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Ab Initio Quantum Chemical Investigation of the Spin States of Some Fused Ring Systems

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The ground-state spins of seven diradicals belonging to the fused ring system have been investigated by ab initio restricted and unrestricted formalisms. The systems under study are (**1**) 4-oxy-2-naphthalenyl methyl, (**2**) 1,8-naphthalenediylbis(methyl), (**3**) 8-imino-1-naphthalenyl methyl, (**4**) 1,8- naphthalenediylbis(amidogen), (**5**) 8-methyl-1-naphthyl carbene, (**6**) 8-methyl-1-naphthalenyl imidogen, and (**7**) 8-methyl-1-naphthyl diazomethane. Out of the seven molecules, only **1** was theoretically investigated earlier. To our knowledge, for **2**−**7**, this work represents the first ab initio investigation. A variety of basis sets have been employed in these calculations. For each spin state, the molecular geometry has been fully optimized at the unrestricted Hartree−Fock (UHF) level using the STO-3G, 4-31G, 6-311G(d), and 6-311G(d,p) basis sets. The UHF optimized geometries have been used for Møller−Plesset (MP) and coupled cluster (CC) calculations as well as the density functional (UB3LYP) treatment. Results in the unrestricted formalism have been given only at UHF and UB3LYP levels for the 6-311G(d) basis. The UHF calculations yield an unrealistically large singlet−triplet (S−T) splitting. Splittings calculated with different bases disagree seriously. The S−T gap is smaller in the split-valence bases. The basis set truncation error can be considerably overcome by calculations involving electron correlation. For these diradicals, any meaningful result would require larger bases with polarization functions. Apart form this difficulty, the optimized geometry turned out to be highly spin-contaminated. The spin-contamination can be significantly reduced by the density functional UB3LYP treatment. Nevertheless, for most of the diradicals, the UB3LYP method did not yield a systematic trend. To avoid spin contamination completely, we have repeated computations in the restricted (open-shell) Hartree−Fock framework. Geometry optimizations were carried out using STO-3G, 6-311G(d), and 6-311G(d,p) bases at the R(O)HF level and 6-311G(d,p) basis at the R(O)B3LYP level for each spin state. The R(O)B3LYP/6-311G(d,p) optimized geometry yields the best total energy for each spin state and hence the most reliable S−T energy difference. Molecules **1**−**6** are found as ground-state triplets. The calculated results are in agreement with the available experimental findings. Molecules **3** and **7** have widely different geometries in the singlet and triplet states. The calculations using 6-311G(d) and 6-311G(d,p) basis sets show that in molecule **3** the substituents of naphthalene are $-NH_2$ and $-CH$ in singlet but $-NH$ and $-CH_2$ in triplet. The two optimized geometries are tautomeric forms. Molecule **7** is expected to be either a ground-state triplet with a very little S−T gap or a ground-state singlet. This prediction is borne out by the computed results. The R(O)B3LYP/6-311G(d,p) calculation yields a S−T splitting of -21.9 kcal mol^{-1}. The singlet state becomes stabilized by forming an additional condensed ring. The UHF spin density plots obtained from the 4-31G optimized geometries manifest the phenomenon of spin alternation in the ground state.

1. Introduction

Non-Kekulé hydrocarbons are known to be diradicals and highly reactive.[1] The presence of degenerate nonbonding molecular orbitals (NBMOs) is responsible for their extraordinary reactivity.[2] A singlet ground-state results when the degeneracy is spoiled. In fact, Hoffmann has shown that when the NBMOs differ by less than 1.5 eV the ground state is a triplet.[3] It is also well-known that a change of the symmetry or a variation of the electronegativity of the diradical termini can be used to control the spin multiplicity in the ground state.[4] These multiplicities can be reliably predicted by ab initio post-Hartree−Fock treatments using large basis sets.[5]

In a previous paper, we have reported the spin nature of the ground states of nine diradicals, four of which are branched chain species and five are monocyclic radicals.[6] In this work, we use ab initio methods to characterize the ground-state spin multiplicity of seven diradicals sharing the naphthalene skeleton. Among these molecules, one (**1**) is a 1,3-substituted naphthalene and the rest (**2**−**7**) are 1,8-substituted naphthalene derivatives. Molecule **1** has two radical centers attached to the same ring, whereas three (**2**−**4**) are species with two radical centers attached to different rings. Each of the species **5** and **6** has one diradical center attached to only one of the rings, whereas **7** has again two radical centers, one on an atom attached to one ring and the other on one of the atoms not directly attached to the other ring. The molecules are explicitly as follows: (**1**) 4-oxy-2-naphthalenyl methyl, (**2**) 1,8-naphthalenediylbis(methyl) or 1,8-naphthaquinodimethane (1,8-NQM), (**3**) 8-imino-1-naphthalenyl methyl, (**4**) 1,8-naphthalenediylbis(amidogen), (**5**) 8-methyl-1-naphthyl carbene, (**6**) 8-methyl-1-naphthalenyl imidogen, and (**7**) 8-methyl-1-naphthyl diazomethane, as shown in Figure 1. Out of these, **2** and **5** are derivatives with homonuclear substituents, and **1**, **3**, **4**, **6**, and **7** have heteroatom

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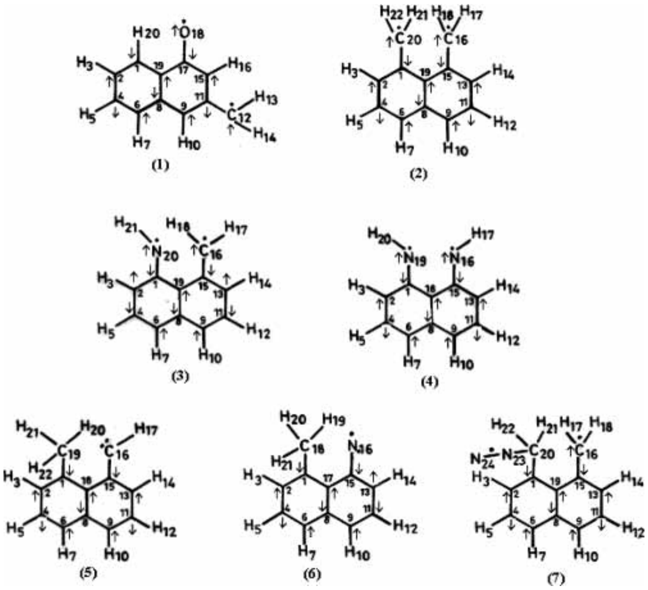

Figure 1. Species investigated in this work: (**1**) 4-oxy-2-naphthalenyl methyl, (**2**) 1,8-naphthalenediylbis(methyl) or 1,8-naphthaquinodimethane (1,8-NQM), (**3**) 8-imino-1-naphthalenyl methyl, (**4**) 1,8-naphthalenediylbis(amidogen), (**5**) 8-methyl-1-naphthyl carbene, (**6**) 8-methyl-1-naphthalenyl imidogen, and (**7**) 8-methyl-1-naphthyl diazomethane.

substituents. These non-Kekulé diradicals exhibit very high reactivity.[4] The species 4-oxy-2-naphthalenyl methyl (**1**) was observed by ESR.[7] Although plausible zwitterionic singlet structures may be drawn for species **1**, a Curie law analysis showed that it has a triplet ground state.[4] Molecule 1,8-naphthalenediylbis(methyl) (**2**) was observed by Pagni et al.[8] using the triplet ESR spectrum. The molecule was postulated to be a ground-state triplet.[4] Fritz et al. also confirmed the triplet ground state by ESR study. INDO calculations for the planar, anti-conformation of 8-imino-1-naphthalenyl methyl (**3**) have been carried out by Platz et al.[4] Molecule 1,8-naphthalenediylbis(amidogen) (**4**) was observed by Platz et al.[4] from ESR and subsequent Curie law plot. The species 8-methyl-1-naphthyl carbene (**5**) was prepared by the photochemical reaction of 8-methyl-1-naphthyl diazomethane at 4 K. Platz et al.[4] predicted molecule **5** to be a ground-state triplet based on the observation of 1-naphthyl carbene to be a ground-state triplet by Trozzolo et al.[9] The species 8-methyl-1-naphthalenyl imidogen (**6**) was matrix isolated by Platz and Burns.[10] Diradical **2** can be prepared through the intermediate formation of **7**.

An accurate calculation of the multiplet splittings in non-Kekulé systems is a challenging task. Based on the calculations on trimethylene methane (TMM), Borden, Davidson, and Feller[11] had initially shown that the restricted (open-shell) Hartree−Fock [R(O)HF] and two-configuration self-consistent-field (TCSCF) calculations generally fail to produce the correct relative energies and geometries although they may provide qualitatively correct molecular orbitals for the two open-shell electrons in diradicals. This is a result of the so-called doublet instability problem in RHF which is most severe when the basis set is small. Hence, these authors advocated the use of the unrestricted Hartree−Fock (UHF) methods for a reasonably correct description of triplet and open-shell singlet geometries. In this area, the most detailed investigations were carried out by Cramer and Smith,[12a] Nachtigall and Jordan,[13c] and Mitani et al.[14h] on the molecules TMM, tetramethylene ethane (TME), and *m*-xylylene, respectively. They all concluded that the singlet−triplet energy differences are highly sensitive to the methodology and the rigor (basis set) employed in the calculations. The most widely studied diradical systems are TMM,[12a−k] TME,[13a−j] *m*-xylylene,[14a−k] polycyclic π-conjugated hydrocarbon polymers,[15a−l] nitroxy radicals,[16] and biphenylene radicals.[17] A number of other diradicals containing π electrons have been described by theoretical[15−25] and experimantal[26a,b] methods.

Species **1**−**4** and **6** in Figure 1 were shown (and **5** was predicted) to be triplet in the ground state. [4,7−10,12d,e,13h,14j,27a−i] Species **7** is an exception. The traditional view of the chemist would be to put one lone electron on the $-CH_2$ substituent and the other on the two nitrogen atoms of the substituent $-CH_2N_2$ in **7**. This would indicate, by the rule of spin alternation,[16] that molecule **7** should be a ground-state singlet or at best a ground-state triplet with very little singlet−triplet energy gap. The main objective of this work is to confirm these observations and generate quantitative data for the S−T energy gap. The present paper is organized in the following way. The method of calculations is described in section 2. Energy differences between the states of different spin multiplicities are given in section 3. Spin alternation in UHF is discussed in section 4. Our conclusions follow in section 5.

2. Methodology

In this paper, we deal with diradical systems that are fairly large in size, and a complete geometry optimization is required for each species in each spin state at both UHF and R(O)HF levels. The STO-3G, 4-31G, 6-311G(d), and 6-311G(d,p) basis sets have been employed in these calculations using the software Gaussian 98 on Windows (G98W),[28] but only the 6-311G(d) and 6-311G(d,p) results are explicitly shown here. Density functional (DFT) calculations have been performed by both UB3LYP and R(O)B3LYP methods while using some of the above-mentioned basis sets. For the post-Hartree−Fock calculations at the unrestricted coupled-cluster UCCSD and UCCSD(T) levels as well as the unrestricted density functional treatment at UB3LYP level, the UHF-optimized geometry has been used for each species in each spin state. The coupled cluster calculations get the sign right and never overestimate the gap. Sometimes the underestimate is serious. All values of the spin-squared expectation value (which should be 2.0) fall in a narrow range 3.2−3.5. Therefore, the coupled-cluster results are included in the Supporting Information. A complete geometry optimization was carried out at the DFT level only in the restricted formalism using the R(O)B3LYP method. The computed energy differences for the singlet and triplet spin states for the systems are discussed in section 3.

A correct description of low-lying singlet and triplet states requires the proper treatment of both static and dynamic correlation energy. The choice of UCCSD and UCCSD(T) post-Hartree−Fock treatments for the present set of calculations is quite reasonable from this standpoint. Using *m*-xylylene, Mitani et al.[14h] showed that the triplet state tends to overstabilize relative to the singlet in a simple UHF calculation, whereas Møller−Plesset (MP) perturbation calculations result in the singlet state being much more stable than the triplet. We have observed the same trends in our previous work[6] as well as in the present work. Due to the near degeneracy of more than one UHF wave function, the MP perturbation theory fails to yield correct results for diradical species. The zeroth-order UHF Hamiltonian is not properly represented in such cases, thereby decreasing the credibility of the ensuing perturbation-theoretic expansion. Coupled-cluster (CC),[14h] multiconfiguration self-consistent-field (MCSCF)[12a,13c] and complete active space perturbation theory (CASPT2N)[12a] methodologies treat correlation in a more sensible way, and by employing these calculational procedures

TABLE 1: (a) Ab Initio Total Energy and the Optimized Geometry for the Spin States of 4-Oxy-2-naphthalenyl Methyl (1) in the Unrestricted Hartree−Fock Formalism and (b) Bond Lengths and Bond Angles in Molecule 1 with Geometry Optimized at R(O)B3LYP/6-311G(d,p) Level[a]

(a)

basis set	method	optimization[b]	molecular geometry S	molecular geometry T	E(T) in a.u.	$\langle S^2\rangle_T$	E(S) − E(T) in kcal mol^{-1}
6-311G(d)	UHF	O	C_s	C_s	−496.1265	3.1744	39.1
	UB3LYP	SP	C_s	C_s	−499.2106	2.0414	−14.7
6-311G(d)	R(O)HF	O	C_s	C_s	−496.0855	2.0000	13.3
6-311G(d,p)	R(O)HF	O	C_s	C_s	−496.1270	2.0000	30.3
6-311G(d,p)	R(O)B3LYP	O	C_s	C_s	−499.2665	2.0000	9.7
6-31G*	CASSCF[c]	O	C_s	C_s	−496.1703	2.0000	14.2
6-31G*	CASPT2N[c]	O	C_s	C_s	−497.6266	2.0000	11.6

(b)

bond (Å)	singlet	triplet	angle (deg.)	singlet	triplet
C_1-C_2	1.382	1.390			
C_2-C_4	1.419	1.402	$H_{20}-C_1-C_2$	122.3	121.5
C_4-C_6	1.367	1.383	$C_1-C_2-H_3$	119.8	120.1
C_6-C_8	1.435	1.415	$C_6-C_4-H_5$	120.5	119.8
C_8-C_9	1.383	1.420	$H_7-C_6-C_4$	120.9	120.3
C_9-C_{11}	1.453	1.424	$H_{10}-C_9-C_{11}$	119.3	118.8
$C_{11}-C_{12}$	1.374	1.402	$C_9-C_{11}-C_{12}$	114.7	121.7
$C_{12}-H_{13}$	1.085	1.082	$H_{13}-C_{12}-H_{14}$	117.3	118.0
$C_{12}-H_{14}$	1.084	1.082	$H_{13}-C_{12}-C_{11}$	121.4	120.8
$C_{11}-C_{15}$	1.414	1.414	$H_{16}-C_{15}-C_{17}$	118.1	116.2
$C_{15}-C_{17}$	1.423	1.445	$C_{15}-C_{17}-O_{18}$	126.0	121.1
$C_{17}-O_{18}$	1.239	1.237			
C_8-C_{19}	1.442	1.442			

[a] S and T indicate singlet and triplet, respectively. Both singlet and triplet are of symmetry C_s. [b] O = optimization; SP = single-point calculation. [c] Reference 27h.

TABLE 2: (a) Ab Initio Total Energy and the Optimized Geometry for the Spin States of 1,8-Naphthalenediylbis(methyl) (2) and (b) Bond Lengths and Bond Angles in Molecule 2 with Geometry Optimized at the R(O)B3LYP/6-311G(d,p) Level[a]

(a)

basis set	method	optimization[a]	molecular geometry S	molecular geometry T	E(T) in a.u.	$\langle S^2\rangle_T$	E(S) − E(T) in kcal mol^{-1}
6-311G(d)	UHF	O	C_{2v}	C_{2v}	−460.2974	3.1408	37.8
	UB3LYP	SP	C_{2v}	C_{2v}	−463.3069	2.0938	16.1
6-311G(d)	R(O)HF	O	C_{2v}	C_{2v}	−460.2328	2.0000	37.8
6-311G(d,p)	R(O)HF	O	C_{2v}	C_{2v}	−460.2516	2.0000	37.8
6-311G(d,p)	R(O)B3LYP	O	C_{2v}	C_{2v}	−463.3178	2.0000	9.4

(b)

bond (Å)	singlet	triplet	angle (deg.)	singlet	triplet
C_1-C_2	1.430	1.429			
C_2-C_4	1.385	1.383			
C_4-C_6	1.383	1.380	$C_{20}-C_1-C_2$	114.5	114.2
C_6-C_8	1.419	1.420	$C_1-C_2-H_3$	117.0	117.2
C_8-C_9	1.419	1.420	$C_6-C_4-H_5$	121.0	120.6
C_9-C_{11}	1.383	1.380	$H_7-C_6-C_4$	121.0	120.7
$C_{11}-C_{13}$	1.385	1.383	$H_{10}-C_9-C_{11}$	121.0	120.7
$C_{13}-C_{15}$	1.430	1.429	$C_9-C_{11}-H_{12}$	121.0	120.6
$C_{15}-C_{16}$	1.391	1.397	$C_{15}-C_{13}-H_{14}$	117.0	117.2
$C_{16}-H_{17}$	1.083	1.083	$C_{13}-C_{15}-C_{16}$	114.5	114.2
$C_{16}-H_{18}$	1.070	1.072	$H_{17}-C_{16}-H_{18}$	115.9	115.7
$C_{15}-C_{19}$	1.458	1.465	$H_{21}-C_{20}-H_{22}$	115.9	115.7
C_1-C_{19}	1.458	1.465	$H_{17}-C_{16}-C_{15}$	118.2	118.1
C_1-C_{20}	1.391	1.397	$C_1-C_{20}-H_{22}$	118.2	118.1
$C_{20}-H_{21}$	1.069	1.072			
$C_{20}-H_{22}$	1.083	1.083			
C_8-C_{19}	1.421	1.438			

[a] S and T indicate singlet and triplet, respectively. Both singlet and triplet are of symmetry C_{2v}. [a] O = optimization; SP = single-point calculation.

with progressively higher level of sophistication, one can overcome the problem of one state being relatively more stabilized than the other. The importance of these methodologies can be visualized from Table 2 in ref 12a (for MCSCF and CASPT2N), Table 3 in ref 13c (for MCSCF), and Table 3 in ref 14h (for CC). Using TMM, Cramer and Smith[12a] also demonstrated the restrictive nature of the density functional treatment (DFT).

TABLE 3: (a) Ab Initio Total Energy and the Optimized Geometry for the Spin States of 8-Imino-1-naphthalenyl Methyl (3) and (b) Bond Lengths and Bond Angles in Molecule 3 with Geometry Optimized at the R(O)B3LYP/6-311G(d,p) Level[a]

(a)

basis set	method	optimization[a]	molecular geometry S	molecular geometry T	E(T) in a.u.	$\langle S^2\rangle_T$	E(S) − E(T) in kcal mol^{-1}
6-311G(d)	UHF	O	C_s	C_s	−476.3133	3.1359	63.3
	UB3LYP	SP	C_s	C_s	−479.3636	2.0931	24.3
6-311G(d)	R(O)HF	O	C_s	C_s	−476.2455	2.0000	20.8
6-311G(d,p)	R(O)HF	O	C_s	C_s	−476.2638	2.0000	19.9
6-311G(d,p)	R(O)B3LYP	O	C_s	C_s	−479.3741	2.0000	16.4

(b)

bond (Å)	singlet	triplet	angle (deg.)	singlet	triplet
C_1-C_2	1.403	1.440			
C_2-C_4	1.398	1.379			
C_4-C_6	1.375	1.387	$N_{20}-C_1-C_2$	120.9	120.6
C_6-C_8	1.418	1.422	$C_1-C_2-H_3$	118.1	117.1
C_8-C_9	1.415	1.418	$C_6-C_4-H_5$	120.3	120.2
C_9-C_{11}	1.382	1.384	$H_7-C_6-C_4$	121.5	120.2
$C_{11}-C_{13}$	1.392	1.384	$H_{10}-C_9-C_{11}$	119.6	120.7
$C_{13}-C_{15}$	1.414	1.427	$C_9-C_{11}-H_{12}$	120.5	120.3
$C_{15}-C_{16}$	1.425	1.399	$C_{15}-C_{13}-H_{14}$	117.5	117.4
$C_{16}-H_{17}$	1.103	1.084	$C_{13}-C_{15}-C_{16}$	119.7	117.0
$C_{16}-H_{18}$	1.858	1.076	$H_{17}-C_{16}-H_{18}$	152.0	119.6
$C_{15}-C_{19}$	1.457	1.453	$C_{15}-C_{16}-H_{17}$	108.1	118.4
C_1-C_{19}	1.442	1.473	$H_{21}-N_{20}-C_1$	119.5	109.1
C_1-N_{20}	1.355	1.317			
$N_{20}-H_{21}$	1.006	1.022			
C_8-C_{19}	1.433	1.431			
$N_{20}-H_{18}$	1.037	2.150			

[a] S and T indicate singlet and triplet, respectively. Both singlet and triplet are of symmetry C_s. [a] O = optimization; SP = single-point calculation.

The unrestricted methods such as UHF, UCCSD, UCCSD(T), etc. introduce some bias due to spin contaminations. It was seen that in all the cases the triplet state UHF optimized geometry had the S^2 expectation value around 3.2 instead of 2.0. Such large deviations in the $\langle S^2\rangle$ values raise questions on the reliability of predictions made using the highly spin-contaminated geometries. There are special methods such as multireference coupled-cluster or nonstandard version of DFT, which are able to treat such systems reliably, concerning the interplay of static and dynamic correlation effects. However, these calculations often require a large amount of data handling and prolonged CPU hours, and their usage seems to have been restricted to the investigation of molecules such as F_2, N_2, HF, HCHO, C_2H_4, and C_6H_8[29a−f] that are much smaller than the systems under consideration here. Therefore, we had to combine an optimally high level of methodology with a suitably large basis set. Because of the problem of an excessively large read−write scratch file in CCSD(T) calculations, the DFT calculations become more reliable. The latter also lead to a vastly reduced spin contamination. Nevertheless, the DFT calculations are generally considered to be more trustworthy in bases larger than STO-3G and 4-31G. Fortunately, these calculations could be performed on the present systems using larger basis sets, namely, 6-311G(d) and 6-311G(d,p), which include polarization functions.

The reason to perform computations in the restricted formalism is to correct the effect of the spin-contaminated geometries in predicting the S−T gaps. Geometry optimization was carried out at the STO-3G, 6-311G(d), and 6-311G(d,p) level using the R(O)HF methodology and at the 6-311G(d,p) level using the R(O)B3LYP methodology. Again, the STO-3G results are incorporated in the Supporting Information.

The time taken for the geometry optimization at the R(O)HF and UHF levels varied from 30 min to 6 CPU hours depending on the molecule, whereas the single point energy calculations at the post-Hartree−Fock level took 3−16 CPU hours for each molecule in each spin state on a Pentium III Xeon Server having 2 GB RAM with Windows 2000 Server as the operating system. Each R(O)B3LYP geometry optimization took about 1−11 CPU hours.

The software HyperChem[30] has been used to get the spin density plots. These contour diagrams can be used to test the spin alternation in UHF, which is discussed in section 4.

3. Energy Differences

Ab initio calculations on species **1**−**7** were performed at various levels, namely, UHF, R(O)HF, UB3LYP, R(O)B3LYP, UCCSD, and UCCSD(T), by employing STO-3G, split-valence as well as a few polarized basis sets. In every case, the singlet−triplet energy gap varies with the rigor of calculation as well as the basis set, and this observation is in agreement with the trends noticed earlier in refs 6, 12a, 13c, and 14h. The UHF methodology generally yields the spin-contaminated geometry, and fails to give the correct singlet−triplet energy gap. As the level of calculation increases, this gap generally converges. For reasons discussed in the previous section, results at the MP level and the UCCSD(T) calculations have not been shown here. As the split-valence basis set imparts a greater variational freedom, we expect the general trend

$$\text{UB3LYP/STO-3G} > \text{UCCSD(T)/STO-3G} > \text{UB3LYP/4-31G} > \text{UCCSD(T)/4-31G} \quad (1)$$

for the S−T gaps. The 6-311G(d) basis sometimes increases and sometimes decreases the energy difference from the 4-31G level. This makes the use of the unrestricted formalism for the calculation of the S−T energy difference somewhat uncertain, unless it is backed by coupled-cluster or perturbation calculations.

Cramer and Smith have demonstrated that the DFT methodology cannot adequately account for the static correlation effects in closed-shell singlets in the limit of degenerate frontier molecular orbitals, where one would expect multi-configurational behavior. The DFT breakdown is expected for molecules **2**, **4**, and **6**. However, for species **4**−**6**, the energy gap has been found to have the trend UB3LYP/4-31G > UCCSD(T)/STO-3G, whereas for **1** and **7**, the trend is UB3LYP/4-31G < UCCSD(T)/4-31G. This again imposes a restriction on the reliability of the energy gaps computed by the UB3LYP method. As a result, the discussion of the calculated results varies from one molecule to another.

One also expects, and observes, the following trend for the S−T gaps:

$$\text{R(O)HF/STO-3G} > \text{R(O)HF/6-311G(d)} > \text{R(O)HF/6-311G(d,p)} > \text{R(O)B3LYP/6-311G(d,p)} \quad (2)$$

The singlet and triplet total energies are seen to follow the trend:

$$\begin{aligned}&\text{R(O)HF/STO-3G} > \text{UHF/STO-3G} > \text{UCCSD/STO-3G} \sim \text{UCCSD(T)/STO-3G} > \\ &\text{UB3LYP/STO-3G} > \text{UHF/4-31G} > \text{UHF/6-311G(d)} > \text{UCCSD/4-31G} \sim \text{UCCSD(T)/4-31G} \sim \\ &\text{R(O)HF/6-311G(d)} \sim \text{R(O)HF/6-311G(d,p)} > \text{UB3LYP/6-311G(d)} > \text{R(O)B3LYP/6-311G(d,p)} \quad (3)\end{aligned}$$

Hence the R(O)B3LYP/6-311G(d,p) calculations invariably give the best results in our work.

In the present work, we have obtained small and realistic values of the S−T energy gaps. The latter are the possible outcome of the complete geometry optimization required in this work. What happens is that the singlet structures are often curiously distorted even when the overall symmetry is C_s or C_{2v}. This results in a greater relative stability of the singlet. In our earlier work[6] too, we found that symmetry breaking leads to a realistically small energy difference. A similar situation holds here, except that the molecules considered in this work are not highly symmetric ones.

3.1. 4-Oxy-2-naphthalenyl Methyl. The molecule 4-oxy-2-naphthalenyl methyl (**1**) is planar with C_s symmetry in both singlet and triplet states. Table 1a shows the energy values computed by the restricted and the unrestricted formalisms, the S^2 expectation value in the triplet state, and the point group. The table also reveals whether the geometry was optimized or not. Table 1b gives the optimized bond lengths and bond angles at the R(O)B3LYP/6-311G(d,p) level. In all calculations on this species, except the UB3LYP/6-311G(d) one, the triplet is found to be the ground state. The best energy gaps obtained by our calculations, 10.5 kcal mol^{-1} at UCCSD(T)/4-31G level and 9.7 kcal mol^{-1} at the R(O)B3LYP/6-311G(d,p) level are in strong agreement with the CASPT2N/6-31G* energy gap (11.6 kcal mol^{-1}) reported by Hrovat et al.[27h] The latter authors found the gap to be 2.3 kcal mol^{-1} greater than that for 3-methylene phenoxyl at the CASPT2N/6-31G* and CASSCF/6-31G* level of calculations. The calculated gap for 3-methylene phenoxyl using the UCCSD(T) method is 9.73 kcal mol^{-1} for the STO-3G basis set and 8.44 kcal mol^{-1} for 4-31G basis set.[6] Thus the gap calculated for **1** is about 1.8 kcal mol^{-1} greater than the gap for 3-methylene phenoxyl at UCCSD(T)/STO-3G level and 2.1 kcal mol^{-1} greater at the UCCSD(T)/4-31G level, which more or less agrees with the observation of Hrovat et al.[27h]

It is observed that the UB3LYP/STO-3G splitting is larger (16.1 kcal mol^{-1}), whereas the 4-31G calculation yields a much smaller gap (8.5 kcal mol^{-1}). This follows the general trend described in relation (1). Nevertheless, the UB3LYP/4-31G gap is too small and it has been somehow underestimated. However, the R(O)B3LYP calculations using a larger basis set including polarization functions yields a more realistic S−T energy gap. Lahti et al.[12e] performed INDO−S/CI calculation on this species and reported a singlet−triplet energy difference of 17.0 kcal mol^{-1}. They also concluded that the combination of MNDO−UHF and INDO−CISD computations are effective in predicting not only the geometries but also the relative energies for the spin states of diradicals. Goodman and Kahn[27i] estimated, by using photoacoustic calorimetry, that the energy difference is about 18.5 kcal mol^{-1}. However, the calculations by Hrovat et al.[27h] and those presented here indicate that this number is likely to be an overestimation.

Three points that clearly emerge are as follows: (i) For this system, UCCSD/STO-3G level of calculation yields a singlet−triplet gap of the same order as that predicted by a CASSCF/6-31G* calculation, and the UCCSD(T)/STO-3G gap is comparable to the gap from a CASPT2N/6-31G* calculation; (ii) The 4-31G UCCSD and UCCSD(T) total energies appear to be superior than the 6-31G* CASSCF and CASPT2N values; (iii) The B3LYP calculation yields a relatively good result in the restricted formalism while the basis set includes polarization functions.

From their work, Hrovat et al.[27h] identified C9 and C11 as the main radical centers, and C17 presumably has a double bond with O18. Thus, it is expected that the major changes in bond length and bond angle would involve C9, C11, C12, C15, and C17. Table 1b that lists the R(O)B3LYP/6-311G(d,p) bond lengths and bond angles shows that the major difference of the singlet structure from the triplet one occurs with the bond lengths C8−C9, C9−C11, C11−C12, and C15−C17 and the bond angles C9−C11−C12, H16−C15−C17, and C15−C17−O18. These distortions relatively stabilize the singlet structure and reduce the S−T energy gap.

A specific comparison of the R(O)B3LYP geometries with the CAS(12,12) geometries of ref 27h is possible. The R(O)-B3LYP estimate of the important C9−C11 and C17−O8 distances (1.453 Å and 1.239 Å in the singlet; 1.424 Å and 1.237 Å in the triplet) seems all the more plausible in the following way. The CAS(4,4)/4-31G* calculations yield 1.445 and 1.233 Å in the singlet and 1.373 and 1.355 Å in the triplet, whereas the CAS(12,12) calculations of Hrovat et al.[27h] indicate 1.489 and 1.216 Å in the singlet and 1.427 and 1.226 Å in the triplet. Thus, the larger-CAS geometries progressively come closer to the R(O)B3LYP geometry. This trend was pointed out by one of the reviewers of this paper.

For the other molecules too, the computed results have been given in the same fashion, that is, for molecule *n*, Table *n*a shows the results from the unrestricted and the restricted formalisms, and Table *n*b shows the R(O)B3LYP/6-311G(d,p) geometrical features.

3.2. 1,8-Naphthalenediylbis(methyl). The molecule 1,8-naphthalenediylbis(methyl) (**2**) has C_{2v} symmetry in both singlet and triplet states. In all of the calculations performed here the triplet has emerged as the ground electronic state (Table 2a), which agrees with the observation of Platz et al.[4] and Pagni et al.[8] The molecule seems to be a prime candidate for the DFT breakdown, but its NBMOs take part in π−orbital formation, thereby making the system simultaneously planar and stable. Hence relation (1) is properly followed for this molecule. The R(O)B3LYP method yields the best result for the singlet−triplet splitting (9.4 kcal mol^{-1}).

The singlet and triplet bond lengths and bond angles are shown in Table 2b. The distance slightly varies for C15−C16, C15−C19, C1−C19, C1−C20, and C8−C19 bonds. The C8−C19 bond length is 1.421 Å in singlet and 1.438 Å in triplet. For the rest of the molecule, the singlet and the triplet optimized geometries do not differ significantly.

3.3. 8-Imino-1-naphthalenyl Methyl. The species 8-imino-1-naphthalenyl methyl (**3**) is a planar molecule with C_s point group in both singlet and triplet states. Table 3a shows the computed singlet−triplet energy gap by different methodologies. The molecule is found to be a ground-state triplet in accordance with the observation of Platz et al.,[4] who relied on INDO calculations. The INDO method, however, is grossly inadequate to give rise to the correct S−T splitting. The splitting calculated by Platz et al.[4] was 60 kcal mol^{-1}. The S−T energy gap follows the trends mentioned earlier, and the best value calculated in the present work is 16.4 kcal mol^{-1} [R(O)B3LYP/6-311G(d,p)]. The two substituents on the naphthalene ring (−CH$_2$ and −NH) are of an entirely different nature. The methylene NBMO is mixed with the π orbitals. The −NH group has the lone electron in a σ orbital. The most remarkable point about the optimized geometries is that the singlet has −NH$_2$ and −CH substituents whereas the triplet has −NH and −CH$_2$ substituents.

The optimized bond lengths and bond angles found by the R(O)B3LYP/6-311G(d,p) method are given in Table 3b. There are large changes in bond lengths and bond angles as observed for C1−C2, C2−C4, C4−C6, C13−C15, C15−C16, C16−H18, C1−C19, C1−N20, and especially N20−H18 bonds, and H17−C16−H18, C15−C16−H17, and H21−N20−C1 angles. One may notice from the change in the angles that the nitrogen is in the state of sp^2 hybridization in singlet and sp^3 hybridization in triplet whereas the substituent carbon is in sp^3 hybridization in singlet and sp^2 hybridization in triplet. Thus, the optimized singlet and triplet geometries are in reality tautomeric forms. Incidentally, this observation has been made from UHF/6-311G-(d), ROHF/6-311G(d), and ROB3LYP/6-311G(d,p) geometry optimizations. The two structures are shown in Figure 2a.

3.4. 1,8-Naphthalenediylbis(amidogen). The molecule 1,8-naphthalenediylbis(amidogen) (**4**) is a symmetric molecule with C_{2v} optimized geometry in each spin state. The triplet state is found to be the overall ground state at each level of calculation. However, when dealing with such systems, one cannot rely fully on nonpolarized bases. The molecule appears to be a prime candidate for DFT breakdown. The nitrogen atoms of the diradical have three available electrons out of which two electrons take part in π-bond formation while one electron is still left in a nonbonding orbital. These NBMOs are degenerate, leading to difficulties in obtaining a consistent energy gap by B3LYP or other DFT methods in the unrestricted formalism. Indeed, the general trend UCCSD(T)/STO-3G > UB3LYP/4-31G is not obeyed here. DFT breakdown does not occur in the restricted (open-shell) calculations. The best S−T value is 8.7 kcal mol^{-1} that has been obtained from the R(O)B3LYP/6-311G(d,p) calculation [Table 4a].

Unlike **3**, the singlet and triplet C−C bond lengths hardly vary except for the C8−C18 bond. This is manifest in Table 4b. Similarly, the bond angles vary only slightly in the two spin states.

3.5. 8-Methyl-1-naphthyl Carbene. The species 8-methyl-1-naphthyl carbene (**5**) has the point group C_1 but the framework has C_s symmetry. The species can be derived from molecule **2** by [1,8] migration of a hydrogen atom so that it can be viewed as a slightly higher-energy isomer of molecule **2**. It is found to have a triplet ground state, in agreement with the prediction of Platz et al.[4] Unlike the earlier species, the diradical center lies at a single atom. Table 5a shows the computed energy gap between singlet and triplet states. The best value for the energy difference is 7.4 kcal mol^{-1} [R(O)B3LYP/6-311G(d,p)]. The post-Hartree−Fock CC calculations involving the split-valence bases were performed with the orbitals 27−124 active in the CC expansion. However, for the minimal basis, the CC expansion apparently stabilizes the singlet to a greater extent than the triplet, thus reducing the S−T energy gap drastically. This happens whenever the diradical is centered on a single atom, that is, also for molecule **6**. In such cases, the CC calculation on the triplet using the minimal basis set is not at par with the singlet state calculation, but the DFT calculations exhibit a systematic trend.

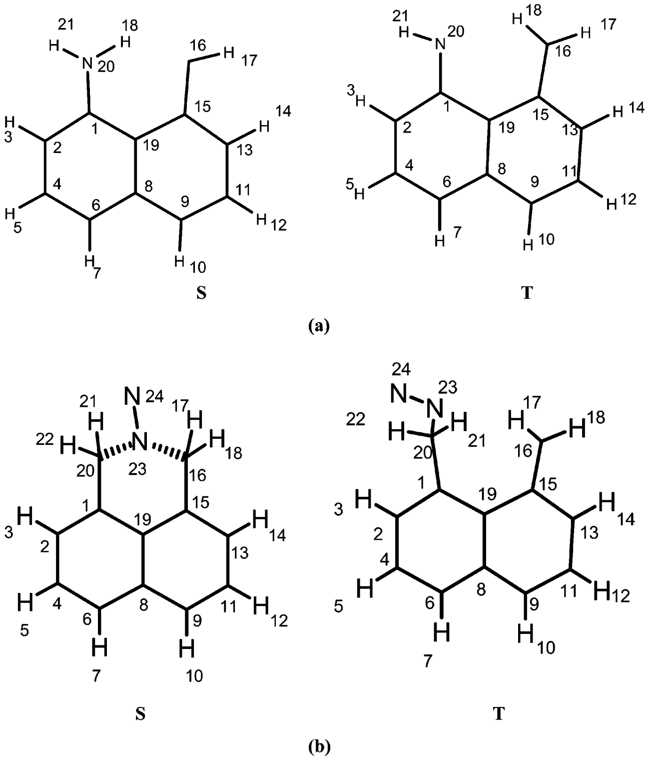

Figure 2. Optimized singlet (S) and triplet (T) structures for (a) molecule **3**, (b) molecule **7**.

The S−T gap for this molecule is found to be generally higher than that for molecule **2** in the unrestricted formalism and lower in the restricted (open-shell) calculations. The NBMOs are nondegenerate, and DFT gives rise to fairly good energy differences. Table 5b shows the optimized bond lengths and bond angles at the R(O)B3LYP level using 6-311G(d,p) basis. Most of the C−C bonds in the fused ring are shorter in the singlet state, the only exceptions being C1−C2, C11−C13, C15−C16, C15−C18, C18−C1, and C1−C19 bonds. The major changes in bond lengths involve the atoms C13, C15, and C16. The C13−C15 bond contracts by 0.010 Å in the singlet state, whereas the C15−C16 bond expands by 0.050 Å. The major variation in bond angles involves the angle C15−C16−H17, and there are minor distortions in C19−C1−C2, C1−C19−H20, and C1−C19−H21 bond angles. The singlet state emerges as slightly more symmetric than the triplet state.

3.6. 8-Methyl-1-naphthalenyl Imidogen. The molecule 8-methyl-1-naphthalenyl imidogen (**6**) has a planar framework in both singlet and triplet states with symmetry C_s, the overall point group being C_1. Table 6a shows the computed energy gap between singlet and triplet states. From all levels of calculation, the triplet state emerges as the ground state. A single atom is

TABLE 4: (a) Ab Initio Total Energy and the Optimized Geometry for the Spin States of 1,8-Naphthalenediylbis(amidogen) (4) in the Unrestricted Hartree−Fock Formalism and (b) Bond Lengths and Bond Angles in Molecule 4 with Geometry Optimized at the R(O)B3LYP/6-311G(d,p) Level[a]

(a)

			molecular geometry				
basis set	method	optimization[a]	S	T	E(T) in a.u.	$\langle S^2\rangle_T$	E(S) − E(T) in kcal mol^{-1}
6-311G(d)	UHF	O	C_{2v}	C_{2v}	−492.3102	3.1644	80.8
	UB3LYP	SP	C_{2v}	C_{2v}	−495.3982	2.1019	17.3
6-311G(d)	R(O)HF	O	C_{2v}	C_{2v}	−492.2395	2.0000	36.4
6-311G(d,p)	R(O)HF	O	C_{2v}	C_{2v}	−492.2577	2.0000	36.2
6-311G(d,p)	R(O)B3LYP	O	C_{2v}	C_{2v}	−495.4077	2.0000	8.7

(b)

bond (Å)	singlet	triplet	angle (deg.)	singlet	triplet
C_1-C_2	1.449	1.438			
C_2-C_4	1.381	1.381			
C_4-C_6	1.389	1.385	$H_{20}-N_{19}-C_1$	108.5	108.1
C_6-C_8	1.421	1.421	$N_{19}-C_1-C_2$	120.9	120.9
C_8-C_9	1.421	1.421	$C_1-C_2-H_3$	116.4	116.9
C_9-C_{11}	1.389	1.385	$H_5-C_4-C_6$	120.8	120.2
$C_{11}-C_{13}$	1.381	1.381	$H_7-C_6-C_4$	120.7	120.3
$C_{13}-C_{15}$	1.449	1.438	$H_{10}-C_9-C_{11}$	120.7	120.3
$C_{15}-N_{16}$	1.314	1.322	$C_9-C_{11}-H_{12}$	120.8	120.2
$N_{16}-H_{17}$	1.024	1.025	$H_{14}-C_{13}-C_{15}$	116.4	116.9
$C_{15}-C_{18}$	1.459	1.468	$C_{13}-C_{15}-N_{16}$	120.9	120.9
$C_{18}-C_1$	1.459	1.468	$C_{15}-N_{16}-H_{17}$	108.5	108.1
C_1-N_{19}	1.313	1.322			
$N_{19}-H_{20}$	1.024	1.025			
C_8-C_{18}	1.411	1.428			

[a] S and T indicate singlet and triplet, respectively. Both singlet and triplet are of symmetry C_{2v}. [a] O = optimization; SP = single-point calculation.

TABLE 5: (a) Ab Initio Total Energy and the Optimized Geometry for the Spin States of 8-Methyl-1-naphthyl Carbene (5) in the Unrestricted Hartree−Fock Formalism and (b) Bond Lengths and Bond Angles in Molecule 5 with Geometry Optimized at the R(O)B3LYP/6-311G(d,p) Level[a]

(a)

			molecular geometry				
basis set	method	optimization[a]	S	T	E(T) in a.u.	$\langle S^2\rangle_T$	E(S) − E(T) in kcal mol^{-1}
6-311G(d)	UHF	O	C_1	C_1	−460.2737	3.1921	45.2
	UB3LYP	SP	C_1	C_1	−463.2758	2.0385	8.0
6-311G (d)	R(O)HF	O	$C_1(C_s)$	$C_1(C_s)$	−460.2330	2.0000	22.3
6-311G(d,p)	R(O)HF	O	$C_1(C_s)$	$C_1(C_s)$	−460.2504	2.0000	19.8
6-311G(d,p)	R(O)B3LP	O	$C_1(C_s)$	$C_1(C_s)$	−463.2940	2.0000	7.4

(b)

bond (Å)	singlet	triplet	angle (deg.)	singlet	triplet
C_1-C_2	1.390	1.387			
C_2-C_4	1.402	1.403			
C_4-C_6	1.370	1.372	$C_{19}-C_1-C_2$	115.6s	118.2
C_6-C_8	1.417	1.422	$C_1-C_2-H_3$	117.6	118.7
C_8-C_9	1.412	1.420	$C_6-C_4-H_5$	121.0	120.5
C_9-C_{11}	1.376	1.379	$H_7-C_6-C_4$	121.2	120.8
$C_{11}-C_{13}$	1.395	1.393	$H_{10}-C_9-C_{11}$	120.0	120.5
$C_{13}-C_{15}$	1.411	1.421	$C_9-C_{11}-H_{12}$	121.0	120.3
$C_{15}-C_{16}$	1.431	1.381	$C_{15}-C_{13}-H_{14}$	117.0	118.3
$C_{16}-H_{17}$	1.106	1.081	$C_{13}-C_{15}-C_{16}$	118.1	117.5
$C_{15}-C_{18}$	1.471	1.462	$H_{17}-C_{16}-C_{15}$	106.0	132.7
$C_{18}-C_1$	1.433	1.427	$C_1-C_{19}-H_{20}$	112.0	111.8
C_1-C_{19}	1.516	1.508	$C_1-C_{19}-H_{21}$	109.5	111.8
$C_{19}-H_{20}$	1.086	1.094	$C_1-C_{19}-H_{22}$	109.5	110.3
$C_{19}-H_{21}$	1.095	1.094			
$C_{19}-H_{22}$	1.095	1.092			
C_8-C_{18}	1.444	1.432			

[a] S and T indicate singlet and triplet, respectively. Both singlet and triplet are of symmetry C_1. [a] O = optimization; SP = single-point calculation.

the diradical center, and again we observe that the computed S−T energy gaps from CC calculations are unreliable while using small bases. The species can be viewed as an analogue of molecule **5**, but the computed energy gaps are a lot different from those of **5** because of the presence of a heteroatom. It can also be considered as a higher-energy isomer of molecule **3**. The best calculated S−T gap is 27.2 kcal mol^{-1} [R(O)B3LYP/6-311G(d,p)].

The [R(O)B3LYP/6-311G(d,p) optimized bond lengths and bond angles for this species are shown in Table 6b. Like

TABLE 6: (a) Ab Initio Total Energy and the Optimized Geometry for the Spin States of 8-Methyl-1-naphthalenyl Imidogen (6) in the Unrestricted Hartree−Fock Formalism and (b) Bond Lengths and Bond Angles in Molecule 6 with Geometry Optimized at the R(O)B3LYP/6-311G(d,p) Level[a]

(a)

			molecular geometry				
basis set	method	optimization[a]	S	T	E(T) in a.u.	$\langle S^2 \rangle_T$	E(S) − E(T) in kcal mol^{-1}
6-311G(d)	UHF	O	$C_1(C_s)$	$C_1(C_s)$	−476.3248	3.2048	70.5
	UB3LYP	SP	$C_1(C_s)$	$C_1(C_s)$	−479.3681	2.0641	32.2
6-311G(d)	R(O)HF	O	$C_1(C_s)$	$C_1(C_s)$	−476.2719	2.0000	37.4
6-311G(d,p)	R(O)HF	O	$C_1(C_s)$	$C_1(C_s)$	−476.2923	2.0000	40.7
6-311G(d,p)	R(O)B3LYP	O	$C_1(C_s)$	$C_1(C_s)$	−479.3773	2.0000	27.2

(b)

bond (Å)	singlet	triplet	angle (deg.)	singlet	triplet
C_1-C_2	1.392	1.390			
C_2-C_4	1.406	1.403			
C_4-C_6	1.371	1.375	$C_{18}-C_1-C_2$	118.1	118.9
C_6-C_8	1.419	1.415	$C_1-C_2-H_3$	118.1	118.7
C_8-C_9	1.415	1.423	$H_5-C_4-C_6$	120.8	120.4
C_9-C_{11}	1.387	1.383	$C_4-C_6-H_7$	121.2	120.8
$C_{11}-C_{13}$	1.387	1.390	$H_{10}-C_9-C_{11}$	119.3	120.3
$C_{13}-C_{15}$	1.440	1.434	$C_9-C_{11}-H_{12}$	120.3	120.1
$C_{15}-N_{16}$	1.307	1.305	$H_{14}-C_{13}-C_{15}$	114.3	117.3
$C_{15}-C_{17}$	1.488	1.473	$C_{13}-C_{15}-N_{16}$	118.0	117.5
$C_{17}-C_1$	1.421	1.420	$C_1-C_{18}-H_{19}$	111.5	111.6
C_1-C_{18}	1.508	1.507	$C_1-C_{18}-H_{20}$	111.5	111.6
$C_{18}-H_{19}$	1.091	1.093	$C_1-C_{18}-H_{21}$	109.7	110.3
$C_{18}-H_{20}$	1.091	1.093			
$C_{18}-H_{21}$	1.094	1.092			
C_8-C_{17}	1.435	1.429			

[a] S and T indicate singlet and triplet, respectively. Both singlet and triplet are of symmetry $C_1(C_s)$. [a] O = optimization; SP = single-point calculation.

molecule **5**, species **6** has almost the same singlet and triplet geometries. The singlet state has slightly elongated bonds compared to the triplet state, with the differences varying up to 0.15 Å. The bond angles hardly vary in the two spin states.

3.7. 8-Methyl-1-naphthyl Diazomethane. The molecule 8-methyl-1-naphthyl diazomethane (**7**) shows a large difference in its singlet and triplet optimized structures. The singlet has C_s symmetry, whereas the point group for the triplet is C_1. See Table 7a. The NBMOs in this case are somewhat degenerate leading to a slight DFT breakdown. Because of the presence of the bonds between the heteroatoms, the UHF calculation using the STO-3G basis very confusingly indicates the triplet as the ground state. However, this is corrected by using the split-valence basis which shows the singlet and triplet to have almost the same energy. The post-Hartree−Fock calculations invariably point out the singlet to be the more stable species. Here again, the density functional treatment leads to a systematic trend in the S−T energy difference. Calculations were also performed using the polarized basis sets to yield the best S−T gap as −21.9 kcal mol^{-1} at the R(O)B3LYP/6-311G(d,p) level.

Table 7b reveals the optimized bond lengths and bond angles at the R(O)B3LYP level using the 6-311G(d,p) basis set. In the singlet state, the molecule takes up a very interesting geometry. One of the nitrogen atoms becomes equidistant from the two CH_2 groups with the length of the C−N bond of the same order as that of a carbon−nitrogen single bond. This points out the formation of a stable six membered ring by one nitrogen and five carbon atoms. This happens in all of the calculations, both restricted and unrestricted. The nitrogen atoms, however, remain out of the plane of the carbon atoms so that the point group is only C_s. This situation does not hold for the triplet case where the nitrogen atom points away from the carbon atom C16 to which it is not directly bonded. The optimized structures are shown in Figure 2b.

4. Spin Alternation

The basis of conventional qualitative resonance theory[31,32] is formed by different classical patterns of bonding. For example, in the case of benzene, each carbon is supposed to have a single π electron that shows singlet spin pairing with the adjacent π electrons. That the ground-state spin pairing takes place between atoms having opposite spin density was noted by Rumer[33a] and co-workers.[33b] This idea was extended to spin doublet manifold by Pauling[34] and later to arbitrary spin multiplicities.[35a,b] This is consistent with the predictions of the ground-state spins of a Heisenberg model as shown by Lieb and Mattis.[36] According to the valence bond (VB) model, stability increases with the number of a low-energy spin-pairing pattern. Klein and co-workers have pointed out that, in order to maximize the total stabilization energy, there should be maximum numbers of locally paired sites and like-energy canonical structures.[15l] Ovchinnikov has shown that for an alternant system containing n* starred π centers and n^0 unstarred π centers, the numbers of unpaired electrons u is given by[21a,b]

$$u = |n^* - n^{\circ}| \tag{4}$$

This simple rule predicts $u = 2$ for systems **1**−**6** but when the rule is judiciously extended we find $u = 1$ for molecule **7**.

Several authors have used the concept of spin alternation by considering alternating up and down spin on successive atoms followed by the averaging of results with a balanced VB wave function for the singlet state.[12i,13g,15,18,21] These methodologies can predict the triplet ground state of various species with ease, but the situation for a singlet ground-state remained unclear.

Borden and Davidson formulated a similar qualitative theory, whereby disjointness of the frontier one-electron MOs favors the singlet ground state where triplet was otherwise expected.[2] Borden, Davidson, and Feller[11] showed that the UHF is capable

TABLE 7: (a) Ab Initio Total Energy and the Optimized Geometry for the Spin States of 8-Methyl-1-naphthyl Diazomethane (7) in the Unrestricted Hartree−Fock Formalism and (b) Bond Lengths and Bond Angles in Molecule 7 Optimized at the ROB3LYP/6-311G(d,p) Level[a]

(a)

basis set	method	optimization[a]	molecular geometry S	molecular geometry T	E(T) in a.u.	$\langle S^2 \rangle_T$	E(S) − E(T) in kcal mol^{-1}
6-311G(d)	UHF	O	C_s	C_1	−569.1994	3.3101	12.9
	UB3LYP	SP	C_s	C_1	−572.8201	2.0563	−17.9
6-311G(d)	R(O)HF	O	C_s	C_1	−569.1501	2.0000	−18.0
6-311G(d,p)	R(O)HF	O	C_s	C_1	−569.1676	2.0000	−17.3
6-311G(d,p)	R(O)B3LYP	O	C_s	C_1	−572.8337	2.0000	−21.9

(b)

bond (Å)	singlet	triplet	angle (deg.)	singlet	triplet
C_1-C_2	1.378	1.391			
C_2-C_4	1.411	1.400			
C_4-C_6	1.373	1.374	$C_{20}-C_1-C_2$	120.7	115.5
C_6-C_8	1.418	1.416	$C_1-C_2-H_3$	119.6	118.6
C_8-C_9	1.418	1.422	$C_6-C_4-H_5$	120.2	120.8
C_9-C_{11}	1.373	1.380	$H_7-C_6-C_4$	120.5	120.6
$C_{11}-C_{13}$	1.411	1.389	$H_{10}-C_9-C_{11}$	120.5	120.7
$C_{13}-C_{15}$	1.378	1.422	$C_9-C_{11}-H_{12}$	120.2	120.3
$C_{15}-C_{16}$	1.506	1.392	$C_{15}-C_{13}-H_{14}$	119.6	117.6
$C_{16}-H_{17}$	1.096	1.077	$C_{13}-C_{15}-C_{16}$	120.7	117.1
$C_{16}-H_{18}$	1.088	1.083	$H_{17}-C_{16}-H_{18}$	109.2	116.9
$C_{15}-C_{19}$	1.426	1.468	$C_{15}-C_{16}-H_{18}$	112.6	118.8
C_1-C_{19}	1.426	1.429	$C_1-C_{20}-H_{22}$	112.6	113.4
C_1-C_{20}	1.506	1.498	$H_{22}-C_{20}-N_{23}$	105.4	104.3
$C_{20}-H_{21}$	1.096	1.087	$C_{20}-N_{23}-N_{24}$	124.7	121.5
$C_{20}-H_{22}$	1.088	1.089	$C_{16}-N_{23}-N_{24}$	124.7	159.5
$C_{20}-N_{23}$	1.521	1.589			
$N_{23}-N_{24}$	1.202	1.162			
C_8-C_{19}	1.431	1.436			
$C_{16}-N_{23}$	1.521	3.227			

[a] S and T indicate singlet and triplet, respectively. Singlet is of symmetry C_s, whereas the triplet is of symmetry C_1. [a] O = optimization; SP = single-point calculation.

of producing the correct optimized geometries in different spin states and often indicate the ground-state spin. Using this observation in mind, it was shown in ref 16 that the UHF method gives rise to spin alternation in the ground state. This gives us a powerful tool to qualitatively predict the spin nature of the ground state of any diradical species. The UHF spin density pattern obviously relates to the nodal patterning of the many-body wave function that has been theoretically demonstrated in the VB approach.[15]

The spin alternation in UHF is shown along the π extension in Figure 3. The pictures on the left show the spin alternation in the ground state of the respective species. These plots have been generated at the PM3 level by the software HyperChem by using the 4-31G optimized geometry. Spin alternation is manifest for triplets of **1**−**6** and singlet of **7** in Figure 3. It is also observed that, except for the ground spin states, the presence of one node is very common. The node gives rise to a higher energy, thereby rendering the singlets less stable for molecules **1**−**6** and the triplet less stable for species **7**. Molecule **7** reveals an apparent spin alternation for its triplet structure. However, both C20 and N23 belong to the same spin density region. Thus, the rule of spin alternation in UHF is robust for all the species studied here.

5. Conclusions

The diradicals TMM, TME, and *m*-xylylene were investigated earlier by a large number of researchers in great detail.[12a−k,13a−j,14a−k] On a previous occasion, we discussed the spin nature of some chain and monocyclic diradicals, and found the UCCSD(T) methodology with split-valence basis sets to be a dependable approach to the calculation of the S−T energy difference for diradicals.[6] Here we have explored the ground electronic spin state of seven organic diradicals belonging to the condensed ring system.

Though the UHF method gives a more or less correct, optimized molecular geometry in each spin state, the relative energies calculated by the UHF method are not reliable. Hence, the method often yields significantly wrong S−T energy differences. The calculated S−T splitting vastly improves by the application of coupled-cluster methods on the UHF optimized geometry. The other alternative, Møller−Plesset perturbation theory, generally yields misleading results for the S−T gap. This is also in general agreement with the observations of Mitani et al.[14g,h] Results from the MP calculations are not shown in this paper. The S−T energy gap calculated with small basis sets such as STO-3G and 4-31G at the UCCSD(T) level is not very realistic. One has to use larger basis sets, especially those with polarization functions. This imposes a limit on the computing ability using coupled-cluster methods. So, one can resort to the density functional treatment as a workable solution.

There is another aspect of the problem. The unrestricted formalism gives rise to a very high spin contamination as can be seen from the S^2 expectation value computed for the triplet state. The post-Hartree−Fock methods do not significantly rectify this error. However, the density functional treatment such as UB3LYP reduces spin-contamination and yields $\langle S^2 \rangle_T$ of the order of 2.1. This spin-contamination effect is best avoided by the restricted formalism. The RHF formalism suffers from the difficulty that a much larger basis set is needed to obtain the correct triplet geometry. This is why we have carried out single-

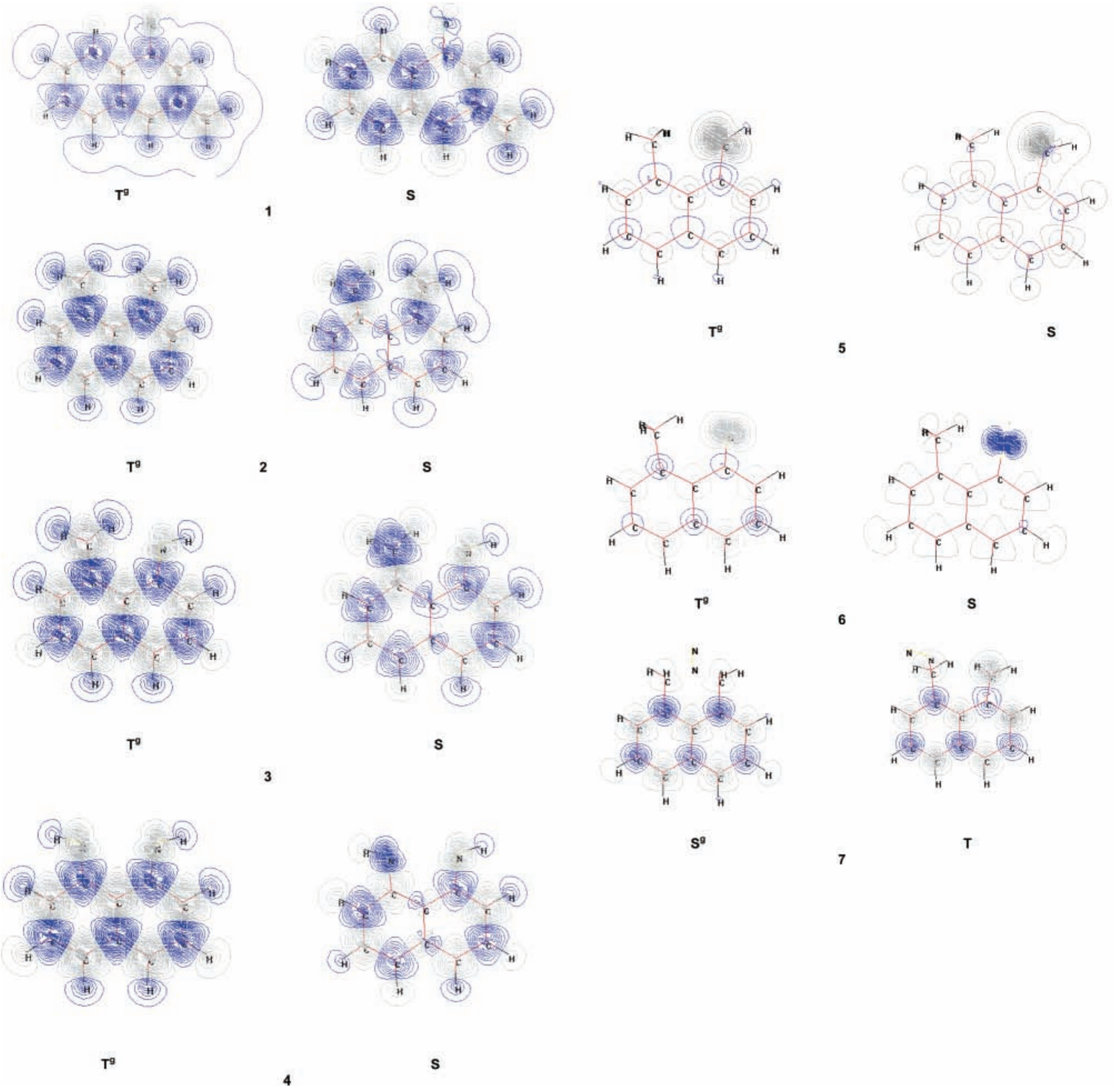

Figure 3. PM3 spin density contours for molecules **1**−**7** in singlet (S) and triplet (T) states. The superscript g indicates the calculated ground state.

point UB3LYP calculations using 6-311G(d) basis sets but optimized geometries by R(O)B3LYP calculations using 6-311G-(d,p) basis sets.

The DFT methodology does not always work in the unrestricted formalism. In fact, we have noticed more or less a systematic trend in the UB3LYP calculations only for molecules **5**−**7**. Our best results are, therefore, from the R(O)B3LYP/6-311G(d,p) calculations. The experimental gaps, once they are measured, are predicted to be found within a few kcal mol^{-1} of the values calculated here. The calculated spin ordering in the ground states are in excellent agreement with the observations discussed in section 1.[4,7−10,12d,e,13h,14j,27a−i]

All of the molecules except species **7** have triplet ground states. Molecule **7** is the only species investigated here in which one of the diradical centers is not directly attached to the ring. This indicates a very low S−T gap or even a ground-state singlet. This prediction is borne out by all of the calculations except the UHF ones. A summary of the computed S−T energy difference vis-à-vis spin-contamination is given in Table 8.

The prominent isotropic Fermi contact coupling constants calculated here are given in Table 9 for any possible comparison with the ESR line shapes of the triplet species. The ESR splitting and the number of lines are not explicitly available from the current literature. The computed LUMO−HOMO energy gaps for the singlet species are given in Table 10.

The optimized structures in the singlet and triplet states vary from each other. Symmetry breaking has been found to be essential in obtaining a correct estimate of the S−T splitting that is usually of the order of only a few kcal mol^{-1}. The variation has been found to be the largest for molecules **3** and **7**. The structure of molecule **3**, as shown in Figure 1, is representative of the stable, that is, the triplet state. The stable singlet is a tautomeric form with substituents $-NH_2$ and $-CH$ in lieu of $-NH$ and $-CH_2$. The singlet of molecule **7** has a three-fused-ring nonplanar structure that has been evidenced by geometry optimization by all the methods indicated in Table 7a. Finally, the rule of spin alternation in UHF is again found

TABLE 8: Summary of the Computed $S - T$ Energy Difference

	$S - T$ energy (kcal mol^{-1}) ($\langle S^2\rangle_T$)		
molecule	UCCSD(T) 4-31G[a]	UB3LYP 6-311G(d)	R(O)B3LYP 6-311G(d,p)
1	10.5	−14.7	9.7
	(3.19)	(2.04)	(2.00)
2	3.7	16.1	9.4
	(3.21)	(2.09)	(2.00)
3	3.5	24.3	16.4
	(3.21)	(2.09)	(2.00)
4	3.5	17.3	8.7
	(3.23)	(2.10)	(2.00)
5	10.9	8.0	7.4
	(3.27)	(2.04)	(2.00)
6	4.5	32.2	27.2
	(3.31)	(2.06)	(2.00)
7	−14.0	−17.9	−21.9
	(3.5)	(2.06)	(2.00)

[a] These calculations were carried out by keeping the orbitals 13−110 active in the CC expansion. Geometry optimization were carried out at the 4-31G UHF level.

TABLE 9: Prominent Isotropic Fermi Contact Coupling Constants Computed by UHF/4-31G Method for the Triplets of Species 1−6

species	prominent isotropic Fermi contact coupling constants (Gauss)
1	H3: −15.84; H5: 15.29; H7: −16.45; H10: −20.13; H13: −23.10; H14: −23.07; H16: −20.40; H20: 16.00
2	H3: −18.18; H5: 15.60; H7: −18.02; H10: −18.02; H12: 15.60; H14: −18.18; H17: −22.68; H18: −22.29; H21: −22.29; H22: −22.68
3	H3: −18.10; H5: 15.70; H7: −18.10; H10: −17.98; H12: 15.59; H14: −18.10; H17: −22.29; H18: −22.55; N20: 12.42; H21: −20.87
4	H3: −18.15; H5: 15.78; H7: −18.09; H10: −18.09; H12: 15.78; H14: −18.15; N16: 12.21; H17: −21.11; N19: 12.21; H20: −21.11
5	H3: −15.39; H5: 15.02; H7: −16.02; H10: −17.79; H12: 16.26; H14: −18.44; H17: −21.03; H20: −8.67; H22: −8.67
6	H3: −15.77; H5: 15.05; H7: −16.10; H10: −17.99; H12: 16.58; H14: −19.39; N16: 20.83; H20: −10.04; H21: −10.04

TABLE 10: Computed LUMO−HOMO Energy Gaps from Various Calculations on the Singlet Diradical Species in Atomic Units

	6-311G(d)		6-311G(d)	6-311G(d,p)	
species	UHF[a]	UB3LYP[a]	RHF	RHF	RB3LYP
1	0.2144	0.0352	0.2143	0.2141	0.0341
2	0.1743	0.0331	0.1744	0.1742	0.0345
3	0.2922	0.0870	0.2920	0.2920	0.0807
4	0.1901	0.0356	0.1901	0.1899	0.0361
5	0.3326	0.0812	0.3330	0.3321	0.0778
6	0.3268	0.0341	0.3267	0.3264	0.0306
7	0.3759	0.1308	0.2089	0.3754	0.1287

[a] For α as well as β spin.

to be robust. It can be used to identify the correct spin nature of the ground state without fail for the diradical systems.

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Supporting Information Available: The optimized atomic coordinates for all the species in each spin state along with the corresponding UHF, MP-levels, UB3LYP, UCCSD, UCCSD(T), R(O)HF and R(O)B3LYP energy values are included in the Log files. Tables showing the ab initio total energies for the spin states of each species in the unrestricted Hartree−Fock formalism at the STO-3G and the 4-31G bases have been included in the Log files. The Log files from all the 24 calculations for each of the 7 molecules discussed in the paper are available free of charge via the Internet at http://pubs.acs.org.

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