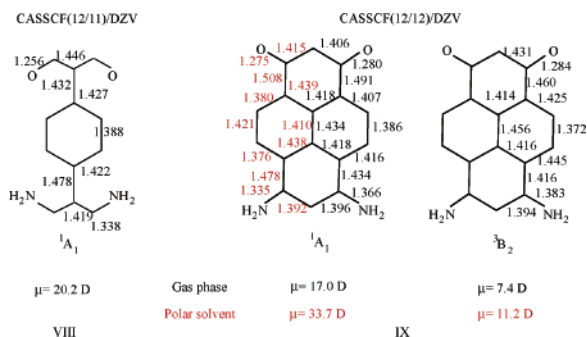
**Figure 5.** Structure and dipole moments of two 'extended' structures in which the donor D$_N$ is separated from the acceptor A$_O$ by a larger distance than in Ia. The data marked in red are results obtained in a polar solvent, discussed in the next section.

**Table 5.** CASSCF Results for the D$_N$–A$_O$ Pair with Different Spacers

| molecule | 1$^1$A$_1$ | 1$^3$B$_2$ | ΔE, kcal/mol | comments |
|---|---|---|---|---|
| VIII | −719.85719 | −719.85189 | 3.3 | CASSCF(12/11)/DZV |
| IX | −870.20718 | −870.22716 | −12.6 | CASSCF(12/12)/DZV |

a delicate balance between different factors determines the nature of the ground state of these 12 π-electron systems.

**Larger Systems.** It is of some interest to check whether a stable zwitterion state with a larger dipole moment can be designed. For this purpose, we inserted a spacer between the two radicals as shown in Figure 5. The calculations indicate that such species are indeed stable molecules. At the CASSCF level, the energy of the zwitterion is not necessarily lower than of the triplet biradical in the gas phase, but the very large dipole moment is expected to stabilize them in a crystal or in a polar solvent. Table 5 lists the results for VIII which may be considered as VII formed by inserting a benzene spacer and for IX which is an extended Ia 'stretched' by inserting a naphthalene spacer, converting it to a pyrene derivative

## VII. Discussion

The goal of this paper is to establish the main factors required for efficient charge separation in molecules having a formal biradical structure. In particular, it is intended to propose design parameters that will help in preparing molecules that have a zwitterionic ground state with a large dipole moment. A biradical formed by 1,2,4,5 substitution of benzene can be considered as being formed from the union of two pentadienyl radical fragments. The tendency to assume a zwitterion form in the ground state depends as we have seen on the ionization potential and electron affinities of the donor and acceptor fragments. Our CASSCF calculations show that for a molecule in which the donor radicals is D$_N$ and the acceptor A$_O$, the lowest singlet state is a zwitterion at *short inter-nuclear distance* in the gas phase. The charge-separated species is the lowest singlet state whether the two radicals are bound chemically or not; in other words the 12 electrons tend to rearrange so that each fragment carries six of them, rather than 7 and 5 as required to maintain charge neutrality in each fragment.

**VIIa. Design Considerations for a Charge-Separated System.** Inspection of Tables 3 and 4 shows that among the molecules shown in Figure 1, Ia appears to be the best choice for the purpose of a charge separation in a ground state molecule. None of the other donor/acceptor combinations proved to be

nearly as efficient for charge separation in the isolated molecule as Ia. It is noted that for this molecule, one electronic configuration dominates in the ground state, whereas in most others, the contribution of a second configuration is larger than in Ia. This is reflected by the longer CC separation between the two radicals—in Ia it is 1.517 Å, whereas in the others, it is less than 1.5 Å. The lengths of these CC bonds reflect the conversion of the phenyl ring to an anti-quinoid structure in which resonance stabilization is mainly within the two separate 'pentadienyl'-type radicals. The symmetrically substituted molecules (D$_N$–A$_N$, III and D$_O$–A$_O$, IV) appear to be the next best choices, based of the crude model (Table 2). Of the others, only II was calculated to have a singlet zwitterionic ground state whose energy is lower than that of the triplet at the CASSCF level, but the energy gap is quite small (Table 4). It is noted that for this molecule the leading configuration has a much larger coefficient than the second, and that the CC bonds are rather long, suggesting that the structure found is close to the true zwitterion, and that higher level calculations might lead to a more realistic result. A CASSCF calculation does not properly treat the electron dynamic correlation,[17] which is important mostly for the ionic contributions. A MP2 correction partly compensates for this artifact, and inspection of Table 4 shows that it affects mostly Ia and III, considerably increasing the S$_0$–T$_1$ energy gap. (These calculations were performed point-wise, using the structure obtained by the CASSCF optimization). In the CASSCF-MP2 calculation the S$_0$–T$_1$ gap increased from 0.6 to 13.6 kcal/mol for molecule III, strongly suggesting that this molecule would have a zwitterion character in the ground state.

Molecule IV, whose calculated dipole moment is as large as that of Ia, is an interesting case. The energy of the singlet is slightly lower that of the triplet, in their optimized CASSCF structures and MP2 does not change the ordering. This reflects the fact that the calculated structure is too far from the optimized one required for charge separation, considering that the OH group is a less efficient electron donor than the NH$_2$ one. The crude model of Section III predicts that IP(donor)–EA(acceptor) should be of the order of 2∼3 eV for the system to have a zwitterion ground state. The CASSCF calculation for IP(D$_N$)–EA(A$_O$) yields 2.74 eV a value that decreases to 1.97 eV when MP2 correction is applied. In the case of IV, the IP(D$_O$)–EA(A$_O$) gap is much larger in the gas phase and the MP2 correction is insufficient in this case. Nonetheless, for this molecule the contribution of one electronic configuration is much larger that the other for the singlet state (Table 3), suggesting a potential charge separated species under appropriate conditions. A promising way to facilitate charge separation is by introducing electrostatic stabilizing interactions. We checked this option for molecule IV by calculating the solvent effect using the simple reaction field model.[14,15] It was found that the optimized structure of the molecule when solvated by aceto-nitrile (ε = 36.5) was significantly changed: the CC bonds' lengths increased to 1.501 Å and the dipole moment increased from 9.7 to 12.5 D. The changes in the triplet state were much smaller, and the energy gap between the singlet and the triplet increased to 10.0 kcal/mol. This molecule can therefore be considered as a charge separated species when solvated in a polar solvent.

(17) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

The lowest singlet states of molecules V and VI were calculated to have roughly equal contribution from the two leading configurations. The triplet was found to the lowest energy state for these molecules at the CASSCF level of theory, and MP2 correction did not change this order. The dipole moment of the singlet was small — the tendency to separate charges is weak. In V, this is due to the fact that fluorine atoms are not good enough donors — their p-electrons are too strongly bound. In the case of VI, $CH_2$ is a weak acceptor. These energetic factors are expressed by the relatively large IP(D)−EA(A) listed in Table 2.

The basic model also predicts correctly the effect of changing the nature of the connection between the donor and acceptor groups. In VII, the donor and acceptor are joined in an 'inverted' fashion. Their separation is much smaller (about 1.5 Å) but the stabilization of the zwitterionic state increases dramatically compared to Ia, even at the CASSCF level. The molecular dipole moment decreases somewhat, but indicates an almost complete transfer of one electron. Placing a longer spacer between the donor and acceptor, it is possible to increase the dipole moment, but since the Coulomb attraction term is reduced, also to destabilization of the singlet with respect to the triplet. VIII may be viewed as a 'stretched' Ia, and IX as VII with a benzene spacer added. The calculated dipole moment was found to be about the same for these two molecules (∼20 D). This translates to the transfer of 0.7 and 0.6 electronic charges, respectively. The energies of the lowest triplet and singlet states of VIII were approximately equal, whereas for IX the triplet was found to have a lower energy than the zwitterionic state in the gas phase. Therefore, IX was chosen to check the effect of polar solvents on the structure, dipole moment and stabilization of the zwitterionic state compared to the triplet. As shown in Figure 5, the solvent has a considerable effect on the bond lengths in this case. The SCRF calculations with acetonitrile solvent showed that the dipole moment of Ia increased from 9.7 to 11.8 D and of IX from 17.0 to 33.7 D, respectively. In this solvent, the calculated energy of the $1^1A_1$ state (CASSCF(12/11)/DZV) was 40 kcal/mol *lower* than the triplet in this solvent (whose energy is hardly affected by solvation), inverting the gas-phase energy ordering. This calculation suggests that for such charge separated states, the environment can stabilize the singlet state to a considerable degree, making it the dominant ground-state species, even for molecules whose triplet is the more stable state in the gas phase.

**VIIb. Application to Other Systems.** Several ground state zwitterionic systems related to the model proposed in this paper have been reported in the literature. In the case of the parent molecule III, the quinoid isomer is more stable than the proton transferred molecule.[18] However, the same electronic structure has been shown to lead to a zwitterionic ground state under proper substitution. Thus, the tetra-azapentacene family of heterocycles was studied by Wudl and co-workers,[19,20] who showed that they form zwitterionic structure rather than a diradical singlet. These molecules can be considered as derivatives of III, to which benzene rings were attached at either side.

A system that has been reported to have a zwitterionic ground state and is not derived from an aromatic precursor can be treated within the model presented in this paper. Thiooxalic acid 2-amide-1-hydrazide-2-hydrazone (X)[21] was shown by X-ray analysis to have a zwitterionic character. As seen from Figure 1, its structure is related to compound VII: in the biradical there would be an excess electronic charge at the 'bottom' donor part and shortage in the acceptor 'upper'. Charge transfer from the amino side to the imino-thio one relieves this charge disparity, leading to a stable zwitterion.

**VIIc. Need for Configuration Interaction.** Ia and its analogues presented in Tables 3 and 4 are non-Kekulé hydrocarbons and as such their two HOMOs are almost degenerate (Figure 2). The two configurations in which one of these orbitals is doubly occupied, whereas the other is empty are nearly iso-energetic and may contribute almost equally to the stabilization of the singlet.[2,3] Under these conditions, a configuration interaction scheme must be used in order to calculate the proper ground singlet state wave function of these $12\,\pi$ electron species. Single configuration calculations such as HF have been shown to reproduce the structure and dipole moment of I reasonably well.[4−6] In view of the above analysis, this is due to the fact that indeed a single configuration is dominant in this case. Considering the delicate balance between electron−electron repulsion on one hand and resonance stabilization on the other, only a CI calculation can verify whether a zwitterions character predicted by a single configuration method is fortuitous or not (regardless of the level of calculation). To demonstrate this point we carried out simple CASSCF(2,2)/DZV calculations on VI, the fluoro-substituted molecule (Table 3). Under $C_{2v}$ symmetry, we included in the calculation only the two electrons and the two orbitals $U_3 − D_3$ ($b_1$) and $U_4 + D_4$ ($a_2$). This simple calculation reproduced nicely the structure and dipole moment shown in Table 3 using a much larger active space. The coefficients of the $(b_1)^2(a_2)^0$ and $(b_1)^0(a_2)^2$ configurations obtained for the optimized structure were 0.74 and −0.61 respectively, i.e., almost equal. When an HF−SCF calculation was carried out using the $(b_1)^2(a_2)^0$ configuration only, the system was found to have a stable minimum with a large dipole moment of 6.1 D, and central CC bond lengths of 1.541 Å! This calculation would therefore erroneously predict a zwitterionic structure and a large dipole moment for the ground state of VI (and also of V), which in fact are typical biradicals. For V, a single configuration calculation yields a dipole moment of 7.2 D, with the central CC bond lengths 1.494 Å, namely also a typical zwitterion state. More detailed results are available from the authors on request.

## VIII. Summary

1,2,4,5-Substitution may change the character of the benzene ring—instead of benzene resonance, the system is stabilized by two separate pentadienyl resonances. Electron donor and acceptor groups, when placed at opposite sides of the ring can result in charge redistribution, resulting in a zwitterionic ground state. The driving force for the redistribution is the low ionization potential of the donor and the high electron affinity of the acceptor. The two substituted pentadienyl fragments can be combined to form a molecule in different ways, and the

(18) Rumpel, H.; Limbach, H.-H. *J. Am. Chem. Soc.* **1989**, *111*, 3429.
(19) Wudl, F.; Koutentis, P. A.; Weitz, A.; Ma, B.; Strassner, T.; Houk, K. N.; Khan, S. I. *Pure Appl. Chem.* **1999**, *71*, 295.
(20) Riley, A. E.; Mitchell, G. W.; Koutentis, P. A.; Bendikov, M.; Kazynski, P.; Wudl, F.; Tolbert, S. H. *Adv. Funct. Mater.* **2003**, *12*, 531.

(21) Heinemann, F.; Hartung, H. Acta Crystallogr. **1995**, *C51*, 442.

resulting dipole moment differs depending on the distance between them. The environment can also affect the efficiency of the charge separation by stabilizing the ionic form with respect to the biradical form. The best donor group is the $D_N$ radical, and the best acceptor, the $A_O$ one. Therefore, Ia appears to be the preferred molecule among 1,2,4,5-substituted phenyl rings. Furthermore, since oxygen atoms are better sigma electron acceptors than nitrogen atoms, in this molecule the sigma and pi electron attractions operate in concert.

The analysis presented in this paper shows that charge separation is in fact not related to the aromatic character of the precursor, but to the ease of ionization of the amino group, and the large electron affinity of the dioxoallyl radical. The ingenious preparation of I by Siri and Braunstein[1] used an aromatic molecule as a starting material. However, this molecule is only one representative of a large family of organic molecules in which the ground state is characterized by charge separation.