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FEATURE ARTICLE

Triradicals

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By using novel spin-flip approach, we characterized electronic structure of several prototypical triradicals. Interaction of unpaired electrons in triradicals results in unusual bonding patterns. We determined structural, spectroscopic, and thermochemical consequences of the partial bonds formed between the radical centers. The strength of these bonds varies from a rather weak (but stabilizing) interaction of about 0.5 kcal/mol up to 32 kcal/mol, which is one-third of a typical chemical bond energy. The structural signature of these bonds is shorter distances between the radical centers relative to the closed-shell precursors. Depending on the nature of triradical's molecular orbitals, the ground state in these species varies from quartet, to closed- or open-shell doublet.

1. Triradicals: What Are They?

Triradicals are molecules with three unpaired electrons, as those prototypical systems shown in Figure 1. From the electronic structure point of view, they are species where three electrons are distributed in three (near) degenerate orbitals. This definition is an extension of Salem's definition of diradicals as molecules with two electrons occupying two (near) degenerate orbitals.[1] Similarly to diradicals, different electron distributions result in several closely lying electronic states with different bonding patterns, which have distinct structural, spectroscopic, and chemical signatures. The complexity of electronic structure of triradicals provides a sharpening stone for our understanding of bonding and electron interactions and opens possibilities for tuning their properties to match specific applications. Practical interest to tri- or, more generally, polyradicals is fueled by their potential role as building blocks of organic magnets (see, for instance, refs 2−6).

Figure 2 shows all Slater determinants with a positive projection of the total spin, which can be generated for three-electrons-in-three-orbitals system. The high-spin determinant (1) has $M_s = {}^3/_2$. Nine determinants have $M_s = {}^1/_2$, six of them [(5)−(10)] being of a closed-shell type (these are the eigenfunctions of $\hat{S}^2$), and three [(2)−(4)] of an open-shell type (these are not the eigenfunctions of $\hat{S}^2$). Figure 3 shows valid wave functions that can be constructed from the determinants of Figure 2. From the open-shell determinants (2)−(4), one can construct one quartet (b) and two doublet states (c)−(d). These wave functions are eigenstates of both $\hat{S}_z$ and $\hat{S}^2$. Regardless of the spatial symmetry of the orbitals ϕ_1−ϕ_3, the closed-shell determinants can form several doublet wave functions (e)−(j), as shown in Figure 3. The values of λ's depend on the energy separation between the orbitals, i.e., large λ values correspond to nearly degenerate orbitals. For example, when ϕ_2 and ϕ_3 are exactly degenerate, two different doublet states, (i) and (j), are obtained by taking the normalized sum and the difference of determinants (7) and (8). An additional factor affecting λ's is a nodal structure of orbitals. For example, if the two lowest orbitals are of σ and π character, respectively, the coefficients λ' in the wave functions (e) and (f) will be small even for nearly degenerate MOs. The symmetries of the MOs define which of the configurations shown in Figure 3 can interact and mix further in the triradical wave functions.

Ultimately, the ordering of states from Figure 3 and the properties of the resulting wave functions are defined by the character of MOs and energy gaps between them. For example, if ϕ_2 and ϕ_3 are a bonding and an antibonding combination of orbitals from two different radical centers, e.g., as in a homosymmetric diradical, the open-shell doublet (d) is of ionic nature, whereas the ionic vs covalent character of states (i) and (j) can be continuously tuned up by varying the value of λ'''. Alternatively, when ϕ_2 and ϕ_3 are localized on the same or different radical centers (a heterosymmetric case), the doublet (d) is covalent (similarly to the quartet), whereas (i) and (j) either are covalent or exhibit a charge separation (large and small λ''', respectively).

This feature article summarizes our work[7−11] on several prototypical triradicals from Figure 1. We performed electronic structure calculations by employing state-of-the-art methodology developed in our group.[12−14] The main theme of these studies is bonding patterns, which arise from different electron distributions in ground and excited electronic states of triradicals. Indeed, in finite size species, the unpaired electrons are only nominally unpaired. In practice, their interactions can span the whole range from strongly antibonding (repulsion) to an almost complete chemical bond. These interactions have distinct structural, spectroscopic, and chemical signatures, and ultimately determine properties of open-shell compounds. For example, a bonding interaction between the unpaired electrons results in a shorter distance between the radical centers relative to a parent closed-shell molecule, and in more rigid structures, i.e., higher vibrational frequencies. The energetics of these partial bonds can be characterized by the so-called diradical and triradical stabilization energies (DSEs and TSEs), which provide a

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measure of the effect of combining two or more radical centers in the same molecule (which can be stabilizing or destabilizing with respect to the separate noninteracting centers). Finally, the ground-state multiplicity and the energy gap between the high-spin and low-spin states (e.g., the singlet−triplet and doublet−quartet splittings of the diradicals and triradicals, respectively) also represent a measure of the stabilizing or destabilizing interactions between the unpaired electrons. Indeed, a chemical bond is produced by a pair of electrons with antiparallel spins, whereas a system of noninteracting electrons would not show any preference for either high-spin or low-spin states.

2. A Word on Methodology

From a methodological perspective, it is important that all the doublets and the $M_\mathrm{s} = {}^{1}/_{2}$ component of the quartet state are multideterminantal. Therefore, a multiconfigurational method should be employed when the triradical orbitals are nearly degenerate. However, if the triradical orbitals are well separated in energy, some of the states [for example, (g) and, perhaps, (e)] can be described by a single-reference method.

Unlike the $M_\mathrm{s} = {}^{1}/_{2}$ triradical states, the high-spin component ($M_\mathrm{s} = {}^{3}/_{2}$) of the quartet state is single-determinantal. Moreover, all the low-spin determinants are formally single spin-flipping excitations from the high-spin $M_\mathrm{s} = {}^{3}/_{2}$ determinant. Therefore, the SF approach[12,15−20] can be employed to describe triradicals, as explained below.

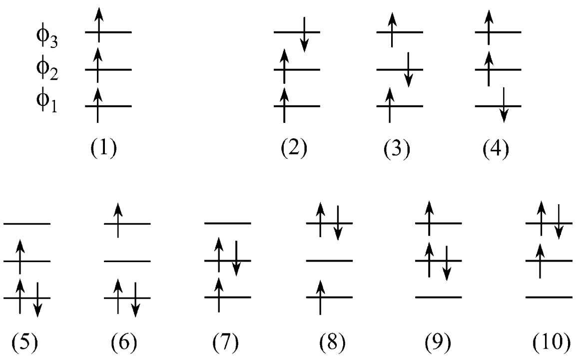

Figure 2. Slater determinants that can be generated by distributing three electrons over three orbitals. Only determinants with a positive projection of the total spin are shown. (1) has $M_\mathrm{s} = {}^{3}/_{2}$, (2)−(10) have $M_\mathrm{s} = {}^{1}/_{2}$. With respect to the high-spin determinant (1), all low-spin determinants (2)−(10) are formally singly excited configurations including the spin-flip of one electron. By reversing the spins of all the electrons, a set of determinants with $M_\mathrm{s} = -{}^{3}/_{2}$; $-{}^{1}/_{2}$ can be generated. Because spin is not present in the nonrelativistic Hamiltonian, determinants with different M_s's do not interact across the Hamiltonian and, therefore, do not mix in the triradical wave functions. (1), (5)−(10) are eigenfunctions of $\hat{S}^2$, whereas (2)−(4) are not (however, their proper linear combinations are).

In the SF approach, one describes low-spin states within a single reference formalism as spin-flipping, e.g., α → β, excitations from a high-spin reference state for which both dynamical and nondynamical correlation effects are much smaller than for the corresponding low-spin states.[12,15−19] In the case of triradicals, we choose the high-spin ($M_\mathrm{s} = {}^{3}/_{2}$) component of the quartet state as a reference. This state is accurately described by single-reference methods. The target states, the low-spin component of the quartet and the open- and closed-shell doublets [(b) and (c)−(j), respectively], are described as single electron excitations including the spin-flip of an electron:

$$\Psi^{\mathrm{d,q}}_{M_\mathrm{s}=1/2} = \hat{R}_{M_\mathrm{s}=-1}\tilde{\Psi}^{\mathrm{q}}_{M_\mathrm{s}=3/2} \tag{1}$$

where $\tilde{\Psi}^{\mathrm{q}}_{M_\mathrm{s}=3/2}$ is the ααα component of the quartet reference state [(a) from Figure 3], $\Psi^{\mathrm{d,q}}_{M_\mathrm{s}=1/2}$ stands for the final ($M_\mathrm{s} = {}^{1}/_{2}$) doublet and quartet states [(b)−(j)], and the operator $\hat{R}_{M_\mathrm{s}=-1}$ is an excitation operator that flips the spin of an electron.

By employing theoretical models of increasing complexity for the reference wave function, one can systematically improve the description of the final states. For example, the simplest SF model employs a Hartree−Fock wave function, and the operator $\hat{R}$ is then truncated at single excitations (SF-CIS or SF-SCF).[12,18] SF-CIS can be further augmented by perturbative corrections [SF-CIS(D) or SF-MP2].[15] A more accurate description can be achieved by describing the reference wave function by a coupled-cluster model, e.g., coupled-cluster singles and doubles (CCSD) or optimized orbitals coupled-cluster doubles (OO-CCD). In this case, the excitation operator $\hat{R}$ consists of single and double excitation operators involving a flip of the spin of an electron (SF-CCSD, SF-OD).[12,19] The accuracy of SF-CCSD can further be improved by including triple excitations.[20] Moreover, the SF idea can be used to extend density functional theory to multireference situations.[17] The attractive feature of the SF approach is that it is a multistate method; i.e., it describes several states in one calculation. Furthermore, both dynamical and nondynamical correlation are included simultaneously. In

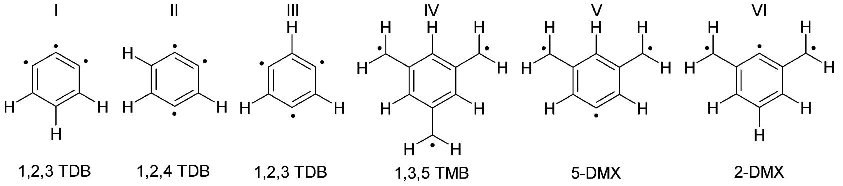

Figure 1. Some prototypical triradicals. In tridehydrobenzenes (TDB) isomers, all three triradical centers belong to the σ system, whereas trimethylenebenzene (TMB) is an example of an all-π triradical. The dehydro-*m*-xylylene (DMX) isomers are σ−π triradicals.

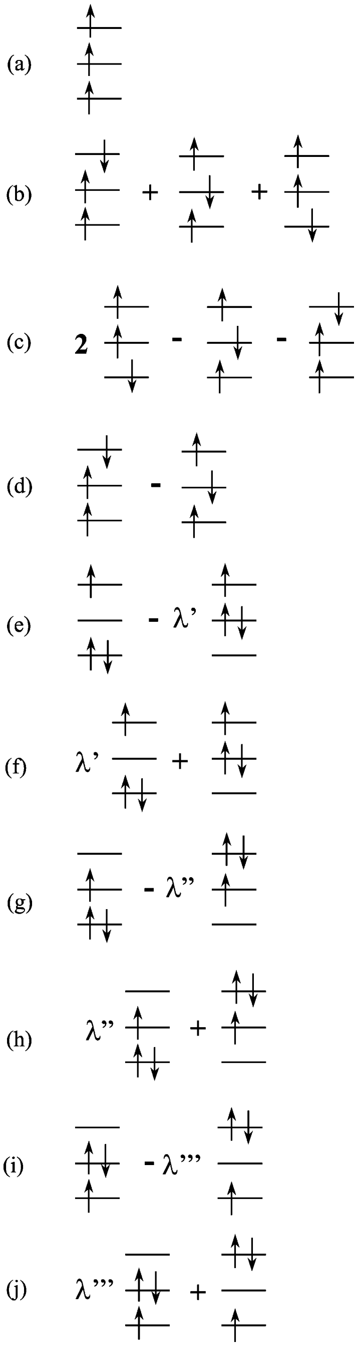

Figure 3. Triradical wave functions that are eigenstates of $\hat{S}_z$ and $\hat{S}^2$. The symmetry of the orbitals determines if these configurations can interact and further mix with each other. All doublets (c)−(j) and the low-spin component of quartet (b) are multiconfigurational, and the high-spin component of quartet state (a) is singly determinantal.

addition to computational effectiveness and simplicity, this scheme yields reliable and accurate energy differences and describes equilibrium properties of all the diradical or triradical states with an accuracy comparable to that of the traditional methods when applied to well behaved molecules. All the SF models are implemented in the Q-CHEM ab initio package.[21] Analytic gradients are available for the SF-CIS, SF-DFT, and SF-CCSD[22] wave functions.

3. Ground-State Multiplicity and Excited States Ordering: Aufbau vs Hund

The relative ordering of electronic states from Figure 3 determines properties of triradicals and, consequently, their practical applications. For example, ground-state multiplicity and energy gaps between high-spin and low-spin states is important for the design of novel magnetic materials.[2] Moreover, the ground-state multiplicity and the quartet−doublet splitting represent a measure of the stabilizing or destabilizing interactions between the unpaired electrons within a finite size molecule. Indeed, a chemical bond is produced by a pair of electrons with antiparallel spins, whereas a system of noninteracting electrons would not show any preference for either high-spin or low-spin states.

From the electronic structure perspective, the type of interaction between the unpaired electrons is derived from the character of the MOs that host these electrons. In many di- and polyradicals, the nominally nonbonding MOs (NBMOs) interact either by direct spatial overlap (through-space interaction) or by overlap with intervening σ and σ^* orbitals (through-bond interaction[23,24]). The bonding interaction lifts the degeneracy between these orbitals, and when the MO splitting exceeds the electron repulsion, a pair of electrons occupies a bonding orbital (as dictated by the aufbau principle), thus producing a partial bond. However, when NBMOs are exactly degenerate, the aufbau principle, which is based on one-electron considerations only, predicts no energy difference between different electron arrangements. In this limiting case, the ground-state electronic configuration is determined by the electron repulsion that is minimal for the same spin electrons. Thus, for degenerate NBMOs the extension of Hund’s first rule[25] to molecules predicts that the lowest energy state is the one with the highest multiplicity, i.e., triplet, quartet, quintet, etc. However, violations of this rule occur when the singly occupied NBMOs are disjoint,[26−28] i.e., localized on different parts of the molecule. In this case, the exchange interactions between these orbitals are small, and low-spin and high-spin states with the same spatial configuration are nearly degenerate. In some cases, mixing with certain singly excited configurations can lower the energy of the low-spin state, but not that of the high-spin state, and the former falls below the latter. This mechanism of reversing the singlet−triplet ordering has been termed dynamic spin polarization.[29,30]

Although these guiding rules (the aufbau principle and extended Hund’s rule) have proved to be extremely useful in predicting the ground-state multiplicity, it is often unclear which one would prevail. Indeed, there is no quantitative criterion of separating the aufbau and Hund’s domains, and the decisive word belongs to either an experiment or predictive electronic structure calculations. Moreover, these simple models do not predict relative order of other low-lying states and fail in the case of substituted species, especially when charge is introduced.[31,32]

We have calculated and analyzed relative state ordering in several prototypical triradicals from Figure 1, i.e., in tridehydrobenzene (TDB) isomers (1,2,3-, 1,2,4-, and 1,3,5-C_6H_3),[7,8] 1,3,5-trimethylenebenzene (TMB),[11] and dehydro-*m*-xylylene (DMX) isomers (5-DMX and 2-DMX).[9,11]

3.1. Low-Lying Electronic States in C_6H_3 Isomers. Molecular orbitals of the C_6H_3, or TDB isomers are shown in Figure 4. The three σ orbitals derived from the three sp^2-hybridized orbitals of the dehydrocarbons are between the bonding and antibonding π-orbitals, which are similar to these of benzene.

If three σ-orbitals were all exactly degenerate, the ground state of the molecule would be a quartet, according to Hund’s rule. If the orbitals are well separated in energy, however, the aufbau principle would predict a doublet ground state, in which

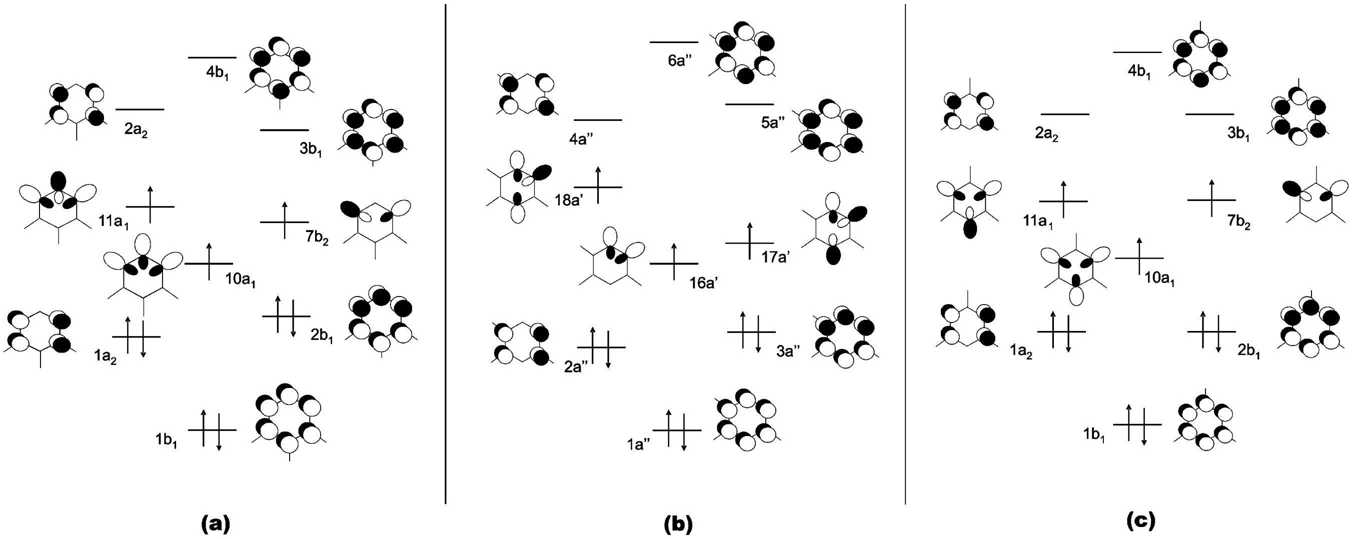

Figure 4. Molecular orbitals of (a) 1,2,3-C_6H_3, (b) 1,2,4-C_6H_3, and (c) 1,3,5-C_6H_3. Only the π-system, which is similar to that in benzene, and the three σ orbitals, which in the lowest quartet state host unpaired electrons, are shown.

the lowest triradical orbital is doubly occupied and the singly occupied orbital is the second lowest.

For the C_6H_3 isomers, the aufbau principle prevails over Hund's rule and their ground states are closed-shell-type doublets, (g) from Figure 3. The ground-state dominant configuration, in all three cases, has the lowest triradical orbital ($10a_1$ in 1,2,3- and 1,2,4-TDB, and $16a'$ in 1,3,5-TDB) doubly occupied and the next orbital ($7b_2$, $17a'$ and $11a_1$ in 1,2,3-, 1,2,4-, and 1,3,5-TDB, respectively) singly occupied. The closed-shell doublet ground state of these triradicals is a signature of a bonding interaction between the unpaired electrons.

In 1,2,3-TDB, the $\tilde{X}^2B_2$ ground state is followed in energy by the 1^2A_1 state, whose wave function is of type e: the dominant configuration has the $10a_1$ orbital doubly and the $11a_1$ orbital singly occupied. Although the vertical energy gap between the two doublets is more than 1 eV, adiabatically these states are nearly degenerate. The next state is the 1^4B_2 quartet, whose $M_s = {}^3/_2$ and $M_s = {}^1/_2$ components are shown in Figure 3, (a) and (b), respectively. The $M_s = {}^3/_2$ component of this state was used as the spin-flip reference. At higher energy, there are two doublet states, 1^2B_1 and 1^2A_2, derived from the excitation of an electron from the $1a_2$ and $2b_1$ π orbitals to the $10a_1$ σ orbital.

In the 1,2,4-isomer, the triradical orbitals are all of the same symmetry (a'), and the low-lying triradical states shown in Figure 3 that are of the same multiplicity can mix. The $\tilde{X}^2A'$ ground state is a closed-shell doublet of type (g). The next in energy is the $2^2A'$ state, which is predominantly of type (i) but has also contributions from configurations in which all the triradical orbitals are singly occupied. The second excited state is the lowest quartet, $1^4A'$, whose $M_s = {}^3/_2$ component was chosen as the spin-flip reference for 1,2,4-C_6H_3. Two states of A'' symmetry that are derived from $\pi \rightarrow \sigma$ excitations lie higher in energy. The dominant configuration in the lowest A'' state has the $3a''$, $17a'$ and $18a'$ orbitals singly occupied and $16a'$ doubly occupied, whereas in the next state the configuration that results from a $2a'' \rightarrow 16a'$ excitation of the reference state is dominant. However, for both states, the configurations resulting from the excitation of an electron from the other occupied π orbitals ($1a''$, $3a''$ and $1a''$, $2a''$ respectively) have rather large coefficients (at the ground-state and lowest quartet geometries).

In 1,3,5-C_6H_3, the $\tilde{X}^2A_1$ ground state is a closed-shell-type doublet [(g) in Figure 3, where the orbitals are $10a_1$, $11a_1$, and $7b_2$ in the order of increasing energy]. Next in energy are the 1^2B_2 state, whose wave function is of type e, and the lowest quartet, 1^4B_2. Similarly to the other isomers, the third and fourth excited states (1^4A_2 and 1^4B_1) are derived from the excitation of one electron from a π orbital ($2b_1$ and $1a_2$, respectively) into the lowest triradical (σ) orbital ($10a_1$). These two states are degenerate in D_{3h} symmetry (e.g., at the equilibrium geometry of the 1^4B_2 state).

The extent of the interaction between the "unpaired" electrons in the ground (low-spin) state and in the lowest high-spin state is reflected in the value of the adiabatic energy separation between these states. Thus, in benzynes, as the distance between radical centers increases (from ortho to meta to para), the energy of the low-spin state becomes higher (as the bonding interaction becomes weaker), and the high-spin state is lowered in energy, due to weaker electron repulsion. This results in a decrease of the singlet−triplet gap as ortho > meta > para. In tridehydrobenzenes, the strongest bonding interaction in the low-spin state and the strongest repulsion in the high-spin state both occur in the 1,2,3-isomer, where the three radical centers are closest together, resulting in the largest doublet−quartet gap. The relative stability of the ground and lowest quartet states of 1,2,4- and 1,3,5-TDB is less obvious a priori. From the EOM-SF-CCSD/cc-pVTZ/cc-pVDZ calculations,[8] we found that the bonding interaction in the $\tilde{X}^2A'$ state of 1,2,4-TDB is stronger than in the $\tilde{X}^2A_1$ state of 1,3,5-TDB, whereas the lowest high-spin states of the two molecules are very close in energy. This results in a larger doublet−quartet gap in the 1,2,4-isomer. In conclusion, the most efficient bonding interaction occurs in the ground state of 1,2,3-TDB, followed by the 1,2,4- and 1,3,5-isomers, respectively. The corresponding adiabatic doublet−quartet gaps are 2.14, 1.79, and 1.20 eV, respectively.[7,8]

3.2. Trimethylenebenzene: A Quartet Triradical. On the first glance, MOs of 1,3,5-TMB are similar to those of 1,3,5-TDB: two of them are exactly degenerate at D_{3h} geometries. However, the bonding character of the lowest orbital is less pronounced because of the smaller overlap between the π radical centers. As a result, the ground state of TMB is quartet, in agreement with Hund's rule.[11,33,34] The lowest doublet state, or rather, a Jahn−Teller pair, is 0.76 eV higher in energy (vertically). Low-lying electronic states of TMB are shown in Figure 6.[11]

3.3. Electronic States of 2-DMX and 5-DMX: A Quartet vs an Open-Shell Doublet Ground State. Two DMX triradi-

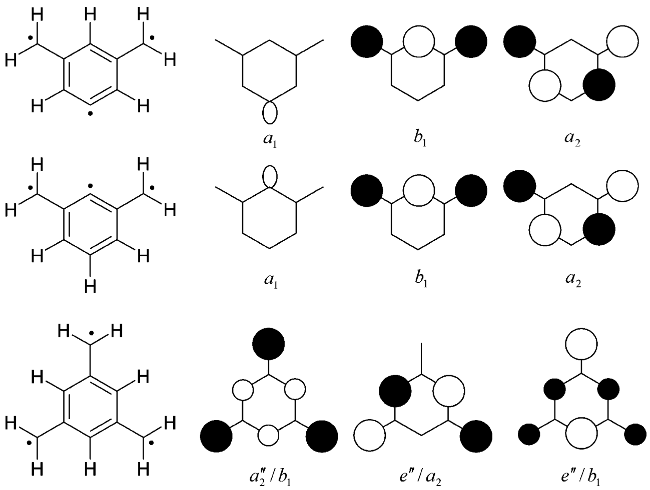

Figure 5. Molecular orbitals of 1,3,5-TMB, 5-DMX, and 2-DMX.

cals, 2-DMX and 5-DMX, belong to the family of $\sigma-\pi$ triradicals. Their MOs and electronic states are shown in Figures 5 and 6, respectively.[9,11] Different nodal structures of these orbitals result in reduced couplings between some configurations from Figure 3, e.g., between pairs of determinants from wave functions (e)−(h). As a result, coefficients λ' and λ'' are very small, which has interesting consequences. For example, small λ's result in wave functions with large charge separations; e.g., states (e) and (g) in which the σ-orbital is doubly occupied correspond to an electron being transferred from the π-system into the σ radical center. Consequently, the corresponding states lie rather high in energy. For example, the 1^2B_1 state, which, by aufbau principle, should be the DMX ground state, is more than 2 eV above (vertically) the ground state in both DMX isomers. Likewise, states of type (e), 1^2A_2, are also high in energy. Thus, due to the $\sigma-\pi$ character of DMX, the only covalent states are open-shell type states (b) and (d), and state (i). This explains a very unusual state ordering shown in Figure 6.

The nature of the ground state of DMX is, perhaps, the most interesting feature of these triradicals. Two covalent wave functions in which the unpaired electrons are localized at the corresponding radical centers are a quartet (b) and an open-shell doublet (c). In the case of noninteracting radical centers, these two states would be exactly degenerate, however, the interactions with core electrons preferentially stabilize one of them, as can be predicted by a qualitative spin-polarization model. In agreement with these predictions, the ground state of 5-DMX is the open-shell doublet 1^2B_2 state, and 2-DMX has a quartet ground state, 1^4B_2. The gaps between open-shell doublet and quartets are 0.16 and 0.44 eV, respectively.

The nodal considerations and charge localization in the σ radical center also explain the high excitation energy of the 2^2A_1 state. In both isomers, the lowest energy closed-shell type doublet (i.e., doublet with one of the triradical orbitals being occupied by a pair of electrons) is the 1^2A_1 state, which resembles the lowest-energy singlet in *m*-xylylene.

Close inspection of Figure 6 reveals another interesting difference between two isomers, that is, a relative order of two states in which σ orbital is doubly occupied, i.e., 1^2B_1 and 1^2A_2. Though in agreement with aufbau principle, in 5-DMX the 1^2B_1 state in which the unpaired electron occupies the lowest π orbital is considerably lower than 1^2A_2; the ordering is reversed in 2-DMX. This can be explained by the symmetry and nodal structure of π orbitals: the lower π orbital has some density on C3, whereas the higher π does not. Thus, in 2-DMX the negative charge on σ center destabilizes an unpaired electron on the lower π orbital but has no effect on an unpaired electron on the higher π orbital.

4. Structural Manifestation of the Interaction between Radial Centers in the C_6H_3 Isomers

Equilibrium structures of the ground and lowest quartet states of TDB isomers[8] reflect bonding interactions between the radical centers, as suggested by the bonding character of the lowest σ molecular orbital (see Figure 4). Indeed, the calculated equilibrium structures manifest considerably contracted distances (relative to benzene) that demonstrate partial bond formation between the radical centers. The magnitude of the distance decrease is related to the strength of these partial bonds. Figure

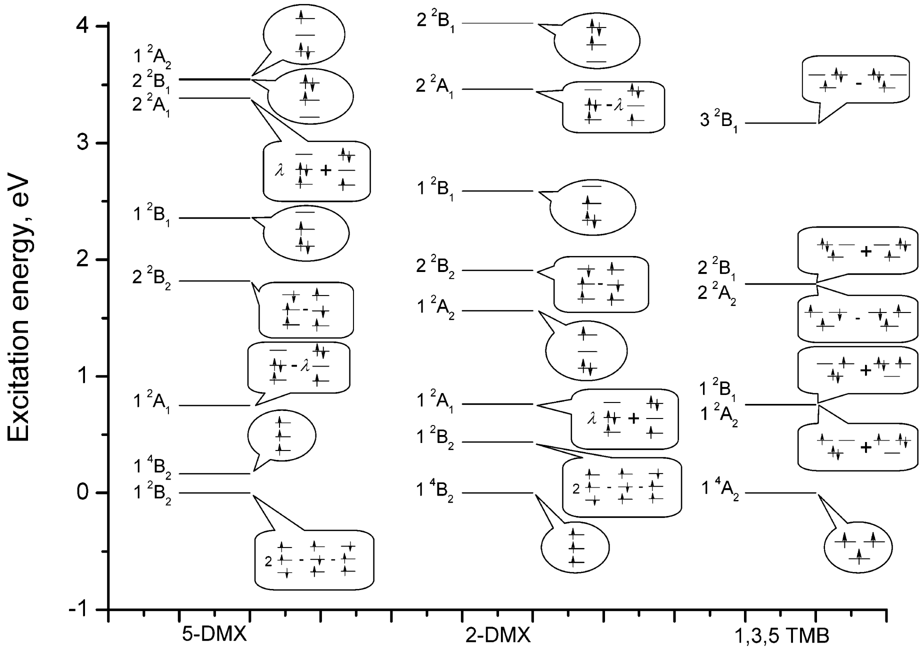

Figure 6. Low-lying electronic states of 1,3,5-TMB, 5-DMX, and 2-DMX calculated at the corresponding equilibrium geometries. MO are shown in Fig. 5.

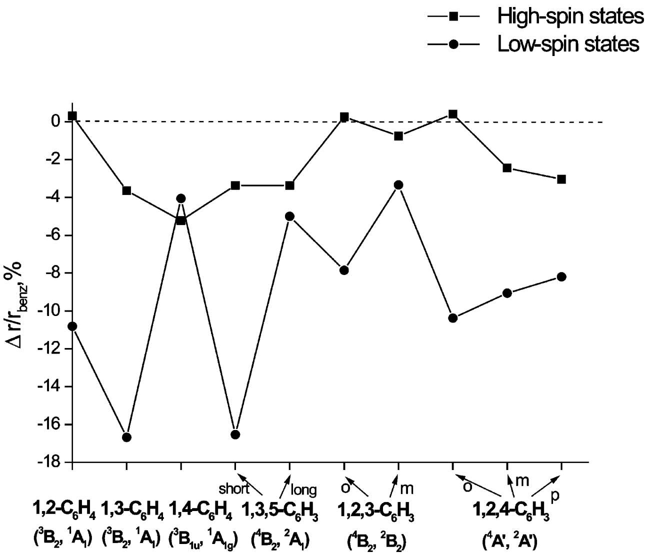

Figure 7. Relative change of the distance between radical centers in benzynes (C_6H_4) and tridehydrobenzenes (C_6H_3) with respect to benzene. For each species, $\Delta r/r_{benz}$ (in %) for the ground (low-spin) state and for the lowest high-spin state is shown. For the C_6H_3 isomers, all possible distances between two radical centers are considered; for example, in 1,2,4-C_6H_3, the distances between centers in ortho (o), meta (m), and para (p) positions are used.

7 shows the relative changes in the distances between tridehydrocarbons (in the C_6H_3 isomers) and didehydrocarbons (in the C_6H_4 species) with respect to the corresponding distances in the benzene molecule. The changes are calculated as $\Delta r/r_{benz}$, where Δr is the deviation of the distance between radical centers in a given triradical or diradical from the distance between carbon atoms situated in the same positions in benzene (denoted by r_{benz}). These values quantify the effect of the interaction between radical centers on the structures of the di- and tridehydrobenzenes.

In the $\tilde{X}^2B_2$ ground state of 1,2,3-TDB, the shortening of the distance between meta radical centers is much less pronounced than in the $\tilde{X}^1A_1$ state of *m*-benzyne, whereas the bond between ortho dehydrocarbons is only slightly longer than the one in the $\tilde{X}^1A_1$ state of *o*-benzyne. This implies that in the ground state of 1,2,3-TDB, the ortho interaction prevails over the meta one but is weaker than the ortho interaction in *o*-benzyne, due to σ delocalization over dehydrocarbons C1, C2, and C3. An interesting bonding pattern arises in the nearly degenrate (adiabatically) $^2A_1$ state, where there is a significant contraction of the C1−C3 and lengthening of C1−C2 distance.

In 1,2,4-C_6H_3 ($\tilde{X}^2A'$ state), the C1−C2 bond is almost as short as the one in o-benzyne, whereas the distance between the meta radical centers at C2 and C4 is considerably longer than that in *m*-benzyne, but shorter than that in 1,2,3-C_6H_3. This suggests that, although the interaction between the ortho radical centers at C1 and C2 prevails, the interaction between the C2 and C4 dehydrocarbons also has a noticeable effect on the structure of 1,2,4-TDB. The fact that the distance between the para dehydrocarbons C1 and C4 is shorter than the distance in *p*-benzyne is probably due to an overall tighter structure rather than a stronger interaction between these radical centers.

In 1,3,5-zTDB, whose $\tilde{X}^2A_1$ ground state is a Jahn−Teller distorted doublet,[7] the distance between the C1 and C3 dehydrocarbons is much shorter than the C1−C5 and C3−C5 distances between the other radical centers in the meta isomer. The C1−C3 distance is only slightly shorter than the one in *m*-benzyne, so it can be concluded that the radical center at C5 interacts very weakly with the diradical moiety in 1,3,5-C_6H_3.[7,35]

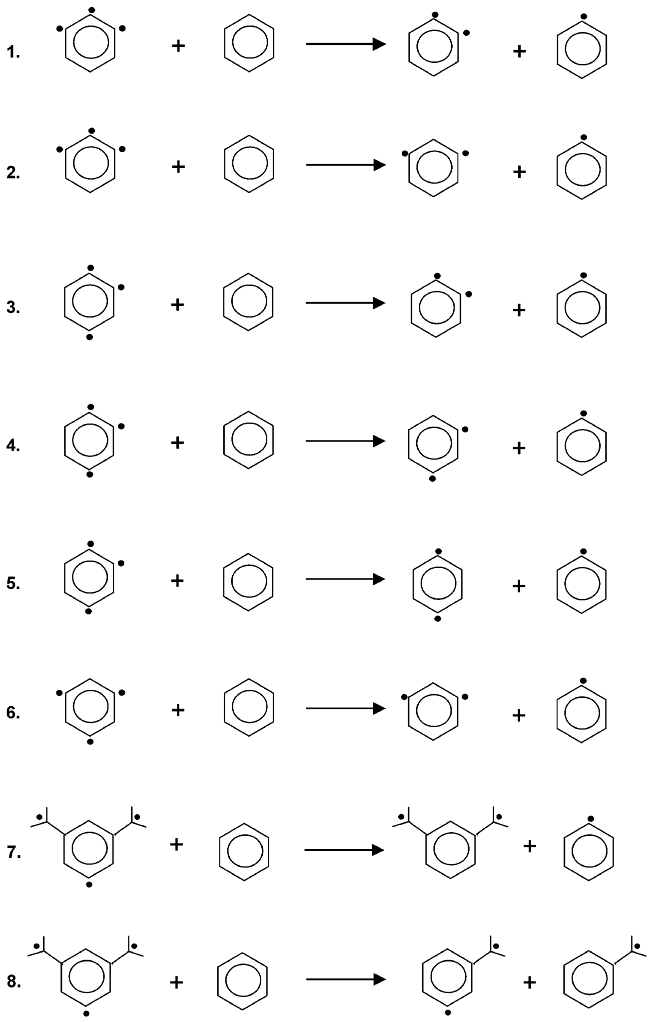

Figure 8. Reactions whose energy changes define the triradical stabilization energies for the C_6H_3 isomers and 5-DMX. Contrary to diradicals, in triradicals there are several ways to separate the third radical center from a diradical moiety.

TABLE 1: Diradical Stabilization Energies (DSEs) for Benzynes (kcal/mol)

	o-C_6H_4	*m*-C_6H_4	*p*-C_6H_4
theory[a]	30.89	16.66	1.30
theory + expt[b]	31.82	17.63	2.09
expt[c]	35.4 ± 3.3	19.4 ± 3.2	3.5 ± 3.0

[a] High-spin DSEs calculated by CCSD(T)/cc-pVTZ (with a ROHF reference). Singlet−triplet gaps, computed by SF-OD with a mixed basis set (cc-pVTZ on C, cc-pVDZ on H), are from ref 39. [b] ROHF-CCSD(T)/cc-pVTZ high-spin DSEs and experimental singlet−triplet gaps[40] were used. [c] Experimental DSEs calculated from heats of formation given in the Appendix of ref 8.

Even in the high-spin states of the C_6H_3 and C_6H_4 isomers, the distances between meta and para radical centers are contracted relative to benzene. This has been explained to be a consequence of an increase in electron density in the central part of these molecules upon C−H bond breaking.[7] For radical centers in ortho isomers, this effect is compensated by the strong electron repulsion and the distance between C1−C2 dehydrocarbons is slightly elongated with respect to benzene.

To summarize, the equilibrium structures of the C_6H_3 and C_6H_4 isomers indicate the formation of partial bonds between the radical centers in these species.

TABLE 2: Reaction Energies at 0 K (kcal/mol) for the Low-Spin[a] Isodesmic Reactions 1−8[b]

TSE	1	2	3	4	5	6	7	8
theory[c]	2.35	17.17	0.43	15.25	28.75	2.75	3.18	3.01
expt[d]	12.3 ± 4.9	28.3 ± 6.7	4.0 ± 5.8	20.0 ± 7.4	35.9 ± 7.3	3.7 ± 5.6	1.0 ± 4.0	1.0 ± 4.0

[a] The ground states (singlet and doublet, respectively) of the diradicals and triradicals are involved in the reactions. [b] See Figure 8. [c] Low-spin TSEs calculated using SF-CCSD (ROHF) gaps for the triradicals and diradicals and ROHF-based CCSD(T)/cc-pVTZ high-spin TSEs. [d] TSEs for reactions 1, 3 and 6 from refs 35 and 37. TSEs for reactions 2, 4 and 5 calculated using the TSEs for reactions 1, 3 and 6 and DSEs for benzynes computed using data from ref 41. TSEs for reactions 7 and 8 are from ref 9.

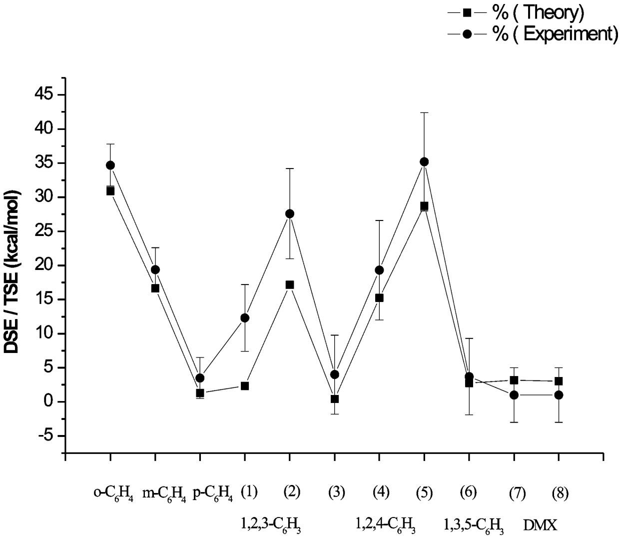

Figure 9. Theoretical and experimental values of DSEs and TSEs for benzynes, TDBs, and 5-DMX. (1)−(8) correspond to the isodesmic reactions in Figure 8.

5. Thermochemical Consequences of the Interaction between the Unpaired Electrons

A measure of the strength of the interaction between one radical center and a diradical moiety is provided by the triradical stabilization energy (TSE).[35] For example, for the TDB isomers TSE is defined as the energy at 0 K (ΔE_0°) of hypothetical isodesmic reactions (see Figure 8) in which a radical center is transferred from a triradical to a benzene molecule, yielding a phenyl radical and a benzyne diradical as products. A positive value of the TSE indicates stabilization of the triradical relative to separated radical centers. This definition of TSE is analogous to that given by Wierschke et al.[36] for the diradical stabilization energy (DSE) of the benzyne isomers. In their paper, DSE is calculated as the energy change in the reaction between a benzyne molecule and benzene, in which two phenyl radicals are formed; this is also the approach we employ in this work for the calculation of the DSEs of benzynes. Experimentally, TSEs and DSEs can be determined from heats of formation.[35,37,38]

Although there is only one way to separate the two radical centers in a diradical, there are, in general, several possible channels for the separation of a radical center from a triradical. For example, in the case of 1,2,3- and 1,2,4-C_6H_3, the reaction with benzene may proceed on two and three different channels, respectively. As can easily be proved, however, for a given triradical the sum of TSE and the DSE of the benzyne product is the same for all the TSE channels—simply because there is only one way to separate all three radical centers.

Low-spin DSE for benzynes and TSEs for TDBs and 5-DMX are given in Tables 1 and 2, respectively, and illustrated in Figure 9. By comparing the TSE values for different reactions, several conclusions regarding the extent of the interaction between radical centers can be drawn. First, as expected, in a given triradical the strength of the interaction decreases as the distance between the radical centers increases (from ortho to meta to para).

In 1,2,3-C_6H_3, the interaction between centers situated in an ortho position is much stronger than the meta interaction, as proved by the small TSE of reaction **1**. In 1,2,4-C_6H_3, the ortho interaction is also dominant (the TSE of reaction **3** is very small). For 1,3,5-C_6H_3, it can be concluded from the small TSE of reaction **6** that the third radical center interacts very weakly with the *m*-benzyne moiety.

TSEs in DMX (reactions **7** and **8**) are rather small, i.e., around 3 kcal/mol, which reflects a weak interaction between all three radical centers.

As follows from Tables 1 and 2, and Figure 9, the overall trend in theoretical TSEs closely follows the experimental one. With estimated error bars of 1 kcal/mol for theoretical values, the calculated TSE and DSE agree with the experimental ones, except for *o*-benzyne, which is discussed in details in ref 8.

6. Conclusions

Interaction of unpaired electrons in triradicals results in unusual bonding patterns. By using advanced ab initio techniques, we characterized electronic structures of several prototypical diradicals and triradicals and determined structural, spectroscopic, and thermochemical consequences of the partial bonds formed between the radical centers. In TDB and DMX isomers the strength of these bonds varies from a rather weak (but stabilizing) interaction of about 0.5 kcal/mol up to 32 kcal/mol, which is one-third of a typical chemical bond energy. The structural signature of these bonds is shorter distances between the radical centers relative to the closed-shell precursor. Depending on the nature of triradical MOs, the ground state in these species varies from quartet, to closed- or open-shell doublet.

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