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Ab Initio Quantum Chemical Investigation of the Spin States of Some Chain and Monocyclic Diradicals

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Ab initio calculations have been performed on nine organic diradicals to find the spin multiplicities in their electronic ground states. Three diradicals, namely, trimethylene methane (TMM), tetramethylene ethane (TME), and *m*-xylylene, were previously investigated in detail by various authors. These have been used as test cases so as to establish the reliability of the calculated results. The basis sets used in this work are mainly STO-3G and 4-31G. For the smaller molecules, the 6-31G basis set has also been tried. In every case, the molecular geometry has been optimized at the unrestricted Hartree−Fock (UHF) level for each basis set and for each spin state. Calculations have also been performed at the post-Hartree−Fock Møller−Plesset (MP) and coupled-cluster (CCSD) levels. Results have been quoted only for the UHF, UCCSD, and UCCSD(T) levels because the MP-level calculations do not generate reliable singlet−triplet energy gaps. The UHF calculation generally yields an unrealistically large splitting, but the UCCSD and especially the UCCSD(T) methods reduce the gap to a significant extent. From a comparison with the best results already reported on the test cases, we find that the UCCSD(T) singlet−triplet energy gaps are of the correct order. In fact, the singlet−triplet energy gaps calculated by the UCCSD(T) method using the 4-31G basis sets are more or less in agreement with the results of previous detailed investigations on TME and *m*-xylylene. Six more diradicals, two of them of the linear chain type (3-methylene pentane-2,4-diyl and tris(methylimino)methane) and four of the monocyclic variety (2-isopropylidene cyclopentane-1,3-diyl, 2,3-bis(methylene) cyclohexane-1,4-diyl, 3-methylene phenoxyl, and tetramethyl *m*-xylylene), have been investigated here. To our knowledge, this work is the first report on an ab initio post-Hartree−Fock calculation of the spin states of these six species. Out of the six diradicals, one has a singlet ground state, and the rest are ground-state triplets. These findings agree with the experimental observations without fail. The UCCSD(T)/4-31G results on tris(methylimino) methane, for which the hyperfine splitting spectrum is available, can explain the number of lines as well as the average hyperfine coupling constant. The molecule 2,3-bis(methylene) cyclohexane-1,4-diyl has been found to have almost degenerate singlet and triplet states, as observed experimentally. The UCCSD(T)/4-31G singlet−triplet gap is −0.84 kcal mol^{-1} for this species. The UHF spin-density plots show that the ground states of all nine diradicals can be successfully predicted by the rule of spin alternation in the UHF treatment.

1. Introduction

Non-Kekulé hydrocarbons have been known for several decades. They were postulated to be diradicals.[1] These molecules are known to be highly reactive. The reactivity can be easily explained in terms of degenerate nonbonding molecular orbitals (NBMOs).[2] The lifting of the degeneracy tends to favor a singlet ground state. A triplet ground state is obtained from a π-electron framework when the splitting of the two NBMOs is less than approximately 1.5 eV.[3] The ground-state spin multiplicity can be controlled either by lowering the symmetry of the molecular structure or by varying the electronegativity of the diradical termini.[4] It is also known that the ground-state multiplicities of diradicals can be reliably predicted from ab initio calculations employing large basis sets and extensive post-Hartree−Fock (HF) considerations.[5]

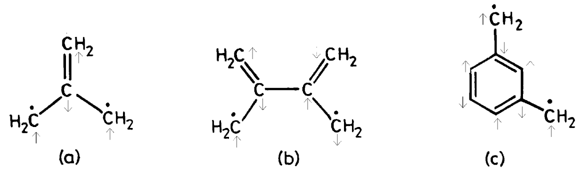

Figure 1. Three molecules that have been extensively investigated so far: (a) trimethylene methane (TMM), (b) tetramethylene ethane (TME), and (c) *m*-xylylene. Arrows show the scheme of spin alternation.

In this work, we investigate the ground-state spin multiplicity of six diradicals by ab initio methods. Detailed reports of the theoretical investigation of two linear-chain diradicals and one monocyclic diradical (molecules a−c in Figure 1) are available in the literature. These three species are trimethylene methane (**1a**, TMM), tetramethylene ethane (**1b**, TME), and *m*-xylylene (**1c**). Here, we investigate the ground-state spin multiplicities of two other linear-chain diradicals (Figure 2a, 3-methylene pentane-2,4-diyl, and b, tris(methylimino)methane) and four other monocyclic diradicals (Figure 2c−f, 2-isopropylidene cyclopentane-1,3-diyl, 2,3-bis(methylene) cyclohexane-1,4-diyl, 3-methylene phenoxyl, and tetramethyl *m*-xylylene, respectively) of π-electron origin. Molecule **2a** was referred to in ref 4. It is suspected that this species is a ground-state triplet. Molecule

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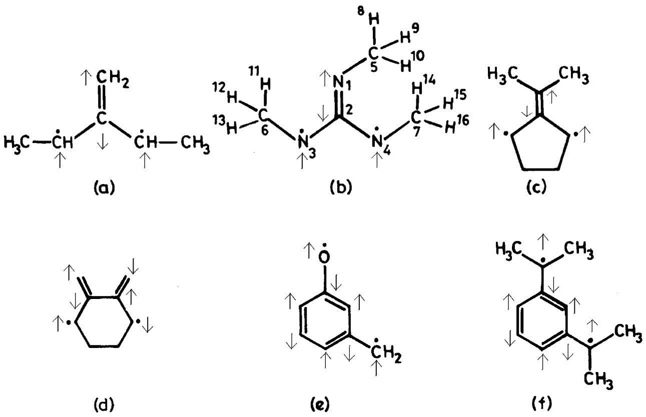

Figure 2. Species investigated in this work: (a) 3-methylene pentane-2,4-diyl, (b) tris(methylimino)methane, (c) 2-isopropylidene cyclopentane-1,3-diyl, (d) 2,3-bis(methylene) cyclohexane-1,4-diyl, (e) 3-methylene phenoxyl, and (f) tetramethyl *m*-xylylene. Arrows show the scheme of spin alternation.

2b was observed by triplet ESR spectroscopy.[6] Molecule **2c** was matrix isolated by Brown et al.[7] These two molecules, **2b** and **2c**, are known to have triplet ground states. Molecule **2d** was observed by low-temperature ESR.[8] From a Curie law plot of the intensity of the ESR spectrum, Dowd et al.[9] concluded that 2,3-bis(methylene)cylcohexane-1,4-diyl is a ground-state triplet. A later study based on magnetic susceptibility and magnetization showed the singlet and triplet states to be almost degenerate.[10] Molecule **2e** was observed by ESR,[11] and from Curie law analysis, it is known that the triplet is the ground state. Molecule **2f** was prepared by Gajewski and Stang.[12]

An accurate calculation of the multiplet splittings in non-Kekulé systems is a challenging task. Using TMM, Borden, Davidson, and Feller[13] showed that RHF and TCSCF calculations, although providing qualitatively correct molecular orbitals for two open-shell electrons in diradicals, generally fail to give correct relative energies, and sometimes they can even lead to incorrect geometries. These authors advocated the use of unrestricted Hartree−Fock (UHF) methods to obtain accurate triplet geometries. The most detailed investigations in this area have been carried out by Cramer and Smith[14] on TMM, Nachtigall and Jordan[15] on TME, and Mitani et al.[16,17] on *m*-xylylene. These authors have shown that the singlet−triplet gaps calculated by different methods and employing different levels of rigor vary widely from each other.

Theoretical investigations carried out on molecules **1a**−**c** have been fairly extensive. Several authors have investigated TMM,[13,14,18−25] TME,[15,18,26−32] and *m*-xylylene.[16,17,33−37] General theoretical[38−47,48a] and experimental[48a,b] work has been reported on a number of other diradicals containing π electrons. The systematic investigation of radical species by Klein and co-workers[44a−k] employing different methodologies is of general interest. The studies of Trindle and co-workers[45a,b;46] on the *m*-phenylene coupler also draws attention in the present context.

In this paper, we first examine molecules **1a**−**c** mainly to determine the limitations of the calculational procedures adopted by us. We then evaluate the merit of the results obtained for species **2a**−**f**. This paper is arranged as follows. The methods of calculation are described in section 2. Energy differences between the states of different spin multiplicities are discussed in section 3. Section 4 is designed to examine the spin alternation in UHF. The conclusions drawn from this work are given in section 5.

2. Methodology

Some of the molecules involved in this work, namely, **2c**−**f**, are fairly large. We require a complete geometry optimization for each of the species in each spin state at the UHF level. Therefore, we have used only STO-3G and 4-31G basis sets, except for the smaller species **1a**, **1b**, **2a**, and **2b** for which the 6-31G basis has also been tried. Gaussian 98 for Windows (G98W)[49] has been used for these calculations. It is apparent that by demanding a complete geometry optimization, symmetry is broken in the UHF singlets to yield a minimum energy that is sometimes far below the closed-shell singlet energy value. This symmetry breaking in the wave function is attended by distorted structures, even when a plane of symmetry is maintained in some of the cases.

For each type of basis set, the UHF-optimized geometry has been used to calculate the total energy at UCCSD and UCCSD(T) levels. However, the post-Hartree−Fock calculations could be performed with the 4-31G basis set for molecules **2c** and **2f** only by choosing a smaller number of active orbitals in the CC expansion. The computed results have been utilized to calculate the energy differences between the spin states. These differences are discussed in section 3.

The reason for the choice of UCCSD and UCCSD(T) post-Hartree−Fock treatments is as follows. The description of low-lying singlet and triplet states is extremely sensitive to the proper treatment of both static and dynamic correlation energy. In fact, Mitani et al.[17] have demonstrated that whereas a simple UHF calculation overstabilizes the triplet state relative to the singlet a Møller−Plesset (MP) perturbation calculation tends to stabilize the singlet state more than the triplet. We too have noticed similar trends by using the G98W software. The failure of the MP perturbation theory (PT) approach is likely due to the circumstance of near degeneracy in some sense; that is, with one UHF solution there is typically at least one other solution belonging to an equivalent conjugate subsymmetry. This type of degeneracy is not properly reflected in the zeroth-order UHF Hamiltonian, so it is not properly accounted for by the ensuing PT expansion. This difficulty does not arise with coupled-cluster,[17] MCSCF,[14,15] and CASPT2N[14] calculations because these methodologies treat correlation in more sensible ways. The latter three methodologies with progressively higher levels of sophistication reduce the relative overstabilization of the triplet from the UHF level. This is borne out by Table 2 in ref 14 (for MCSCF and CASPT2N), Table 3 in ref 15 (for MCSCF), and Table 3 in ref 17 (for CC methodologies). The density functional treatment (DFT) can be quite restrictive, as discussed by Cramer and Smith.[14]

The spin-density plots have been drawn by using the software HyperChem.[50] These are useful in testing the spin alternation in UHF, which is discussed in section 4.

3. Energy Differences

TMM, TME, and *m*-Xylylene (1a−c). An excellent qualitative study of TMM using the UHF method was made by Hashimoto and Fukutome.[18] Auster, Pitzer, and Platz[19] employed open-shell restricted Hartree−Fock (RHF) wave functions and two-configuration self-consistent-field (TCSCF) wave functions for trimethylene methane (**1a**) to find a singlet−triplet energy gap of 10.5 kcal mol^{-1} at the Hartree−Fock level. As mentioned earlier, at about the same time, Borden, Davidson, and Feller[13] stressed the need to rely on the UHF methodology. Cramer and Smith[14] have investigated different multiplets of TMM at a variety of multiconfigurational SCF (MCSCF), complete active space perturbation theory (CASPT), and density functional

TABLE 1: Ab Initio Total Energy and Optimized Geometry for the Spin States of Trimethylene Methane (1a)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	C_s	D_{3h}	−153.0235	33.12
	UCCSD	C_s	D_{3h}	−153.2514	12.95
	UCCSD(T)	C_s	D_{3h}	−153.2537	10.46
4-31G	UHF	C_s	D_{3h}	−154.6823	26.13
	UCCSD	C_s	D_{3h}	−155.0309	12.33
	UCCSD(T)	C_s	D_{3h}	−155.0399	9.36
6-31G	UHF	C_s	D_{3h}	−154.8477	25.91
	UCCSD	C_s	D_{3h}	−155.1942	12.22
	UCCSD(T)	C_s	D_{3h}	−155.2029	9.30
(9s5p/4s), [4s3p/2s]	TCSCF	C_{2v}[b]	C_{2v}[b]	−154.8329	10.5[b]
cc-pVTZ	MCSCF(10,10)	C_s	C_s[c]	−155.0356	15.8[c]
cc-pVTZ	CASPT2N(10,10)	C_s	C_s[c]	−155.6307	16.1[c]

[a] S and T indicate singlet and triplet, respectively [b] Auster, Pitzer, and Platz;[19] geometry optimization for C_{2v} symmetry. [c] Cramer and Smith.[14] The triplet geometry relaxes very slightly from D_{3h} symmetry to C_s symmetry during the calculations.

treatment (DFT) levels of theory. These authors have found that the multiplet splitting varies with the rigor of calculation as well as the methodology. They have issued two caveats—one regarding the interpretation of CASPT2N results and the other, the employment of the DFT method except when the non-Kekulé species has nondegenerate frontier molecular orbitals. The CASPT2N(10,10)/cc-pVTZ calculation predicts the TMM singlet to lie 16.1 kcal mol^{-1} above the triplet ground state. Many other authors have investigated TMM. In the ab initio front, significant contributions have been made by Feller et al. using the configuration interaction (CI) method[20] and Dietz et al. using CISSCF and CISD methods.[21] Other methods that have employed are semiempirical, valence bond, and mixed approaches.[22−25]

The UHF singlet−triplet (S−T) energy differences calculated for TMM (**1a**) are shown in Table 1. The UHF energy differences, calculated by using STO-3G, 4-31G, and 6-31G basis sets, are manifestly unreliable, chiefly indicating the need for electron correlation. A considerable improvement occurs at the UCCSD and especially the UCCSD(T) levels. The UCCSD(T)/STO-3G energy difference equals the TCSCF splitting calculated by Auster, Pitzer, and Platz,[19] but it is lower than the differences computed by Cramer and Smith.[14] The UCCSD/4-31G and UCCSD(T)/4-31G triplet energy values are comparable to the MCSCF(10,10)/cc-pVTZ triplet energy of Cramer and Smith, but the calculated energy gap is again somewhat lower. The UCCSD(T)/6-31G gap is still lower at 9.30 kcal mol^{-1}.

The TMM singlet has C_s symmetry in all of the calculations. The triplet has essentially D_{3h} symmetry, but during the calculations, the geometry relaxes very slightly to that of C_s symmetry, as found by Cramer and Smith.[14] The bond lengths vary at the sixth decimal place.

The molecule tetramethylene ethane (**1b**) was analyzed qualitatively by Hashimoto and Fukutome.[18] It has since been theoretically investigated by a fairly large number of researchers employing a variety of methods such as ab initio Hartree−Fock,[26] MCSCF,[15] CI,[27,28]density functional,[29] and valence bond[30] procedures. These authors mostly concluded that the singlet state is the ground state. The singlet−triplet energy gap was found to be exceedingly small, on the order of 1 kcal mol^{-1}.

TABLE 2: Ab Initio Total Energy and Optimized Geometry for the Spin States of Tetramethylene Ethane (1b)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	D_{2h}	C_{2v}	−228.9568	−13.30
	UCCSD	D_{2h}	C_{2v}	−229.3330	−0.27
	UCCSD(T)	D_{2h}	C_{2v}	−229.3379	−0.40
4-31G	UHF	D_{2h}	C_{2v}	−231.4419	−9.95
	UCCSD	D_{2h}	C_{2v}	−231.9884	−1.80
	UCCSD(T)	D_{2h}	C_{2v}	−232.0056	−1.36
6-31G	UHF	D_{2h}	C_{2v}	−231.6897	−9.96
	UCCSD	D_{2h}	C_{2v}	−232.2328	−1.91
	UCCSD(T)	D_{2h}	C_{2v}	−232.2496	−1.49
3-21G	UHF	D_{2d}	D_{2d}	−230.4907	0.0[b]
3-21G	MCSCF(6,6)	D_2	D_2	−230.5268	−1.20[b]
DZP	MCSCF(6,6)	D_2	D_2	−231.8331	−1.36[b]

[a] S and T indicate singlet and triplet, respectively. [b] Nachtigall and Jordan.[15]

The zero-field splitting has also been calculated by employing semiempirical methods.[31] To date, the most accurate calculations on TME have been performed by Nachtigall and Jordan who, from their ab initio MCSCF calculations,[15] showed that the species has singlet and triplet geometries of D_2 symmetry and a singlet ground state lying about 1.4 kcal mol^{-1} below the triplet state. Furthermore, a CI study carried out by the same authors indicates the triplet to be slightly more stable.[27] This kind of anomaly, first observed by Nachtigall and Jordan, has also been witnessed in the classic studies made by Cramer and Smith on TMM.[14] The singlet and triplet potential energy surfaces have been recently calculated by Pittner et al. by using the coupled-cluster (CC) methodology.[32] The singlet surface lies below the triplet surface, and the minimum gap at the same twist angle was found to be 1.3 kcal mol^{-1}, which more or less vindicates the MCSCF results of Nachtigall and Jordan.[15]

Table 2 shows the singlet−triplet energy differences calculated for TME. All basis sets, namely, STO-3G, 4-31G, and 6-31G, yield an optimized singlet of symmetry D_{2h} and an optimized triplet of symmetry C_{2v}. The G98W software failed to yield for either spin state D_2 geometry, as discussed in ref 15. The total energies reported in ref 15 lie between the total energies calculated here by using the STO-3G and 4-31G bases. This observation merely reflects the order of superiority of the involved basis sets. The UHF S−T energy differences calculated by us again turn out to be in large error. However, the UCCSD and UCCSD(T) calculations vastly improve these energy differences. The difference of −1.36 kcal mol^{-1} calculated by using the UCCSD(T)/4-31G method is identical to the best result of −1.36 kcal mol^{-1} obtained by Nachtigall and Jordan employing the MCSCF(6,6)/DZP methodology. But the use of the 6-31G basis set increases the splitting to 1.49 kcal mol^{-1}.

The molecule *m*-xylylene (**1c**) has also attracted the attention of many investigators. Kato et al. performed UHF and TCSCF calculations using the STO-3G basis set, and from their double-ζ plus CI calculations, they found the triplet state to lie 10 kcal mol^{-1} lower in energy than the singlet state.[33] They found the variational π CI energy-difference calculation to be more accurate than an all-valence electron (AVE) CI calculation that was made using a small number of selected single and double excitations. The molecule was theoretically analyzed by Karafiloglou.[34a,b] The triplet state of *m*-xylylene was found by Fort et al.[35] to be 9.5 kcal mol^{-1} more stable than the singlet at the π-SDCI level. Fang et al. performed ab initio calculations

TABLE 3: Ab Initio Total Energy and Optimized Geometry for the Spin States of *m*-Xylylene (1c)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	C_s	C_s	−303.8588	42.06
	UCCSD	C_s	C_s	−304.3290	11.52
	UCCSD(T)	C_s	C_s	−304.3382	9.54
4-31G	UHF	C_s	C_s	−307.1423	27.06
	UCCSD	C_s	C_s	−307.8387	9.63
	UCCSD(T)	C_s	C_s	−307.8632	7.11
STO-3G/DZ	TCSCF	C_{2v}[b]	C_{2v}[b]	−303.8586	48.95[b]
STO-3G/DZ	11-π SDTQ-CI	C_{2v}[b]	C_{2v}[b]	−307.5375	10.0[b]
6-31G*	π-SDCI	C_{2v}[c]	C_{2v}[c]	−307.6289	9.5[c]
6-31G*	UBLYP				4.46[d]

[a] S and T indicate singlet and triplet, respectively. [b] Kato et al.;[33] geometry optimization for C_{2v} symmetry. [c] Fort et al.;[35] geometry optimization for C_{2v} symmetry. [d] Mitani et al.;[16] geometry not fully optimized.

TABLE 4: Ab Initio Total Energy and Optimized Geometry for the Spin States of 3-Methylene Pentane-2,4-diyl (2a)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	C_s	C_s	−230.1907	31.12
	UCCSD	C_s	C_s	−230.5531	12.41
	UCCSD(T)	C_s	C_s	−230.5565	10.54
4-31G	UHF	C_s	C_s	−232.6416	23.56
	UCCSD	C_s	C_s	−233.1984	11.22
	UCCSD(T)	C_s	C_s	−233.2129	8.99
6-31G	UHF	C_s	C_s	−232.8886	21.16
	UCCSD	C_s	C_s	−233.4423	10.66
	UCCSD(T)	C_s	C_s	−233.4564	8.30

[a] S and T indicate singlet and triplet, respectively.

with dihedral angles of $\varphi = 90°$ between the benzene ring and the hydrogen of the methylene groups.[36a] In this case, the singlet state was found to be more stable than the triplet state. Similar results were quoted by Baumgarten et al., who found that the singlet−triplet gap tends to zero or even becomes negative when the methylene radical is sufficiently twisted out of conjugation.[36b] Of late, *m*-phenylene and its polymers have been extensively studied by Mitani et al.[16] The difference in energy between the low- and high-spin states of *m*-xylylene has been calculated using UHF/4-31G, UB3LYP/4-31G, UBLYP/4-31G, and UBLYP/6-31G* methodologies. These authors have extended their work further by employing density functional calculations and unrestricted molecular orbital methods including Mϕller−Plesset (MP) and coupled-cluster corrections.[17] Like Cramer and Smith[14] and Nachtigall and Jordan,[15,27] Mitani et al.[16,17] found that the singlet−triplet gaps calculated by different methods and employing different levels of rigor vary widely from each other. The best result has been calculated using the UBLYP method with the 6-31G* basis set, which yielded an energy gap of approximately 4.5 kcal mol^{-1}. The zero-field splitting of *m*-xylylene was studied by a few authors.[37a−c]

The computed energy gaps for *m*-xylylene are shown in Table 3. The UHF gaps are again too large, like the TCSCF gap computed by Kato et al.[33] However, the UCCSD(T)/STO-3G gap is comparable to the 11-π SDTQ/CI splitting calculated by Kato et al.[33] and the π-SDCI/6-31G* splitting calculated by Fort et al.[35] At first glance, the UCCSD/4-31G and UCCSD(T)/4-31G total energies for the triplet appear to be comparable to, or even better than, the 6-31G* π-SDCI total energy computed by Fort et al. However, the comparison is strictly misleading. Kato et al.[33] as well as Fort et al.[35] carried out only a partial geometry optimization; that is, they optimized the geometry for the C_{2v} point group. Similarly, the optimization of the molecular geometry, as discussed by Mitani et al.,[16,17] has been only partial. This gives rise to a difficulty in comparing the energy gaps computed by various methods in this case. The situation is unlike the previous cases of TMM and TME. We can conclude only that the UCCSD(T)/4-31G S−T energy gap is of the right order.

An effective spin-aligning coupler between spin sites serves as a building block for a high-spin material. The *m*-phenylene residue has turned into the most useful organic ferromagnetic coupler to design high-spin organic radicals and polyradicals in the laboratory.[51a−d] The coupling of different groups at substituted and unsubstituted *m*-phenylene sites has been theoretically investigated by Trindle and co-workers.[45a,b;46] It was initially reported that the ferromagnetic coupling of local triplets of methylene with the *m*-phenylene coupler leads to a stable quintet state.[51a] Subsequent analyses of *m*-phenylene-coupled carbenes have established a similar trend, with the quintet being more stable than triplet and in turn the triplet being more stable than the singlet.[16,17] Thus, the *m*-phenylene coupler is known to produce the highest possible spin state. For *m*-xylylene that is in reality *m*-phenylene bis(methyl), the triplet can be the highest spin state in the ground state. Indeed, the results calculated here and in previous treatments[16−17,23,33] clearly indicate *m*-xylylene to have a triplet ground state.

From the analysis of these three cases, one can easily see that by itself the UHF method does not suffice to yield reliable singlet−triplet energy gaps for diradical systems. The method can generate splitting of the correct order only when a relatively large basis set is employed and the molecular geometry is only partially optimized, as evidenced from the TCSCF calculation by Auster et al.[19] on TMM (Table 1), but such an agreement is strictly fortuitous. In general, a somewhat extensive post-Hartree−Fock treatment is required to compute the correct energy gap. This has also been the contention of the authors of refs 14−17. The post-Hartree−Fock methodologies such as UCCSD and UCCSD(T) provide much better results and generate a splitting of the correct order even with a small basis set. It is seen that the UCCSD(T)/4-31G gives the correct splitting for TME (Table 2). The choice of 6-31G or higher basis sets would, of course, yield an improved energy gap, but the prohibitively large size of the read−write scratch file generated by the G98W software restricts their use to smaller molecules.

Molecules 2a−f. The singlet−triplet energy differences for species **2a**−**f** are shown in Tables 4−9. We make the following observations:

(1) The species 3-methylene pentane-2,4-diyl (**2a**) has an effectively planar structure in both the singlet and triplet states, and only the hydrogen atoms of the two methyl groups remain out of the plane. The molecule has C_s symmetry in its singlet and triplet states (Table 4). It has a triplet ground state, which agrees with the prediction in ref 4. The UCCSD(T)/4-31G and UCCSD(T)/6-31G energy gaps of 8.99 and 8.30 kcal mol^{-1} are a little lower than the energy gaps of 9.36and 9.30 kcal mol^{-1} calculated for the parent species TMM using the same methods of calculation. The slight lowering is an outcome of the extension of the parent molecule, which affects the mixing of the s orbitals of the out-of-plane hydrogen atoms of methyl substituents with the π orbitals of the molecular frame. This can be qualitatively understood as discussed below. The substitution of two hydrogen atoms that are attached to two

TABLE 5: Ab Initio Total Energy and Optimized Geometry for the Spin States of Tris(methylimino)methane (2b)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	C_1	C_1	−316.0592	42.61
	UCCSD	C_1	C_1	−316.4688	8.53
	UCCSD(T)	C_1	C_1	−316.4750	3.78
4-31G	UHF	C_1	C_1	−319.5065	32.09
	UCCSD	C_1	C_1	−320.1988	14.28
	UCCSD(T)	C_1	C_1	−320.2190	8.28
6-31G	UHF	C_1	C_1	−319.8421	32.38
	UCCSD	C_1	C_1	−320.5295	14.35
	UCCSD(T)	C_1	C_1	−320.5493	8.35

[a] S and T indicate singlet and triplet, respectively.

TABLE 6: Ab Initio Total Energy and Optimized Geometry for the Spin States of 2-Isopropylidene Cyclopentane-1,3-diyl (2c)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	C_s	C_s	−306.2109	23.31
	UCCSD	C_s	C_s	−306.6989	13.53
	UCCSD(T)	C_s	C_s	−306.7042	12.38
4-31G	UHF	C_s	C_s	−309.4375	21.18
	UCCSD[b]	C_s	C_s	−310.1879	12.61
	UCCSD(T)[b]	C_s	C_s	−310.2091	10.85
(9s5p/4s), [4s3p,2s]	TCSCF	C_{2v}[c]	C_{2v}[c]	−309.7512	11.7[c]

[a] S and T indicate singlet and triplet, respectively. [b] These calculations were performed by keeping orbitals 9−96 active in CC calculations. [c] Auser, Pitzer, and Platz;[19] geometry optimization was carried out only for the C_{2v} point group.

TABLE 7: Ab Initio Total Energy and Optimized Geometry for the Spin States of 2,3-Bis(methylene)cyclohexane-1,4-diyl (2d)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	C_1	C_1	−304.9888	−12.47
	UCCSD	C_1	C_1	−305.4871	−0.37
	UCCSD(T)	C_1	C_1	−305.4937	−0.51
4-31G	UHF	C_1	C_1	−308.2514	−8.92
	UCCSD	C_1	C_1	−308.9887	−1.27
	UCCSD(T)	C_1	C_1	−309.0124	−0.84

[a] S and T indicate singlet and triplet, respectively.

TABLE 8: Ab Initio Total Energy and Optimized Geometry for the Spin States of 3-Methylene Phenoxyl (2e)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	C_s	C_s	−339.1537	40.61
	UCCSD	C_s	C_s	−339.5959	11.62
	UCCSD(T)	C_s	C_s	−339.6055	9.73
4-31G	UHF	C_s	C_s	−342.9238	24.14
	UCCSD	C_s	C_s	−343.6356	11.12
	UCCSD(T)	C_s	C_s	−343.6602	8.44

[a] S and T indicate singlet and triplet, respectively.

TABLE 9: Ab Initio Total Energy and Optimized Geometry for the Spin States of Tetramethyl *m*-Xylylene (2f)[a]

basis set	method	molecular geometry S	molecular geometry T	E(T) (au)	E(S) − E(T) (kcal mol^{-1})
STO-3G	UHF	C_s	C_s	−458.1884	38.88
	UCCSD	C_s	C_s	−458.9303	9.60
	UCCSD(T)	C_s	C_s	−458.9424	8.22
4-31G	UHF	C_s	C_s	−463.0549	23.71
	UCCSD[b]	C_s	C_s	−463.7056	6.76
	UCCSD(T)[b]	C_s	C_s	−463.7241	5.12

[a] S and T indicate singlet and triplet, respectively. [b] These calculations were performed by keeping orbitals 13−100 active in CC calculations.

different carbon atoms by methyl groups has two effects. On one hand, the process introduces delocalization and stabilizes one of the degenerate π orbitals of the TMM frame. On the other hand, repulsion by the C−H σ-bond pairs tends to increase the energy of the degenerate π orbitals by unequal amounts. Because the TMM singlet suffers from Jahn−Teller distortion, its HOMO is spatially nondegenerate. The HOMO is the NBMO far from the points of substitution, and the NBMO near the same points is the LUMO. The HOMO energy changes from −0.300 to −0.280 au on substitution (6-31G results). The TMM triplet has spatially degenerate HOMOs—the two possible NBMOs with an energy of −0.351 au. On substitution, these HOMOs become nondegenerate with energies of −0.335 au for the far NBMO and −0.320 au for the near NBMO. Thus, the increase in the orbital energy of the singlet HOMOs (α and β) is less than the increase for the triplet HOMOs (both α). This causes a slight reduction in the calculated S−T energy gap.

(2) Tris(methylimino)methane (**2b**) is largely a nonplanar species in both the singlet and triplet states, the preferred geometry being C_1 (Table 5). The STO-3G-, 4-31G-, and 6-31G-level calculations predict the molecule to be a ground-state triplet, in agreement with the ESR observations of Quast et al.[6] The spin densities calculated from the UCCSD(T)/4-31G method (1N: −0.02; 2C: −0.82; 3N: 0.96; 4N: 1.93; see Figure 2 for the numbering of atoms) show that there are in effect four unpaired electrons, one with a down spin on one of the carbon atoms, one with an up spin on one of the nitrogen atoms, and two with up spins on another nitrogen atom. The overall spin state is triplet. The calculated isotropic Fermi contact couplings are 14.45 G for 3N, 19.84 G for 4N, 12.91 G for 11H, and 13.71 G for 12H. The Fermi contact coupling constants are smaller for other atoms. Considering that each nitrogen nucleus has a spin of 1 and each proton has a spin of $^1/_2$ and that the Fermi contact couplings for two nitrogen atoms and two hydrogen atoms are roughly equal to each other, one would expect approximately nine equidistant lines in ESR. In fact, this is the hyperfine structure found by Quast et al.[6]

The average coupling constant (calculated by multiplying the Fermi contact coupling constants and the respective atomic spin densities, followed by summation over all atoms and division by the total number of effectively unpaired electrons, that is, four) turns out to be 13.27 G, which more or less matches the average coupling constant of 11.7 ± 0.5 G found by Quast et al.[6] from ESR spectroscopy.

Quast et al., however, have tried to simulate the ESR spectrum by using results from INDO calculations. They could not get satisfactory agreement with the observed spectra. Therefore, we carried out INDO geometry optimizations. We found the INDO method to be not at all suitable for predicting the ground-state spin of this molecule. In fact, the INDO-optimized geometries indicate the ground state to be predominantly a singlet with a singlet−triplet energy gap equal to −49.9 kcal mol^{-1}. The ab initio calculations also show the CN_3 framework to be manifestly nonplanar in both the singlet and triplet states.

(3) The molecule 2-isopropylidene cyclopentane-1,3-diyl (**2c**) was earlier theoretically investigated by Auster, Pitzer, and Platz[19] using the (9s5p/4s), [4s3p/2s] Gaussian basis sets. These authors reported the singlet−triplet energy gap to be 11.7 kcal mol^{-1} for the C_{2v} point group. This energy gap is comparable to the value of 12.38 kcal mol^{-1} obtained here using the UCCSD(T)/STO-3G calculations (Table 6). That the triplet is the ground state agrees with experiment.[4,7] The UCCSD(T)/STO-3G gap is 12.38 kcal mol^{-1}. The post-Hartree−Fock treatment were performed with the 4-31G basis set by using orbitals 9−96. The UCCSD(T)/4-31G splitting turned out to be 10.85 kcal mol^{-1}, that is, about 1.53 kcal mol^{-1} less than the STO-3G value.

One may view this molecule as a derivative of species **2a**. A comparison can be made between the S−T energy differences calculated for these two species. The STO-3G difference for **2c** is about 1.84 kcal mol^{-1} greater than the difference for **2a** at the UCCSD(T) level. At the same level, the 4-31G difference for **2c** is 1.86 kcal mol^{-1} larger. A TCSCF calculation using a large basis set[19] gives a S−T gap of the same order.

A few comments on the triplet being the ground state are due here. The local radical orbitals at sites 1 and 3 of the ring in cyclopentadiyl can form one symmetric and one antisymmetric hybrid. The CH_2 σ bonds mix with the symmetric hybrid and push the latter higher in energy. Thus, the triplet state has been shown to be favored in cyclopentadiyl by 0.61 kcal mol^{-1} (UHF-PM3),[45a] which agrees with experiment.[52a] The 2,2-difluoro analogue of cyclopentadiyl has a symmetric combination of CF_2 σ bonds. This combination is stabilized more than the combination of CH_2 σ bonds in the parent compound, so it elevates the symmetric radical hybrid to a lesser extent. Thus, the difluoro analogue has been shown to possess a singlet ground state (S−T energy difference = −0.29 kcal mol^{-1} at the UHF PM3 level),[45a] as observed earlier.[52b] This explanation appears at first glance to be somewhat different from the conditions laid down by Dougherty.[43] But, finally, the requirements that the radical orbitals should be nearly degenerate and coextensive stand out. The σ and π orbitals used in coupling the isopropylidene fragment in **2c** significantly increase the energy of the symmetric radical hybrid, and the UCCSD(T)/STO-3G S−T gap shown in Table 6 is much larger than that for the difluoro analogue.

(4) Species 2,3-bis(methylene) cyclohexane-1,4-diyl (**2d**) is a nonplanar molecule with singlet as the ground state. In fact, it has been speculated that the molecule has almost degenerate singlet and triplet states.[10] The rather small UCCSD(T)/4-31G energy gap of −0.84 kcal mol^{-1} points along the same direction (Table 7). The molecular symmetry is C_1 for both of the spin states. It is seen that this TME derivative has a singlet−triplet gap that is lower than that for the parent molecule. This can be rationalized by arguments similar to those used for TMM and its derivative (**2a**).

(5) The molecule 3-methylene phenoxyl (**2e**) is planar and possesses a C_s structure in both its singlet and triplet states (Table 8). The triplet state is clearly the ground state, in agreement with ref 11 and the previous discussion on the *m*-phenylene coupler.[45a,b] The UCCSD(T)-calculated splittings are slightly larger than those of the analogous species **1c**. This is the effect of heteroatom substitution, and the effect becomes more pronounced while using the split-valence basis set. The oxygen atom, being more electronegative than the methylene group, tries to pull the unpaired electron, thereby stabilizing the triplet state relative to the singlet state.

(6) Tetramethyl *m*-xylylene (**2f**) has a planar framework in both its singlet and triplet states. Only the methyl hydrogen atoms can be out of the molecular plane, with the point group relaxing to C_s. See Table 9. As expected, the molecule is a spin triplet in the ground state. This is in agreement with experiment.[12] The coupled-cluster calculations at the 4-31G level were carried out using orbitals 13−100. The UCCSD(T)/4-31G computations yield a S−T gap of 5.12 kcal mol^{-1}, which is about 3.1 kcal mol^{-1} less than the value from the corresponding STO-3G calculations.

Like **2e**, **2f** is analogous to **1c**. But **2f** is obtained by replacing the hydrogen atoms attached to the radical centers with methyl groups, which are known to be electron-repelling groups. The effect of substitution here is opposite to that in the previous case. The unpaired electrons become slightly more free to delocalize on the π framework, and the singlet state becomes relatively more stabilized. Thus, we find the trend of S−T energy gaps to be **2e** > **1c** > **2f** both at the UCCSD and UCCSD(T) levels. The trend becomes more marked by using the split-valence basis. The UCCSD(T)/4-31G S−T gap is 8.44 kcal mol^{-1} for **2e**, 7.11 kcal mol^{-1} for **1c**, and 5.12 kcal mol^{-1} for **2f**.

4. Spin Alternation in UHF

The idea of spin alternation is quite native in valence bond theory. In fact, several researchers have prepared their valence bond methodologies by considering alternative up and down spins on successive atoms and then averaging the results with a balanced wave function for the singlet state.[25c,30,38,41,44] Although in most cases the valence bond procedure would show with alacrity spin alternation in the triplet state when the triplet is the ground state, the situation for a singlet ground state remains justifiably unclear. For a long time, the molecular orbital treatment remained largely silent on this issue.

It was shown in ref 45a that the UHF method gives rise to spin alternation in the ground state in a natural way. Furthermore, it was demonstrated with ample examples that the spin alternation in UHF is a powerful tool for predicting the spin multiplicity of radical ground states.[45a,b] These findings provide a basis for the earlier observation of Borden, Davidson, and Feller[13] that the UHF methods are capable of reproducing correct optimized geometries for different spin states. The UHF calculations performed here are no exceptions.

The spin alternation in UHF is shown by upward (spin up) and downward (spin down) arrows in Figures 1 and 2. Because these are π-electron species, the spin alternation is shown only along the π extension. Figures 3a−c and 4a−f show 2D contours of spin density in the UHF ground states (pictures on the left). These plots have been generated by the software HyperChem using the STO-3G-optimized geometry. Because of software or Windows limitations, Figure 4, parts e and f have been drawn by using the PM3 spin-density contours of the respective molecules at the STO-3G optimized geometries. The left side of Figure 3a−c is to be compared with Figure 1a−c. Similarly, the left side of Figure 4a−f is comparable to Figure 2a−f. The other spin states for which the spin density contours are shown on the right side of Figures 3 and 4 do not conform to the spin alternation. This is manifest in their corresponding spin-density plots (shown alongside). Thus, the rule of spin alternation in UHF is robust for all of the species studied here, and it correctly predicts the ground spin states.

The UHF patterning of spin densities obviously relates to the relative many-body nodal patterning of the wave function,

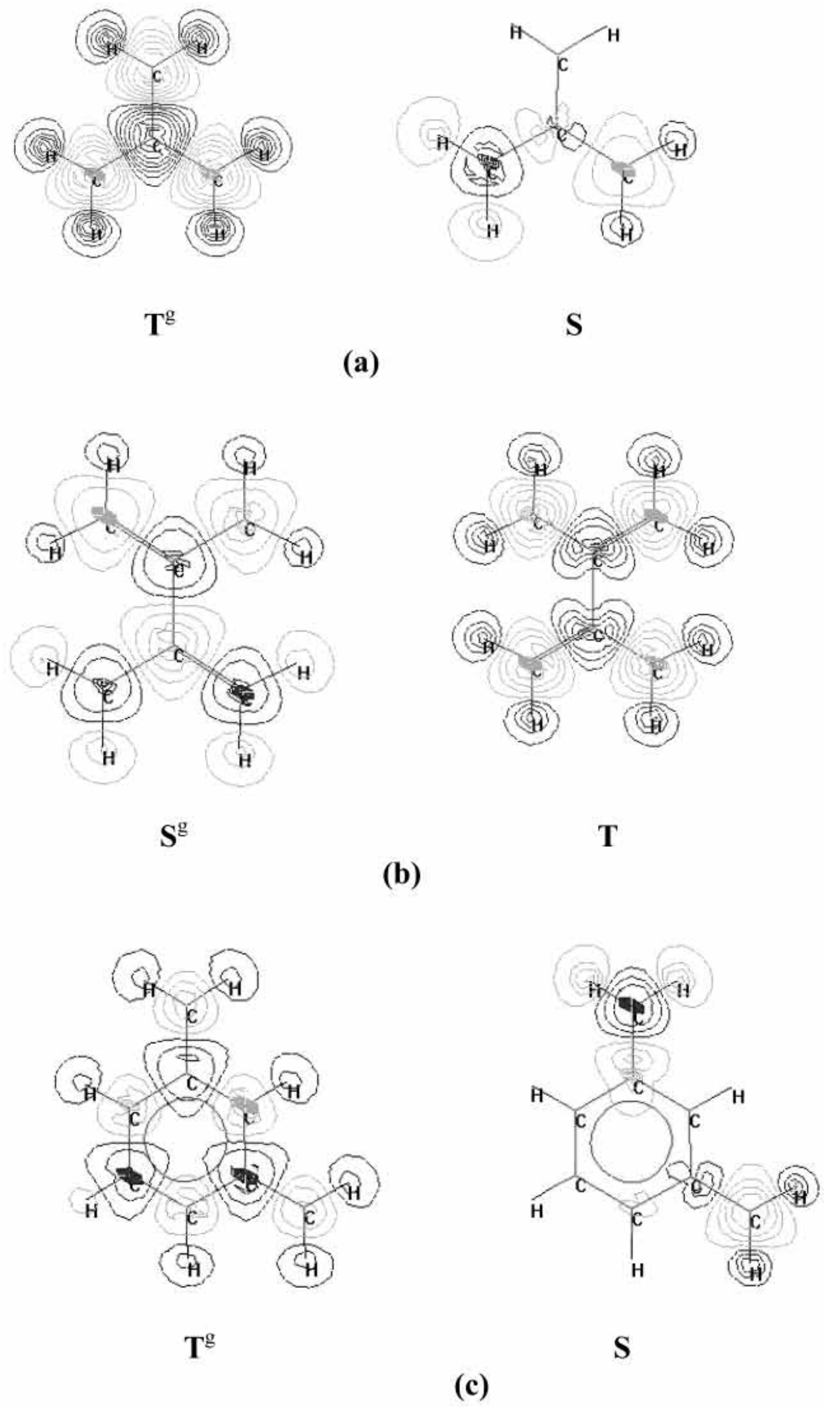

Figure 3. Spin-density contours for molecules (a) **1a**, (b) **1b**, and (c) **1c** in singlet (S) and triplet (T) states. The superscript g indicates the calculated ground state. The spin densities have been calculated using STO-3G-optimized geometries.

which has been known in terms of a rigorous theorem for the nearest-neighbor valence bond model.[44]

5. Conclusions

In this paper, we have examined nine diradicals of organic origin. Three of the molecules, namely, **1a**−**c**, were investigated earlier by other authors in great detail. These have served as test cases for ascertaining the reliability of the methodologies used in this work. After establishing the credibility of the methods of calculation for this kind of diradical system, we have explored the possible spin in the ground states for a set of six other molecules, **2a**−**f**.

One of the main conclusions in this work is that by itself the UHF method yields a significantly wrong estimate of the singlet−triplet splitting, but the optimized molecular geometry in each spin state is more or less correct. The calculated splitting vastly improves by using the coupled-cluster technology whereas the MP-level calculations often yield misleading results (not explicitly shown in this paper). This is also in agreement with the observations of Mitani et al.[16,17] The UCCSD(T)-level calculations yield very realistic values of the S−T energy gap even with small basis sets such as STO-3G and 4-31G, as evidenced by the three test cases **1a**−**c**. The calculated gaps may be numerically in error by a few kcal mol^{-1}, but they are

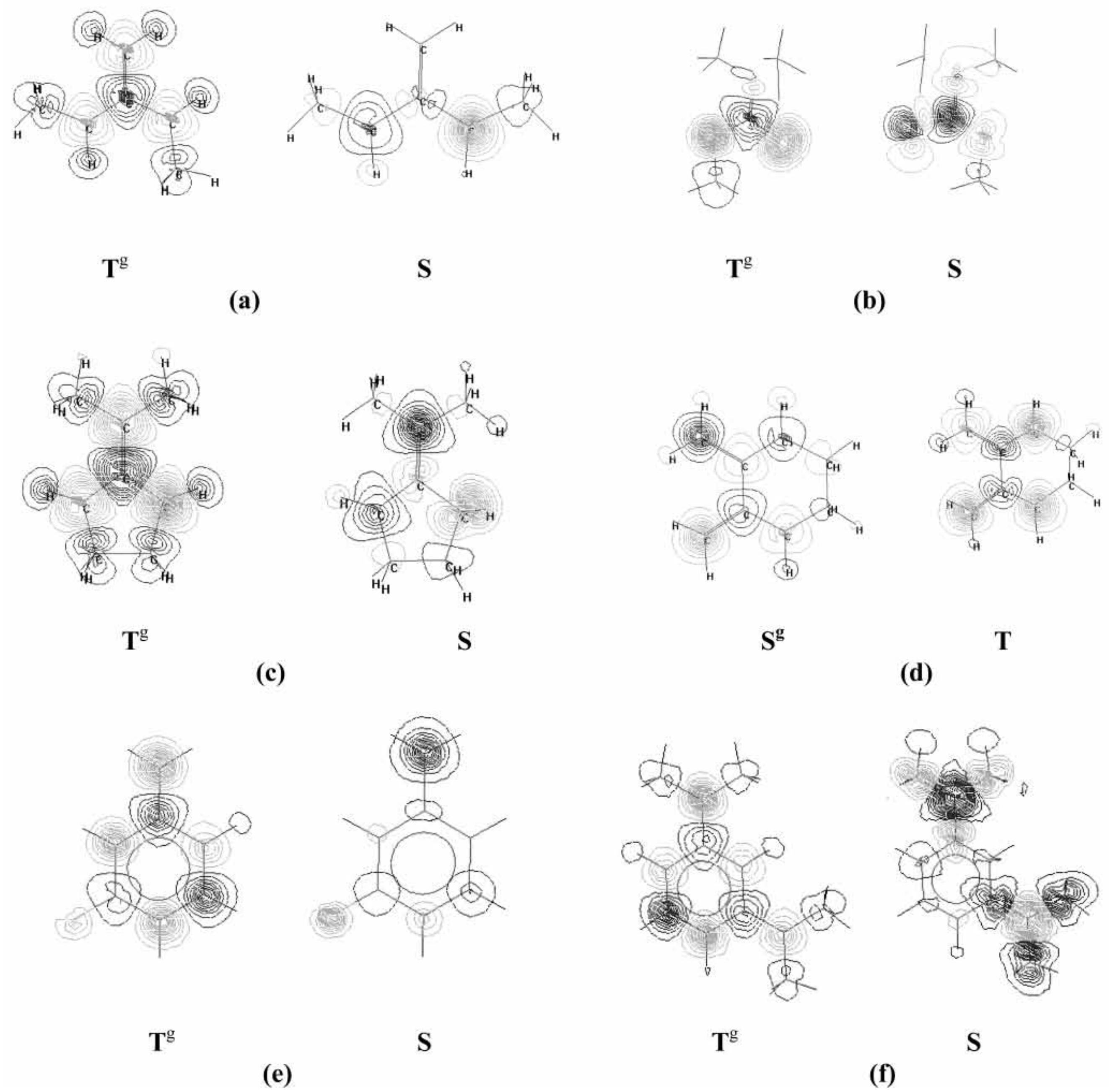

Figure 4. STO-3G spin-density contours for molecules (a) **2a**, (b) **2b**, (c) **2c**, and (d) **2d** and PM3 spin-density contours for (e) **2e** and (f) **2f** in singlet (S) and triplet (T) states. The superscript g indicates the calculated ground state.

certainly of the correct order and sign. The theoretical spin states of the species thoroughly agree with the experimental observations discussed in section 1.[6−12]

From the calculations reported here, we have found that the rule of spin alternation in UHF is robust, and it identifies the correct spin nature of the ground state without fail. The magnitude of the two-electron exchange integral is another valuable indication because a positive value tends to stabilize the triplet radical. However, the twin requirements of the degeneracy of the NBMOs (or HOMOs) and their small but nonvanishing coextensivity cannot be overlooked. If these requirements are violated either by a lack of symmetry of the species or because of an extensive conjugation, which generally happens (except when the molecule is very small), then the exchange integral cannot serve as an index for identifying the correct ground state.

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Supporting Information Available: Optimized atomic coordinates for each species in each spin state along with the corresponding UHF, MP levels, UCCSD, and UCCSD(T) energy values are included in the log files. The log files from all calculations discussed in the paper are available from *J. Phys. Chem. A*. This material is available free of charge via the Internet at http://pubs.acs.org.

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