Non-Kekulé *N*-Substituted *m*-Phenylenes: *N*-Centered Diradicals versus Zwitterions[†]

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The relationship between the structures and electronic ground state properties of non-Kekulé-type *N*-substituted *m*-phenylenes was studied utilizing density functional theory (DFT), with the aim of determining the factors that lead to ground state triplet diradicals. At B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) we identified octahydropyridoquinoline with an exceptionally large singlet−triplet energy separation of $+27.9$ kcal mol^{-1}, in favor of the triplet. The high-spin structures can readily be obtained by interruption of the full cyclic π-delocalization that avoids cross-conjugation of the nitrogen radical centers. Introduction of additional heteroatoms, on the other hand, preferentially stabilizes the singlet zwitterionic resonance contributors in these systems. The identified diradicals show strong ferromagnetic exchange interactions between two radical centers.

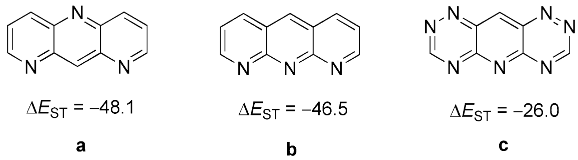
Introduction

The extended π-conjugation and the unusual frontier molecular orbitals of oligoacenes make these compounds attractive as building blocks in the design of organic electronic materials.[1] However, oligoacenes larger than anthracene are unstable toward oxidation as well as dimerization and are poorly soluble;[2] to utilize their potential as electronic materials, a large number of functionalized acenes have been prepared and tested.[3] Substituted oligoacenes have received considerable attention,[4] while acenes incorporating heteroatoms only came into focus over the past decade.[5] In contrast to the linear heteroacenes, there are many extended ladder-type structures containing fused cycles based on thiophene[6] and pyrrole subunits.[7]

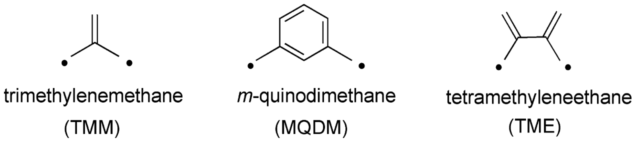
Nitrogen containing acenes (azaacenes) are known to be more stable than their parent hydrocarbons against photooxidation and dimerization; their electronic properties, solubilities, and crystal structures have been examined.[5b,8] Boron- and lithium-doped polycyclic aromatic hydrocarbons have also been investigated.[9] Recently, Winkler and Houk considered $4n + 2$ π-electron azaacenes in the structural models **a** and **b** (Scheme 1) computationally to elucidate their potentials as n-type semiconductors.[5b] Among the azaacenes studied, tetraazatetracenes and larger analogues showed larger singlet−triplet energy separations ($\Delta E_{\mathrm{ST}} = E_{\mathrm{S}} - E_{\mathrm{T}}$) than their corresponding hydrocarbons. A pentacene with at least seven nitrogen atoms reached both the minimum required levels for the electron affinity (EA $\sim$ 3.0 eV) and reorganization energies for electron transport ($\lambda_{-} \sim 0.20$ eV) to be useful for applications in molecular electronics.[5b] With the help of unpublished DFT computations we identified Kekulé-type azaanthracene **c** involving seven nitrogen atoms with $\Delta E_{\mathrm{ST}} = -26.0$ kcal mol^{-1} (anthracene: $\Delta E_{\mathrm{ST}} = -39.5$ kcal mol^{-1}). No aromatic azaanthracene involving less than eight nitrogen atoms could be obtained with $\Delta E_{\mathrm{ST}} > -25$ kcal mol^{-1}.

In comparison to Kekulé-type nitrogen-rich acenes, non-Kekulé structures show considerable narrowing of their singlet−triplet energy separations, thereby making these types of π-conjugated fused heterocycles fascinating candidates for the design of organic electronics and molecule-based magnetic substances.

SCHEME 1: B3LYP/6-311G(d,p) ΔE_{ST} Values (kcal mol^{-1}) for Kekulé-Type Azaanthracenes[10]

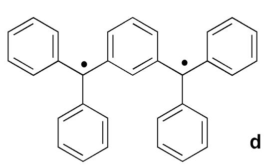


SCHEME 2: Examples of Non-Kekulé Diradicals



"Non-Kekulé" structures have been coined by Dewar for π-conjugated hydrocarbons that cannot be assigned to classical Kekulé resonance structures, since they have at least two atoms that are not π-bonded[11] and the spin centers in such systems act independently (Scheme 2). Hence, such structures are prime candidates for constructing molecules with open-shell character.

π-Conjugated *m*-quinonoid diradicals[12] are known to be fascinating ferromagnetic non-Kekulé couplers because they cannot form diamagnetic quinonoids, in contrast to their ortho- and para-analogues.[13] Schlenk[12a] in 1915 synthesized the first *m*-quinonoid diradical **d** based on Gomberg's[14] triphenylmethyl radical. In 1975, Migirdicyan and Baudet irradiated frozen *m*-xylene and assigned *m*-quinodimethane (Scheme 2) as the parent of *m*-quinonoid diradicals.[15]



d

To date, there are only scattered experimental reports of ground state triplet *N*-substituted derivatives with *m*-quinonoid

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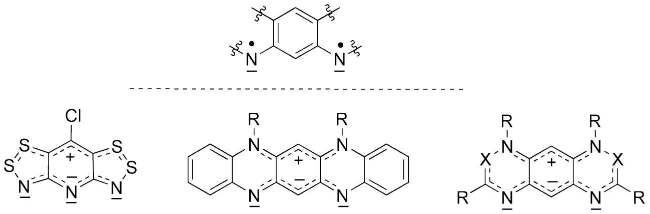
10.1021/jp9028672 CCC: \$40.75

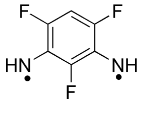
SCHEME 3: Aza Derivatives of *m*-Phenylene in Their Singlet Ground States



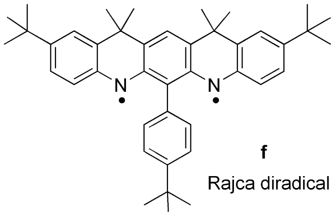
1 **2** **3** X = N
4 X = CH

R = substituent groups

character. In 1989 Platz et al. photolyzed 2,4,6-trifluoro-1,3-diazidobenzene and identified the first nitrogen-centered diradical **e** at 77 K.[16] Rajca and co-workers prepared in 2007 the second example of this class (**f**), which is stable in solution at low temperature, and does not react with oxygen.[17a] Their EPR spectroscopic and SQUID magnetometric studies showed strong ferromagnetic coupling for this nitrogen-substituted *m*-quinonoid. Previously, this group had synthesized and characterized the carbon analogue of **f** that is considerably less stable.[17b]



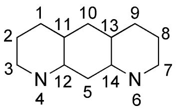
e
Platz diradical



f
Rajca diradical

On the other hand, 4n π-aza-*m*-phenylenes **1**−**4** are expected to have diradical ground states but were found to be best described as closed-shell zwitterions (Scheme 3).[18−20] It should be emphasized that the types of exchange interactions through phenylene coupling units depend appreciably on the mutual arrangement of the singly occupied molecular orbitals (SOMOs) that are affected by substitution and molecular topology. Through perturbations of the SOMOs, the energy gaps between the high- and low-spin states change, and the systems often display several nearly isoenergetic electronic states.

We focus our present work on nitrogen-substituted non-Kekulé *m*-quinonoids with the aim of identifying open-shell species, ideally with a large singlet−triplet energy separation favoring a triplet ground state; the linear tricycles were utilized as models (see below). Anthracene and its derivatives reveal electronic and photonic properties that can find a variety of applications in data storage or for molecular switches.[21]



The non-Kekulé pyridine-bridged bis-1,2,3-dithiazole (**1**),[18] diphenyltetraazapentacene (**2**),[19] and tetraphenylazaanthracenes (**3** and **4**),[1b,e,20] are examples of the biscyanine zwitterionic families displaying singlet ground states. A way for such molecules to reduce their antiaromatic character and to avoid the open-shell ground state, is the partitioning of the overall 4n π-electrons into two charged separately conjugated subsystems (cyanines) that are structurally connected by σ-bonds (Scheme 4).[22]

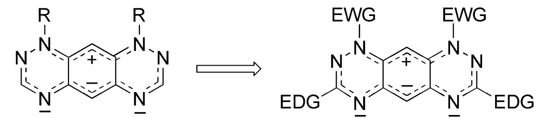
SCHEME 4: Diradical and Zwitterionic Forms of Non-Kekulé Structures 3 and 4

triplet singlet

3 X = N
4 X = CH

R = substituent groups

SCHEME 5: B3LYP/6-31G(d) Substituent Effects on Arising the Diradical Character of Zwitterion 3[1b] (Relative Energies in kcal mol^{-1})



R = OCH_3 $\Delta E_{ST} = -19.5$
H $\Delta E_{ST} = -18.8$
NO_2 $\Delta E_{ST} = -9.3$

16 π closed shell
$\Delta E_{ST} \sim -10$

Experiments and computations indicate that in **1**−**4** the lowest-lying triplet states are energetically close to the singlet zwitterionic ground states and that they display unusual photophysical properties.[5b,23] Haas and Zilberg computationally showed that these zwitterions can be envisioned as the union of two independent radical sites.[23] They indicated that electron donor and acceptor substituents placed at opposite sides of a benzene ring (1,2,4,5-substitution) can result in charge redistribution favoring a zwitterionic ground state.[23] The partitioning of the π-electrons in aza derivatives of benzenoid hydrocarbons have been studied in detail.[24]

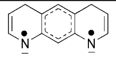
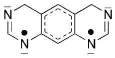
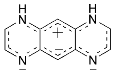
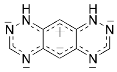
Koutentis et al. have reported that introducing electron withdrawing groups (EWG) para to the negative cyanine in the central ring of **2** and electron donating groups (EDG) in the para-position to the positive cyanine ribbon increases the ΔE_{ST} in favor of the triplet state.[22a] We recently showed that in zwitterion **3** the nitrogen bonded σ-/π-acceptors considerably reduce singlet−triplet energy gaps (Scheme 5).[1b] Indeed, the σ-/π-acceptor substituents connected to electron donating ribbon attenuate the polarization of the ribbons resulting in smaller singlet−triplet energy gaps and higher diradical character.

As it appears to be difficult to bring biscyanine zwitterions **3** and **4** into their triplet states through substitution,[1b] we focus in the present work on the design of non-Kekulé nitrogen-substituted *m*-phenylenes. In our presentation of the triplet ground states, we consider only intramolecular magnetic exchange couplings between two spin-centers.

Computational Methods

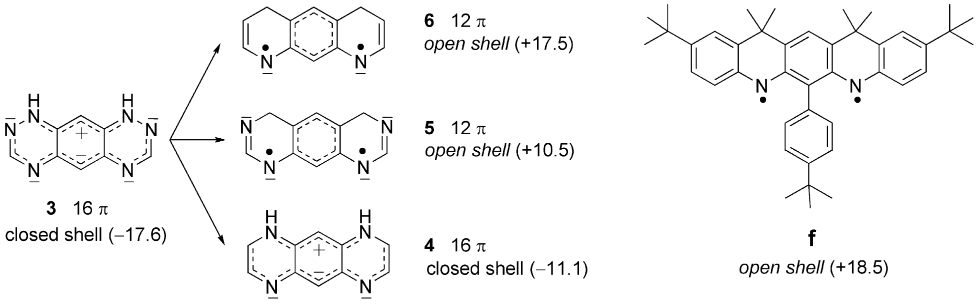
Density functional theory (DFT) using the Becke's three-parameter hybrid functional[25] (U)B3LYP within the Gaussian 03 program suite[26] was employed to optimize all structures. We utilized a 6-311G(d,p) basis set for computing all geometries and energies for closed-shell singlet (spin-restricted wave functions), broken-symmetry open-shell singlet (spin-unrestricted wave functions), and triplet states (spin-unrestricted wave functions).[27] The computed vibrational frequencies showed that all stationary points are minima.

TABLE 1: Singlet-Triplet and First Excited Singlet State Energy Separations as well as Zero Point Vibrational Energies (kcal mol^{-1}), Spin Contaminations, and Dipole Moments (D)

		GS	S_0–T_1[a]	S_0–S_1	ZPVE		$<S^2>$ S_0	$<S^2>$ S_1	$<S^2>$ T_1	μ_{S0}	μ_{S1}	μ_{T1}	$\Delta\mu_{ST}$
					S_0, S_1	T_1							
6		diradical	+17.5	+15.5	117.5	117.7	0.00	1.02	2.08	6.26	4.94	4.76	+1.5
5		diradical	+10.5	+9.1	103.2	103.2	0.00	0.93	2.08	4.49	3.34	2.78	+1.7
4		zwitterion	–11.1	0.0	105.6	104.0	0.00	0.05	2.04	7.91	7.88	7.14	+0.8
3		zwitterion	–17.6	0.0	91.5	89.8	0.00	0.00	2.03	5.08	5.08	4.63	+0.5

[a] Positive value indicates a triplet ground state; GS = ground state description.

SCHEME 6: Replacing of Nitrogen Atoms with Carbon Atoms Leading to Diradical Ground States (ΔE_{ST} Values in Parentheses in kcal mol^{-1})



For evaluating the validity of the B3LYP functional for these types of structures, Truhlar's recent M06-2X density functional[28] has been utilized for comparison on the zwitterion ground state **3a** and on the diradical **6i** as reference systems. The ΔE_{ST} values for **3a** are −17.8 and −17.6 kcal mol^{-1} at M06-2X/6-311G(d,p) and B3LYP/6-311G(d,p), respectively. The M06-2X/6-311G(d,p) functional shows an even higher diradical character for the ground state of **6i** and yields a ΔE_{ST} of +33.8 vs +27.9 kcal mol^{-1} at B3LYP/6-311G(d,p).

Nucleus-independent chemical shieldings NICS(1) were determined as the negative value of the absolute isotropic magnetic shielding[29] utilizing GIAO[30]-B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) by locating a ghost atom 1 Å above the plane of each ring. To predict the intramolecular magnetic exchange couplings, the broken symmetry (BS) approach was used for determining the spin coupling constants *J*, which describes the effective exchange interaction between spin-carrier sites.

Results and Discussion

Diradicals from 4*n* π-Electron Zwitterions. Wudl et al.[19c] previously reported a significant increase in ΔE_{ST} when the nitrogens at the 2- and 8-positions of hexaazaanthracene **3** were replaced with carbon atoms to give tetraazaanthracene **4**. The present B3LYP/6-311G(d,p) computations show also ΔE_{ST} values of −17.6 and −11.1 kcal mol^{-1} for zwitterions **3** and **4**, respectively (Scheme 6). Our present investigations indicate that replacing the nitrogens located at the 1- and 9-positions has a much larger effect on the ΔE_{ST} values so that tetraazaanthracene **5** is predicted to have a low-lying *triplet* ground state (ΔE_{ST} = +10.5 kcal mol^{-1}). The diazaanthracene **6** involving no extra

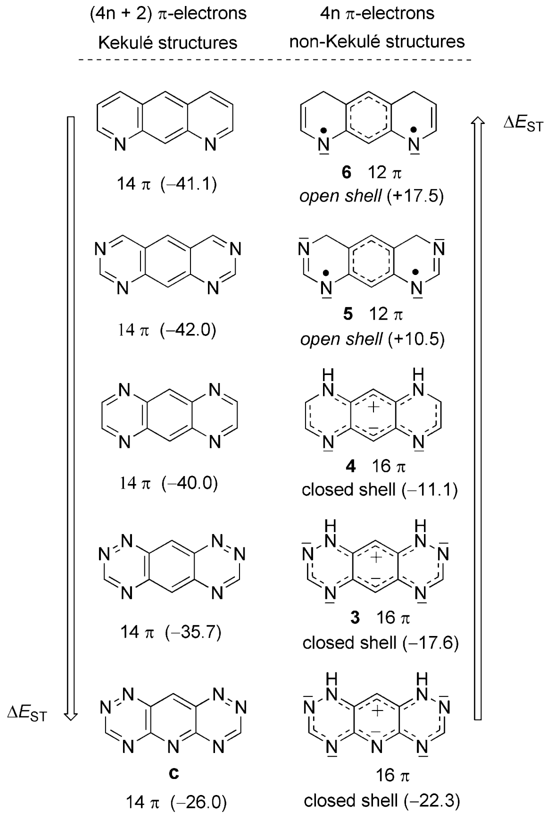


Figure 1. Trends of increasing ΔE_{ST} values (kcal mol^{-1}) of Kekulé and non-Kekulé azaacenes depending on the number of nitrogen atoms and substitution pattern. The computed ΔE_{ST} for parent anthracene is −39.5 kcal mol^{-1}.

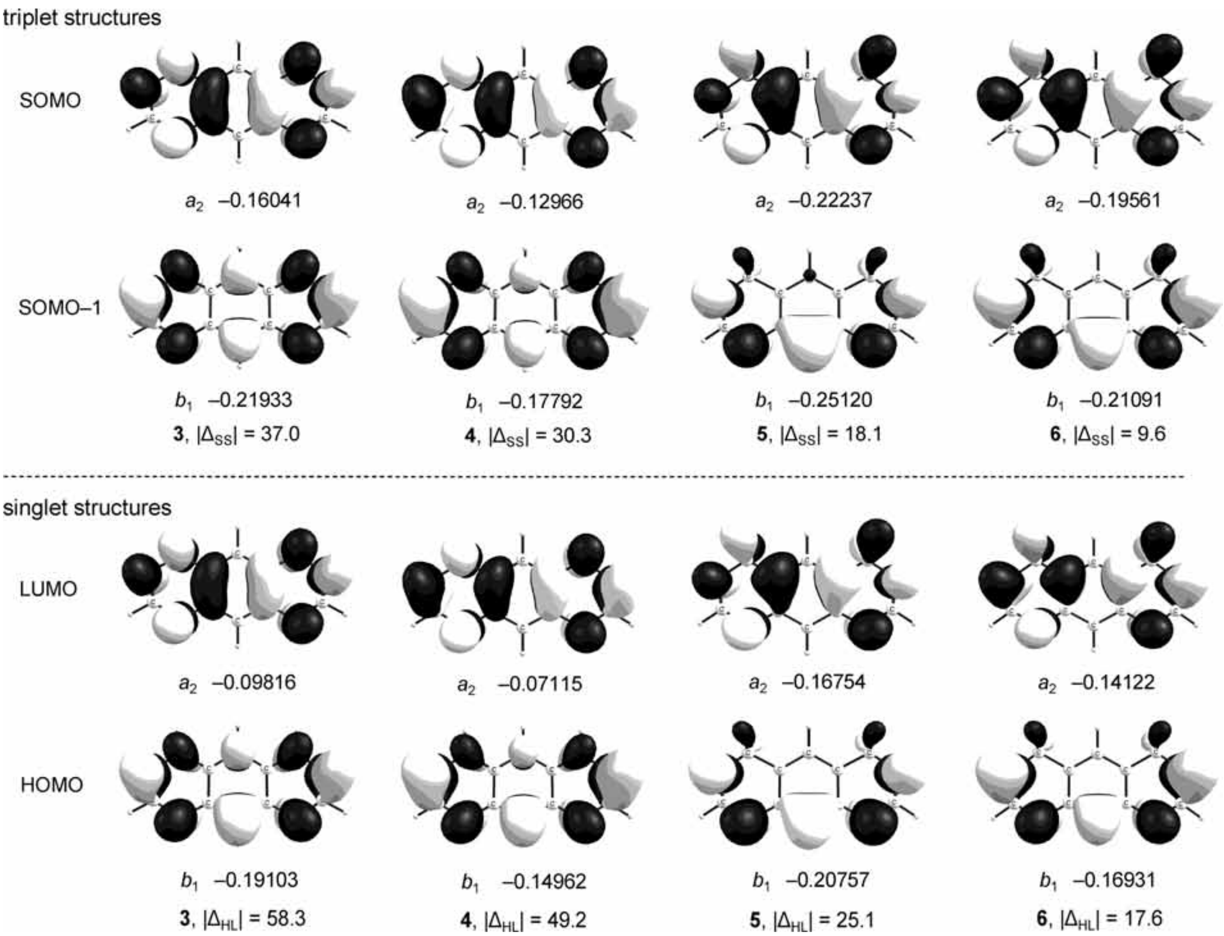


Figure 2. Isosurface plots for the frontier molecular orbitals of singlet and triplet structures of **3**−**6**. Absolute energies are in hartree, and relative energies, in kcal mol^{-1}; the contour value is ±0.03 au Δ_{SS} and is defined as the energy gap between SOMO−1 and SOMO1.

nitrogen atoms shows an even more positive ΔE_{ST} of +17.5 kcal mol^{-1}. Rajca's aminyl diradical **f** has been considered as a reference system; computations at the same level of theory place the triplet of **f** 18.5 kcal mol^{-1} lower in energy than the singlet state.

Computations show that open-shell singlet states for diradicals **5** and **6** lie moderately higher than their triplet states (1.4 and 2.0 kcal mol^{-1}, respectively). The energy differences of the electronic ground and low-lying excited states of this series and the corresponding spin contaminations are summarized in Table 1. A previously studied, the phenanthrene analogue of **4** by Koutentis et al. has a triplet ground state with ΔE_{ST} value of +14.2 kcal mol^{-1} at B3LYP/6-31G(d).[22a]

Involvement of the N^1 and N^9 donor atoms of structures **3** and **4** in the π-conjugation para to the N^6 and N^4 spin centers, respectively, effectively couples all π-electrons and favors a closed-shell zwitterion. Thus, replacing the N^1 and N^9 atoms with carbon as in the case of **5** and **6** blocks the conjugation efficiently and such ground states are open-shell.

Trends for the ΔE_{ST} values for the non-Kekulé structures considered here, along with their Kekulé analogues are presented in Figure 1. In contrast to highly conjugated azaanthracenes, the smaller number of nitrogen atoms in the 4n π-electron series results in larger ΔE_{ST} values.

The HOMO and LUMO isosurfaces of the closed-shell structures and the two SOMOs of the open-shell isomers are depicted in Figure 2; all structures are C_{2v} symmetric. The electronic states for singlet and triplet structures are $^1A_1$ and $^3B_2$, respectively. By inspection, we conclude that the two

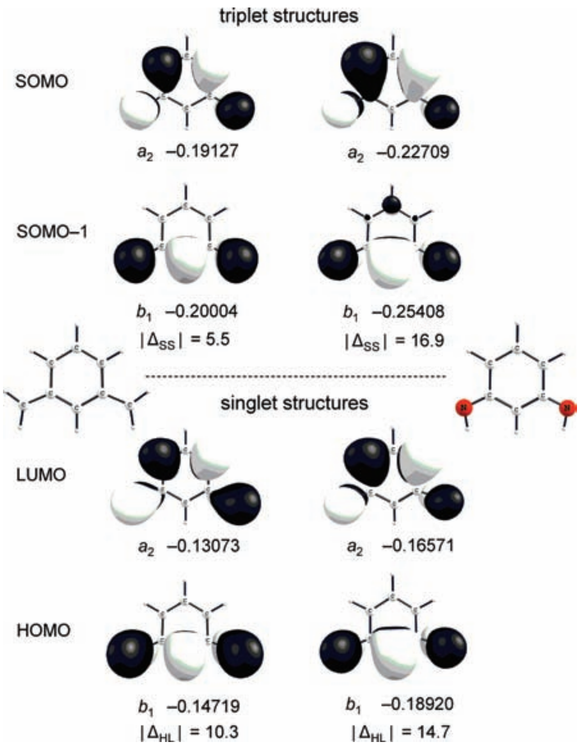
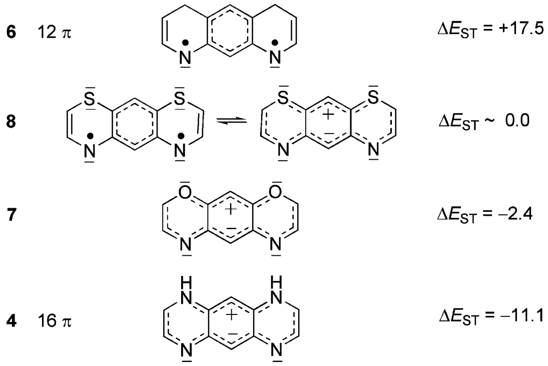


Figure 3. Isosurface plots for the frontier molecular orbitals of singlet and triplet structures of *m*-quinodimethane (left) and the nitrogen-substituted derivative (right). Absolute energies are in au, and relative energies, in kcal mol^{-1}; the contour value is at ±0.03 au.

SCHEME 7: Heteroatom Functionalities at the 1- and 9-Positions Destabilizing of Zwitterionic Ground States (Relative Energies in kcal mol^{-1})



unpaired electrons in the SOMOs both have p-character, and they occupy mutually noninteracting π-orbitals. This trend is in agreement with the observations of Li et al.[31] who described that with decreasing nondisjoint SOMO-coefficients on C^{12} and C^{14} the triplet states are increasingly stabilized in energy. The ΔE_{SS} values for zwitterion **4** and diradical **5** are 30.3 and 18.1 kcal mol^{-1}, respectively.

The computed HOMO−LUMO gap is much smaller in diradicals **5** ($|\Delta_{HL}| = 25.1$ kcal mol^{-1}) and **6** ($|\Delta_{HL}| = 17.6$ kcal mol^{-1}) relative to zwitterions **3** ($|\Delta_{HL}| = 58.3$ kcal mol^{-1}) and **4** ($|\Delta_{HL}| = 49.2$ kcal mol^{-1}). The stabilization for the HOMOs of **3** and **4** can be related to the presence of more electronegative nitrogen atoms involved in the π-delocalization. Thus, a reduction in the number of nitrogen atoms leads to smaller HOMO−LUMO gaps. This is in contrast to results of Winkler and Houk for Kekulé-type azaacenes.[5b] Through replacing N^1 and N^9 with carbon atoms, the molecular orbitals change such that instead of a closed-shell zwitterion a diradical ground state forms.

For comparison, the frontier molecular orbitals of parent *m*-quinodimethane and its nitrogen-substituted diradical are presented in Figure 3. The isosurface plots for the SOMOs of *m*-quinodimethane show no contribution of C^1 in the delocalization. The nitrogen-substituted *m*-phenylene has a small coefficient on C^1 of SOMO−1 and on C^{12} and C^{14} of SOMO. This compound in comparing to *m*-quinodimethane has a larger band gap.

The large exchange coupling constants (J) for diradicals **5** and **6** relative to zwitterions **3** and **4** predict a ferromagnetic exchange mechanism for **5** and **6** (Table 2). Turek et al. have theoretically investigated a series of *m*-phenylene couplers and have shown that the influence of spin polarization and molecular configuration control the exchange coupling constant J.[32]

The singlet and triplet geometries of model systems **3**−**6** are presented in Figure 4. In contrast to larger cyclic compounds and also to monocyclic *m*-phenylene systems containing four separated exocyclic substituents, the conformational mobility of these tricycles is minimal and the radical centers of **5** and **6** are essentially kept in one plane by the condensed terminal rings.

Generally, the singlet states structures show larger dipole moments than their corresponding open-shell structures ($\Delta\mu_{ST} > 0$, Table 1). The $\Delta\mu_{ST}$ values of zwitterions **3** and **4** are much smaller than those of diradicals **5** and **6**. Zwitterions are expected to have larger dipole moments; however, the reverse is true for **3** ($\mu_S = 5.08$ D) and **4** ($\mu_S = 7.91$ D) and also for **5** ($\mu_S = 4.49$ D) and **6** ($\mu_S = 6.26$ D). The reductions in dipole moments of **3** and **5** are due to the presence of electronegative nitrogen atoms at the 2- and 8-positions.

Removal of N^1 and N^9 of **3** giving **5** has a larger effect on the structures than replacing N^2 and N^8 giving **4** (Figure 4). A comparison between the closed-shell structures shows that with an increase of the ΔE_{ST}, the C^3−N^4/N^6−C^7 bonds and N^4−C^{12}/C^{14}−N^6 get longer, while the C^{11}−C^{12} and C^{13}−C^{14} get shorter (1.458 Å in **3** and 1.444 Å in **6**). The alternations between the bond lengths of the central rings are reduced (the largest bond length differences in the central rings of **3** and **6** are 0.064 Å and 0.055 Å, respectively), and the terminal bonds X^2−C^3 and X^8−C^7 become more localized (1.316 Å in **3** and 1.301 Å in **5**).

The zwitterionic structures become increasingly unstable, when the contribution of the nitrogen atoms N^4 and N^6 in the π-delocalization decreases and when the *m*-phenylene rings become more aromatic. The high negative NICS(1) value for the central ring of diradical **6** (−21.9 ppm, Table 2) relative to the *m*-phenylene ring of zwitterion **3** (−2.7 ppm) confirm this.

The NICS(1) values also reveal that the *m*-phenylene rings of zwitterions **3** and **4** are less aromatic than those of the corresponding triplet structures; in contrast, the closed-shell structures of ground state diradicals **5** and **6** are more aromatic in their inner rings.

The NICS(1) value analyses also shows that the substitution pattern significantly affects the aromaticities of *N*-substituted *m*-phenylenes singlets but that it has a much smaller influence on the aromaticities of the corresponding triplets. The C^{11}−C^{12} and C^{13}−C^{14} bonds in all triplet structures are typical aromatic C−C bonds (~1.42 Å). With increasing stabilization of the diradical systems the C^{11}−C^{12} and C^{13}−C^{14} bonds become longer, and the bond length differences in the inner rings increase. These bond length differences in the triplet structures (0.024 Å in **3** to 0.034 Å in **6**) are much smaller than those in the singlets (0.064 Å in **3** to 0.055 Å in **6**).

Heteroatom Functionalities. Different heteroatoms (NH, O, and S) at the 1- and 9-positions of diaza-tricycle **6** were used to determine their ground state multiplicities. Only structure **6** involving carbon atoms at these positions is predicted to have a low-lying triplet ground state. This confirms that π-donor atoms lead to zwitterionic ground state character (Scheme 7 and Table 3).

The ΔE_{ST} values are paralleled by the donor ability of the atoms or groups in the 1- and 9-positions (Scheme 7). The computed large HOMO−LUMO gaps ($|\Delta_{HL}| = 49.2$ for kcal mol^{-1} for **4** and 40.9 kcal mol^{-1} for **7**) and negative magnetic exchange coupling constants ($J = -1949$ cm^{-1} for **4** and −369 cm^{-1} for **7**) are also in the line with high zwitterionic character.

The diradical and zwitterionic isomers of sulfur-doped tricycle **8** reveal energetically degenerate electronic states ($\Delta E_{ST} \sim 0.0$ kcal mol^{-1}), and the exchange coupling constant for this structure is relatively small ($J = +151$ cm^{-1}). The computations predict a HOMO−LUMO gap of 32.9 kcal mol^{-1} and a SOMO−SOMO gap of 20.4 kcal mol^{-1} for this zwitterionic/diradical compound. As Hund's rule hints at an inverse correlation between the ΔE_{ST} and the Δ_{SS} values,[33] Hoffmann et al.[34] on the basis of extended Hückel theory for benzynes diradicals suggested that for $|\Delta_{SS}| < 35$ kcal mol^{-1} (1.5 eV) the ground state is the triplet. Koutentis et al.[22a] noted that for *N*-substituted zwitterions with $|\Delta_{SS}| > 30$ kcal mol^{-1} (1.3 eV) the ground state should be a singlet. On the basis of the computations for zwitterionic/diradical compound **8** ($\Delta E_{ST} \sim 0.0$ kcal mol^{-1}), we suggest a $|\Delta_{SS}| < 20.4$ kcal mol^{-1} (0.9 eV) for the ground state triplet for such compounds.

Increasing Diradical Character by Interruption of Conjugation. By using saturated terminal bonds, the overall number of π-electrons involved in the delocalization is reduced. Two

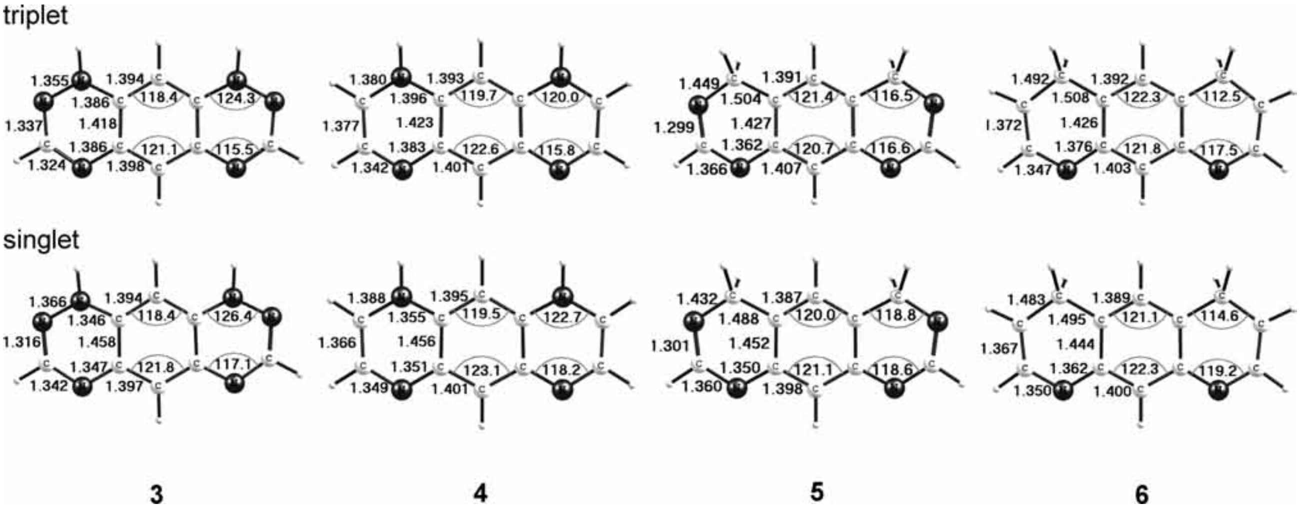
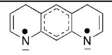
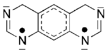
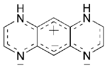
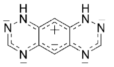


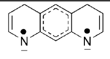
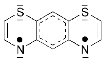
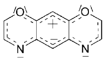
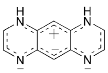
Figure 4. Geometric parameters of non-Kekulé **3**−**6** in singlet (below) and triplet (up) states. Bond lengths are in Å, and angles, in deg.

TABLE 2: NICS(1) Values[a] (ppm) of Inner and Outer Rings and Magnetic Exchange Coupling Constants (cm^{-1})

		GS	$NICS(1)_{in}$ singlet	$NICS(1)_{in}$ triplet	$NICS(1)_{out}$ singlet	$NICS(1)_{out}$ triplet	J
6		diradical	−21.9	−7.5	+10.3	−0.6	+656
5		diradical	−12.2	−6.7	+0.8	−1.3	+421
4		zwitterion	−0.9	−6.4	+5.4	+0.9	−1949
3		zwitterion	−2.7	−7.6	+2.5	−0.4	−3036

[a] The computed NICS(1) values for benzene ring as reference system is −11.1 ppm in the closed-shell (D_{6h}) and +20.6 ppm in the open-shell structure (D_{2h}).

TABLE 3: Singlet-Triplet and First Excited Singlet State Energy Separations as well as Zero Point Vibrational Energies (kcal mol^{-1}), Spin Contaminations, and Dipole Moments (D)

		GS	S_0–T_1[a]	S_0–S_1	ZPVE S_0, S_1	ZPVE T_1	$<S^2>$ S_0	$<S^2>$ S_1	$<S^2>$ T_1	μ_{S0}	μ_{S1}	μ_{T1}	$\Delta\mu_{ST}$
6		diradical	+17.5	+15.5	117.5	117.7	0.00	1.02	2.08	6.26	4.94	4.76	+1.5
8		diradical / zwitterion	+0.4	+0.5	84.7	84.5	0.00	0.00	2.05	4.02	3.98	2.65	+1.4
7		zwitterion	−2.4	−0.2	89.1	88.4	0.00	0.00	2.05	3.71	3.66	2.67	+1.0
4		zwitterion	−11.1	0.0	105.6	104.0	0.00	0.05	2.04	7.91	7.88	7.14	+0.8

[a] Positive value indicates a triplet ground state.

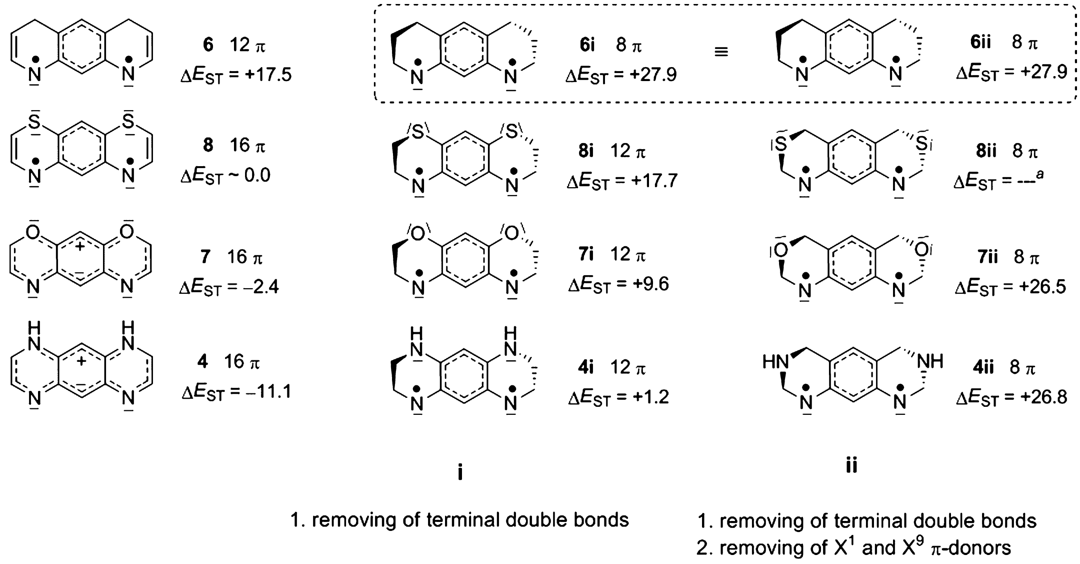
different heteroatomic structural models **i** (12 π-electron species) and **ii** (8 π-electron species) are considered. In Scheme 8, only the trans isomers (C_2 symmetry) are presented, because their ΔE_{ST} values are slightly larger than for the cis isomers.

All new species **i** and **ii** possess triplet ground states. By using saturated terminal bonds, the ΔE_{ST} values increase by about 10 kcal mol^{-1}. The average improvement in the ΔE_{ST} values is much higher for **ii**; for example, the ΔE_{ST} of **4i** is 12.3 kcal mol^{-1} larger than that of **4**, whereas this difference is 3 times larger (37.9 kcal mol^{-1}) between **4ii** and **4**. This indicates that removal of the π-donors at the 1- and 9-positions is more effective to achieve large ΔE_{ST} values than removal of terminal double bonds. The heteroatom functionalities at positions 2 and 8 show no considerable effects on the electronic state energies.

A visualization of the observed trends in the singly occupied molecular orbital changes due to heteroatom substitution and the type of terminal bonds are shown in Figure 5. The electronic states of the singlet closed-shell and triplet open-shell species are ^1A and ^3B, respectively.

The large positive spin coupling constants (J) indicate strong intramolecular ferromagnetic exchange interactions between spin

SCHEME 8: Trend of Increasing Diradical Character by Reduction in Number of Electrons Involved in π-Delocalization (ΔE_{ST} Values in Parentheses in kcal mol^{-1})[a]



[a] ΔE_{ST} is not available for **8ii** because of S^2-C^3 dissociation (1.899 Å) upon optimization in the closed-shell singlet state. This bond length is 1.849 Å in the triplet structure.

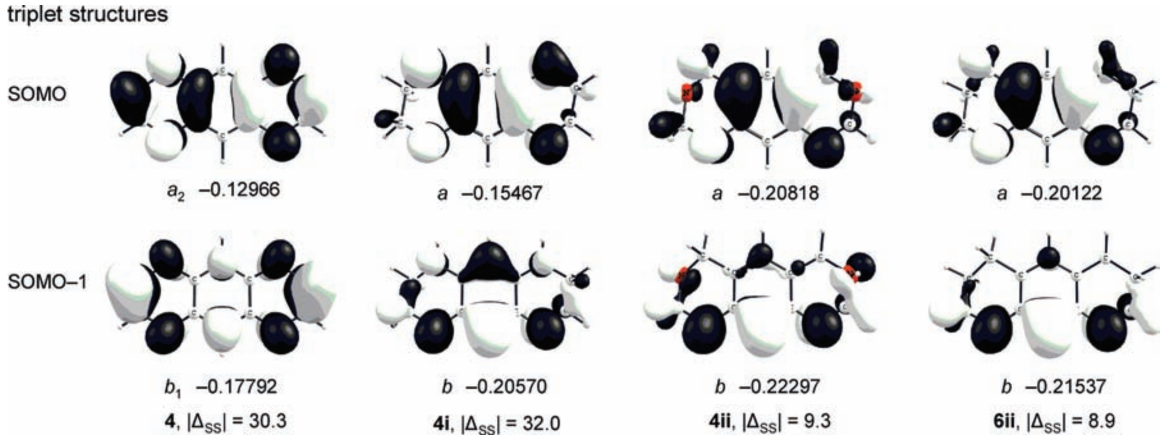


Figure 5. Isosurface plots for the SOMOs of **4**, **4i**, **4ii**, and **6ii**. Absolute energies are in hartree, and relative energies, in kcal mol^{-1}; the contour value is ±0.03 au.

TABLE 4: Singlet-Triplet and First Excited Singlet State Energy Separations as well as HOMO−LUMO Energy Gaps (kcal mol^{-1}), Spin Contaminations, Dipole Moments (D), and Exchange Coupling Constants (cm^{-1})

	S_0-T_1	S_0-S_1	$\langle S^2\rangle$ S_0	$\langle S^2\rangle$ S_1	$\langle S^2\rangle$ T_1	Δ_{HL}	μ_{S0}	μ_{S1}	μ_T	$\Delta\mu_{ST}$	J
6i	+27.9	+20.1	0.00	1.01	2.06	8.6	6.62	4.04	3.90	+2.7	+2281
8i	+17.7	+11.6	0.00	0.97	2.06	16.3	4.64	1.81	1.07	+3.6	+1963
7i	+9.6	+6.4	0.00	0.84	2.06	28.5	4.61	2.87	1.68	+2.9	+902
4i	+1.2	+2.1	0.00	0.57	2.05	36.6	8.74	7.64	5.23	+3.5	−206
8ii	*a*	*a*	*a*	1.01	2.07	*a*	*a*	2.18	2.16	*a*	*a*
7ii	+26.5	+16.8	0.00	0.97	2.07	11.3	5.24	3.04	2.73	+2.5	+3083
4ii	+26.8	+20.0	0.00	1.00	2.07	10.8	5.31	3.04	2.92	+2.4	+2246

[a] The data are not available because of S^2-C^3 dissociation upon optimization in the closed shell singlet state.

sites (Table 4). Structure **4i** with $\Delta E_{ST} \sim 0.0$ kcal mol^{-1} is the only diradical that shows antiferromagnetic coupling in its ground state.

The geometric analyses indicate that the structural model **ii** with smaller torsion angles $N^4-C^{12}-C^{14}-N^6$ (1−5°) show stronger ferromagnetic couplings in comparison with model **ii** (9−19°). Previously, computational studies by Zhang and coworkers suggested that *m*-xylylene coupling units under distortion from planarity show weak ferromagnetic interactions.[35]

Conclusions

We concentrate in this work on the factors that determine the ground state multiplicities of linear conjugated cyclic diradicals containing *N*-spin-centers akin to *m*-phenylene using DFT computations. To maximize the diradical character of such systems, full cyclic conjugation should be avoided to disallow the interactions of the spin centers. π-Donor atoms at the 1- and 9-positions para to the N^6 and N^4 spin centers introduce pronounced zwitterionic character due to cross-conjugation.

Replacing of X^1 and X^9 π-donors with $-CH_2-$ moieties causes smaller SOMO densities on C^{12} and C^{14} and a smaller SOMO-1 coefficient on C^{10}, thereby reducing the contributions of zwitterionic cyanine ribbons. Terminal double bonds or aromatic fused rings decrease the stabilities of the diradical species; however, this effect on the electronic states is much smaller than the presence of π-donor atoms at the 1- and 9-positions. Tricyclic models with overall 12 π-electrons or less possess triplet ground states. In non-Kekulé structures the smaller number of electronegative heteroatoms causes larger ΔE_{ST} values, which the opposite of their Kekulé counterparts. Taken together, our analysis yields a triplet ground state for pyridoquinoline **6ii** that is 27.9 kcal mol^{-1} lower in energy than the zwitterionic singlet state. This energy gap is close to the ΔE_{ST} of parent *m*-quinodimethane (+29.9 kcal mol^{-1} at the same level of theory), indicating an upper limit of this energy separation.

The preparation of the most promising compounds identified in the present study are now underway in our laboratories.

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Supporting Information Available: Computed optimized geometric parameters and energies for all species. This material is available free of charge via the Internet at http://pubs.acs.org.

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