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Biradicals Stabilized by Intramolecular Charge Transfer: Properties of Heterosubstituted Pentalene and Cyclooctatetraene Biradicals†

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Intramolecular charge transfer can lead to substantial stabilization of singlet ground state and a corresponding increase of the singlet−triplet gap for molecules isoelectronic with the dianions of antiaromatic hydrocarbons. The formal biradicals 2,5-di-heterosubstituted-pentalenes and 1,5-di-heterosubstituted-cyclooctatetraenes are theoretically predicted to have the potential to be stable, persistent non-Kekulé molecules, as supported by high-level quantum chemical calculations. The singlet−triplet energy gaps and the S_0-S_1 excitation energies of these molecules are similar to those of aromatic molecules rather than standard biradicals. These formal biradicals have a pronounced zwitterionic character, having a singlet ground state. The marked stabilization of the ground-state singlet for these non-Kekulé molecules is accompanied by a significant destabilization of the highest occupied molecular orbital (HOMO), leading to a low ionization potential (IP). This apparent inconsistency is explained by analyzing the electronic structure of the molecules. In the case of di-aza-pentalene, the energy of the first electronic excited state is only slightly lower than the ionization potential, making it a candidate for molecular autoionization.

I. Introduction

Substantial efforts have been made to design and prepare persistent nonclassical molecules such as diradicals[1] and triplet[2] or singlet carbenes,[3] yet "bottleable" non-Kekulé molecules remain a challenge. A design principle to achieve this goal via a unique substitution of two carbon atoms in formal antiaromatic molecules by heteroatoms is proposed. A highly stable formal aromatic $[4n + 2]$ π-system is formed, even though, as shown by calculations, a possible Kekulé structure is sacrificed.

Non-Kekulé molecules are molecules with a completely conjugated π-system, for which no classical Kekulé structures can be written.[4] A pair of nonbonding molecular orbitals (NBMOs) that are occupied by two electrons is the MO portrayal of the diradical's electronic origin in non-Kekulé hydrocarbons.[5] Tetramethyleneethane (TME) is one of the prototype non-Kekulé molecules. Other types of fully π-conjugated diradicals are antiaromatic species such as cyclobutadiene (CBD), cyclooctatetraene (COT), or pentalene (PNT). Borden and Davidson predicted the violation of Hund's rule for diradicals that have disjoint NBMOs.[5,6] Thus, the ground state of TME is a singlet with a modest singlet−triplet gap $\Delta E_{ST} = E_S - E_T = -2$ kcal/mol, as verified experimentally by negative ion photoelectron spectroscopy.[7] Incorporation of the TME fragment into a five-membered ring, as in the case of 3,4-dimethylenecyclopentane-1,3-diyl, Ia, changes the ground state to a triplet.[8] The singlet−triplet gap ΔE_{ST} for hydrocarbon disjoint diradicals is usually small, consistent with the high reactivity of these molecules. Qualitative MO arguments suggest that the lowest singlet state can be stabilized by replacing a carbon atom by a heteroatom.[9] Thus, the heteroderivatives of Ia (Figure 1) show a substantial stabilization of singlet vs triplet, as has been shown computationally[10,11] and experimentally.[12]

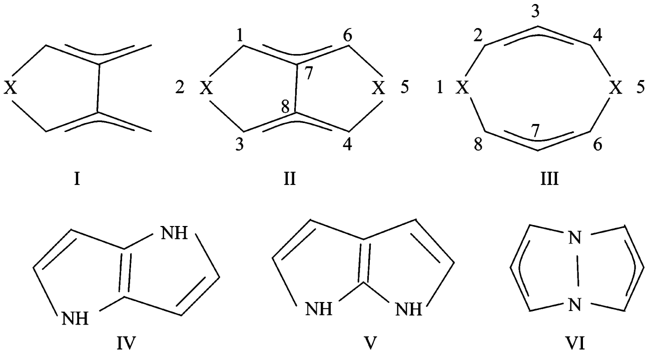

Figure 1. Structures of molecules discussed in the text (X: a = CH_2, b = NH, c = O, and d = S).

Lahti et al.[13] used semiempirical quantum chemical calculations to assess the properties of diradicals (type I) and the related bicyclic derivatives of pentalene (type II). Figure 1 shows their structure and the numbering convention used in this paper. The large ΔE_{ST} computed for type II derivatives led them to discuss criteria for determining whether these systems should be described as biradicals or zwitterions. Through the use of configuration interaction, it was found that the ratio $(C_1/C_2)^2$ of the squares of the coefficients of the two leading configurations in the electronic wave function of the ground-state singlet is a useful criterion for this purpose. If a single configuration is dominant (i.e., $C_1 \gg C_2$), then the system has a pronounced zwitterionic character. Thus, the ratios were found to be 8.05, 3.28, and 2.46 for IIb, IIc, and IId, respectively, showing that IIb is best described as a zwitterion.

Cava and co-workers isolated the tetraphenyl-substituted derivative of IId, tetraphenylthieno(3,4-c)thiophene (hereafter designated as IIe), leading to the elucidation of its electronic spectrum,[14] X-ray structure,[15] and photoelectron spectrum.[16] Derivatives of IIb and IIc, as well as of III, have not yet been

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reported to the best of our knowledge. In this work, we report high-level complete active space self-consistent field (CASSCF) and density functional theory (DFT) calculations on these molecules, predicting that all heterosubstituted derivatives (X= NH, O, or S) are stable (though possibly reactive) compounds with a singlet ground state. The aza-pentalene derivative IIb is calculated to have an exceptionally low ionization potential, due to a high-lying HOMO orbital.

II. Results

All computations were carried out using the GAMESS program suite,[17] with the cc-pVDZ basis set.[18,19] The GAUSSIAN program suite[20] was used for DFT calculations at the B3LYP/cc-pVDZ level. A complete vibrational analysis was performed at the optimized geometry. Calculations on the parent molecules IIa and IIIa were performed only to compare with the substituted derivative. Since their singlet states were found to be planar (D_{2h} symmetry), calculations were performed on the X = CH_2 molecules at this symmetry as well. In general, the CASSCF and DFT results agreed quite well as far as the structure of the minima are concerned. The CASSCF vibrational frequencies were found to deviate a little from the DFT ones (compare Tables S1 and S2 in the Supporting Information); it is well-known that for limited active space and basis sets a correction factor is required for CASSCF calculations. The DFT method fails to calculate singlet biradicals and therefore was not used for IIa and IIIa. For all other molecules, the ground-state singlets were found to be predominantly of zwitterionic character and the DFT results agreed well with the CASSCF ones.

CASSCF[21] calculations (CAS(8/7)/cc-pVDZ with a full π active space) show that the ground states of Ib, Ic, and Id are singlet for all substituents; however, only for the aza-derivative (Ib) does ΔE_{ST} reach the sizable value of −10.1 kcal/mol.

A more substantial stabilization of the singlet ground state and a corresponding increase of the singlet−triplet gap for non-Kekulé molecules can be expected for molecules isoelectronic with the dianions of antiaromatic hydrocarbons. Hückel's ($4n + 2$) rule predicts an aromatic character for dianions of $4n$-annulens, but notwithstanding, isolated COT^{-2} and CBD^{-2} are known to be unstable with respect to electron loss.[22] Substitution of two carbon atoms by two more electronegative heteroatoms, X, adds two electrons to the π-system, while keeping the system electrically neutral. The extent of the interaction of these extra electrons with the rest of the π-electron system depends on the electronegativity of X and on the overlap of the nonbonding electrons of X with the π electronic structure of the TME fragment in IIb−d or of the two allyl fragments in IIIb−d (Figure 1).

Tables 1 and 2 report the calculated absolute energies and the structure of several 2,5-substituted pentalenes and 1,5-substituted cyclooctatetraenes. The parent systems IIa and IIIa are typical disjoint diradicals, because the CH_2 bridges do not take part in the π-delocalization (Tables 1and 2). As seen from Tables 1 and 2, the geometry of the hydrocarbon part does not change much upon substitution. Also, the structures of the singlet and triplet states are very similar, despite the different spin state and charge distribution. This is a first indication that the two extra electrons find themselves in a nonbonding orbital. Table 3 reports the data obtained for the singlet−triplet gap (ΔE_{ST}), the excitation energy of the first electronic excited singlet state ($E(S_1) - E(S_0)$), and the first ionization potential (IP). It is seen that the singlet−triplet energy gaps for the hydrocarbons IIa and IIIa are small, 0.14 and 0.15 eV, respectively, very similar to the gap in the prototype TME.[7]

TABLE 1: Absolute Energies (Hartree), Bond Distances R_{ij} (angstroms), and the Mulliken Charge of X, q_x (electronic charge units), for 2,5-di-X-pentalenes IIa−d (CASSCF(10/8)/cc-pVDZ)

X	state	energy	R_{12}	R_{17}	R_{78}	q_x	$\Delta q_x(ST)^a$
CH_2	1^1A_g (D_{2h})	−307.55414	1.518	1.391	1.449	+0.05	+0.01
CH_2	1^3B_{2u} (D_{2h})	−307.54887	1.516	1.387	1.463	+0.04	
NH	1^1A_g (D_{2h})	−339.62983	1.363	1.405	1.443	+0.25	+0.16
NH	1^3A_u (C_{2h})	−339.56190	1.417	1.394	1.456	+0.09	
O	1^1A_g (D_{2h})	−379.24513	1.341	1.394	1.445	+0.12	+0.11
O	1^3B_{2u} (D_{2h})	−379.20886	1.374	1.388	1.454	+0.01	
S	1^1A_g (D_{2h})	−1024.61791	1.714	1.403	1.452	+0.43	+0.14
S	1^3B_{2u} (D_{2h})	−1024.58510	1.768	1.394	1.461	+0.29	

[a] $\Delta q_x(ST)$ is the excess of charge transferred in the singlet over the triplet. It is a measure of the zwitterionic character of the singlet.

TABLE 2: Absolute Energies (Hartree), Bond Distances R_{ij} (angstroms), and the Charge of X, q_x (electronic charge units), for 1,5-di-X-cyclooctatetraenes IIIa−d (CASSCF(10/8)/cc-pVDZ)

X	state	energy	R_{12}	R_{23}	q_x	$\Delta q_x(ST)^a$
CH_2	1^1A_g (D_{2h})	−308.72286	1.495	1.392	+0.06	+0.01
CH_2	1^3B_{1u} (D_{2h})	−308.71720	1.502	1.393	+0.05	
NH	1^1A_g (D_{2h})	−340.75304	1.355	1.389	+0.25	+0.15
NH	1^3A_u (D_{2h})	−340.70574	1.395	1.390	+0.10	
O	1^1A_g (D_{2h})	−380.39435	1.319	1.385	+0.14	+0.12
O	1^3B_{1u} (D_{2h})	−380.34580	1.354	1.386	+0.02	
S	1^1A_g (D_{2h})	−1025.73221	1.699	1.388	+0.43	+0.15
S	1^3A_u (C_{2h})	−1025.59031	1.763	1.391	+0.28	

[a] $\Delta q_x(ST)$ is the excess of charge transferred in the singlet over the triplet.

TABLE 3: Singlet−Triplet Gap, Excitation Energy ($E(S_1) - E(S_0)$), and the Ionization Potential for 2,5-di-X-pentalene and 1,5-di-X-cyclooctatetraenes Derivatives (CASSCF(10/8)/cc-pVDZ) (in electronvolts)

	PNT derivatives			COT derivatives		
X	ΔE_{ST}	$E(S_1) - E(S_0)$	IP	ΔE_{ST}	$E(S_1) - E(S_0)$	IP
CH_2	0.14	4.30	6.31	0.15	5.25	6.21
NH	1.66	4.89	4.85	2.16	4.54	5.08
O	0.99	5.43	7.16	1.32	5.39	6.02
S	0.89	4.47	6.35	1.29	4.65	6.30

In contrast, the oxygen and sulfur derivatives IIc, IIIc and IId, IIId, and especially the aza-substituted derivatives IIb and IIIb are calculated to have a much larger ΔE_{ST}. The large ΔE_{ST} values computed for the aza-derivatives are in fact typical for aromatic compounds thus confirming the substantial stabilization of the ground singlet state for these non-Kekulé molecules. Further evidence for the large stability of these species comes from comparison of the relative stabilization of IIb with its valence isomers IV, V, and VI (Figure 1). Isomers IV and V have a regular bonding pattern and may be considered as normal Kekulé structures, expected therefore to be quite stable. The relative stability of IIb may thus be estimated by comparison with these isomers: a calculation shows that IV (the most stable isomer) is only 10.7 kcal/mol lower in energy than IIb while V—the other "normal" isomer—is more stable by only 6.3 kcal/mol (CASSCF-MP2 results for IIb, IV, V, and VI; all structures are optimized on the CAS(10/8)/cc-pVDZ level with a full π active space). Moreover, the energy of VI—the other non-Kekulé isomer—is higher than that of IIb by 20.8 kcal/mol. Thus, the thermodynamic stability of IIb is of the same order as the normal aromatic heterocyclic molecules IV and V, despite the loss of one π-bond in IIb.

The IPs of the II-type molecules are calculated to be fairly small, especially for IIb. For this compound, the IP is of the same order as the energy of the first excited state (CASSCF

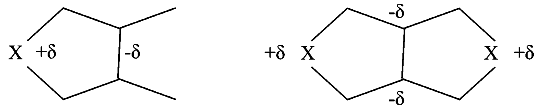

Figure 2. Intramolecular charge separation in I vs II.

and also DFT, see the Supporting Information). Even though CAS is known to overestimate the energy of electronic excited states, the very low ionization potential indicates a facile autoionization for this molecule. The data are summarized in Table 3.

III. Discussion

IIIa. Comparison with Experiment. A large singlet−triplet splitting for a formal biradical, as displayed in Table 3 for the heterosubstituted molecules, was found in the recently prepared di-*tert*-butyl derivative of 2,5-diamino-1,4-benzoquinonediimine, which exists in a persistent zwitterionic form in the singlet ground state.[23,24]

Apart from tetraphenylthieno(3,4-c)thiophene (IIe),[14−16] there is no experimental evidence for molecules IIb−d or their derivatives (though Closs et al. reported[25] experimental evidence for II with X = N) nor for IIIb−d, but crystal structures of potassium and ammonium salts of the dianion of 1,3,4,6-tetranitro-2,5-diazapentalene have been published.[26,27] Compound VI, 7,8-diazapentalene, is the least stable diazapentalene isomer, nevertheless its derivatives were obtained and the crystal structures of nitro-substituted-7,8-diazapentalenes were reported.[28,29]

The calculated structure of IId (Table 1) agrees well with the structure of IIe; the calculated ionization potential (6.35 eV, Table 3) is also in good agreement with experiment (6.19 eV[16]). The lowest-lying excited singlet of IId is calculated to be about 4.47 eV by CASSCF and 2.82 eV by TDDFT. We propose that the lower experimental value (2.24 eV for IIe) reflects a bathochromic shift due to the interaction between the four phenyl groups and the central bicycle moiety.

IIIb. Electronic Structure of IIb and the Rationale for the High Singlet Stability and Low IP. The difference between the calculated charge distributions in the singlet and triplet states Δq_x(ST) (Table 3) shows that about 0.12−0.15 electronic charge is transferred from the donor-heteroatom X to the TME fragment in IIb−d or to the two allyl units and IIIb−d. Significantly, IIa and IIIa (X = CH_2) do not show any differences in the electronic distribution between the singlet and triplet states, as expected. The same donor groups (X) in 2-heterosubstituted-3,4-dimethylenecyclopentane-1,3-diyls, Ib−d, show considerably less tendency for intramolecular charge transfer of this type in the singlet state: $\delta q = q_x(\text{singlet}) - q_x(\text{triplet})$ is +0.08 for aza-derivative, Ib, +0.03 for oxa-derivative, Ic, and +0.06 for thia-derivative. Obviously, the degree of donor−acceptor charge transfer and the relative stabilization of the singlet state in IIb−d and IIIb−d are correlated.

A simple electrostatic model accounts for the physical origin of the extra stabilization of singlet state for IIb−d and IIIb−d. Transferring δ-units of charge from the donor X to the acceptor TME fragment in I leads to a Coulombic stabilization $E_{\text{coul}} = -\delta^2/R$, where R is the distance between the centers of the positively charged X and the negatively charged accepting group. The same amount of charge transferred from X to TME for II results in a much larger Coulombic stabilization, $E_{\text{coul}} = -4\delta^2/R$, four times larger (Figure 2 shows the charge distribution in these molecules).

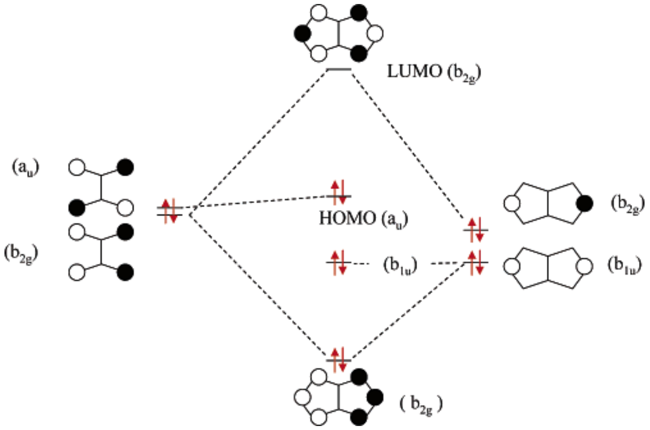

Figure 3. Schematic π-orbital diagram showing the origin of the low ionization potential of 2,5-diheterosubstituted pentalenes IIb−d as well as its high stability as a singlet zwitterion. The left-hand π-orbitals are of the carbon skeleton, and the right-hand ones are of the donor X group. The middle ones are the resulting molecular orbitals of II.

The electrostatic argument cannot account for the low IP of these molecules. An MO-based model can be proposed to explain both the extra stabilization and the low IP. In ref 16, a MO diagram for IIe was used to account for the observed photoelectron spectrum. Figure 3 shows schematically a similar diagram in which the MOs of the IIb molecule are constructed by the interaction between the MOs of the TME fragment and the two donor groups. As seen from the diagram, the only high-lying orbitals that can interact are the b_{2g}-type orbitals. The two b_{2g} and a_u orbitals of the TME biradical fragment are practically degenerate, as are the b_{2g} and b_{1u} orbitals of the two NH groups. In the TME biradical, two electrons occupy the two NBOs; the interaction between the two b_{2g} fragment orbitals lifts the degeneracy of both the TME and NH−NH orbitals. It turns out that the interaction is very strong—the in-phase combination of the two b_{2g} orbitals is stabilized with respect to the a_u orbital by about 9 eV (HF/cc-pVDZ calculation)! The other b_{2g} orbital (formed by out-of-phase combination) is strongly destabilized and becomes the lowest unoccupied molecular orbital (LUMO). This strong interaction is the MO manifestation of the stabilization of the singlet state. It is proportional to the orbital overlap and inversely proportional to the energy gap between the NBO and NH−NH donor orbitals. The oxo-substitution provides effective overlap, but the large energy difference between the TME NBO's level and the p-AO of the O atom reduces the effectiveness of the interaction. The relatively weak stabilization by S-substitution is due to small overlap between the p-orbitals of the small carbon atoms with a big S atom. The interaction is especially strong for the aza substituent since only in this case both conditions for strong stabilization are fulfilled.

The other TME NBO (a_u) does not interact with the donor and becomes the HOMO; it is populated by the two electrons which originally occupied the two different, though isoenergetic, a_u and b_{2g} orbitals. Being now in a single nonbonding orbital, the repulsion interaction between them is stronger, reducing the ionization potential. Moreover, the TME fragment also has a significant additional population on the stabilized b_{2g} MO, as the electrons that occupied the X−X orbital are now partially transferred to the common orbital. These effects lead to the concentration of an electron density on the atoms but not on the bonds between atoms. The strong electron−electron repulsion pushes up this HOMO, and it results in a very low IP.

The electronic structure shown in Figure 3 is compatible with the data of Table 1—the similar geometry of all molecules is due to the fact that the two extra electrons find themselves in a nonbonding orbital and thus their effect on bond lengths is minimal.

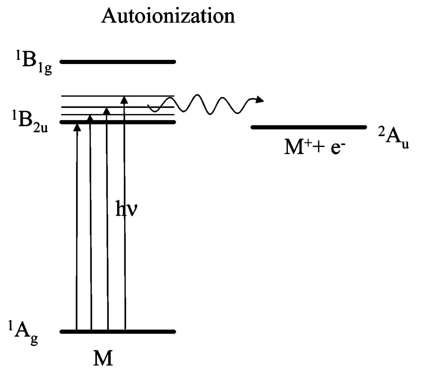

Figure 4. Schematic energy level diagram of IIb showing the S_0-S_1 optical transition with a vibronic progression that can lead to autoionization.

TABLE 4: Squared Ratio of the Coefficients of the Two Leading Configurations of the Singlet CI Wave Function as Obtained by the CASSCF Calculation

molecule	IIa	IIb	IIc	IId	IIIa	IIIb	IIIc	IIId
$(C_1/C_2)^2$	1.1	23.9	9.6	10.3	2.2	23.9	11.3	13.2
$(C_1/C_2)^2$ (ref 12a)		8.05	3.28	2.46				

The dominant ground-state electronic configuration of IIb may be written as $^1A_g = \cdots(b_{1u})^2(a_u)^2(b_{2g})^0(b_{1u})^0$. The removal of one electron yields the cation radical with configuration $^2A_u = \cdots(b_{1u})^2(a_u)^1$. The first excited electronic state has the configuration $^1B_{2u} = \cdots(b_{1u})^2(a_u)^1(b_{2g})^1(b_{1u})^0$; the transition $^1A_g \rightarrow {}^1B_{2u}$ is allowed, with an oscillator strength (TD-DFT/B3LYP-cc-pVDZ) of 0.14. As shown in Figure 4, the system can be readily ionized using UV light.

The high-level CASSCF calculation agrees with the qualitative conclusions of ref 12a, which were based on semiempirical methods: the aza-substituted compound has a much more pronounced zwitterionic character than the oxo- or thio-substituted ones. The squared ratio of the coefficients of the two principal singlet configurations of the singlet ground state $(C_1/C_2)^2$ can serve to estimate the nature of these formal biradicals—for a covalent biradical, it is near unity, and for a zwitterion, it is much larger. Table 4 lists the numerical values for this squared ratio. It is seen that for X = CH_2 the singlet ground states of both pentalene and cyclooctatetraene are largely biradicals, while for X = NH, they are zwitterions. The oxo and thio compounds are of intermediate nature but also mostly zwitterions. When compared with the semiempirical results, it is seen that the $(C_1/C_2)^2$ ratio is much larger, by approximately a factor of 3. Another quantitative difference is the fact that the $(C_1/C_2)^2$ ratio is larger by a factor of 2 for IIb, IIc, and IId as compared with the semiempirical result.

IV. Concluding remarks

In conclusion, it was shown that 2,5-di-heterosubstituted-pentalenes and 1,5-di-heterosubstituted-cyclooctatetraenes are characterized by a strong stabilization due to intramolecular charge transfer; thus, they have the potential to be stable, persistent non-Kekulé molecules. The overall stabilization of the singlet is accompanied by a high-lying HOMO, resulting in a low IP. This is particularly evident in the special case of di-aza-pentalene (IIb) which has an extremely low IP and at the same time a strong zwitterionic character. Both features are related to the strong interaction between the p-orbitals of the N atoms and those of the TME moiety. The low IP (~5 eV) allows in principle facile autoionization in the near UV.

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Supporting Information Available: Table S1 lists the geometries (as Cartesian coordinates) and vibrational frequencies for all of the calculated structures (CASSCF); it also lists the coefficients of the major configurations contributing to the singlet ground state. Table S2 lists the geometries (as Cartesian coordinates) and vibrational frequencies for all of the calculated structures, as well as the energies and oscillator strengths for the low-lying singlet states (DFT). Complete refs 33 and 34 are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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