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Electronic structure of the two dehydro-*meta*-xylylene triradicals and their derivatives

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Abstract

The ground and low-lying excited states of the 5-dehydro-*meta*-xylylene and 2-dehydro-*meta*-xylylene triradicals, as well as their derivatives are characterized by the equation-of-motion spin-flip coupled-cluster method with single and double substitutions. The effect of substituents in the C2, C4, and C6 positions on electronic states ordering is investigated. In the 5-dehydro-*meta*-xylylene triradical, which has the 1^2B_2 ground state, charged substituents at C2 stabilize the closed-shell 1^2A_1 state, whereas the NO substituent lowers the 1^2A_2 and 1^2B_1 states. In the 2-dehydro-*meta*-xylylene triradical with the 1^4B_2 ground state charged substituents also significantly stabilize the 1^2A_1 state and 1^2B_1 state. The observed effects are explained by the nodal structure of the π orbitals and charge localization in the σ radical center.

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1. Introduction

Polyradicals have attracted considerable attention as prospective building units of organic magnets [1]. However, the design of magnetic materials and other practical applications require understanding the electronic structure of these species, e.g. factors that determine their reactivity, multiplicity of the ground state, energy gaps between high-spin and low-spin states, etc. Qualitative structure–property relationships, and simple electronegativity and molecular orbital (MO) considerations provide useful guidelines for the understanding and control of these properties, however, the decisive word often belongs to predictive *ab initio* calculations or experiment.

Since electronic density varies strongly in different electronic states, substituents at specific positions may preferentially stabilize some states and even change the state ordering and the multiplicity of the ground state thus alter-

ing the chemical identity of a molecule. Recently, we presented computational studies of the substituent effects on the state ordering in the *meta*-xylylene (MX) diradical [2], a popular prototypical molecule that features triplet ground state [3–5]. Quite contrary to qualitative MO-based predictions, the singlet–triplet gap was found to be rather insensitive to substituents of varying electronegativity, as well as π or σ donor/acceptor strength. However, in agreement with the Dougherty proposal [6] and the reactivity studies by Kentamaa and coworkers [7], *charged* substituents may reverse state ordering and change the multiplicity of the ground state. Another interesting finding was strong stabilization of an open-shell singlet state in the N-oxidized pyridinium analogue of MX.

This work investigates the effect of substituents on the electronic state ordering in two triradicals derived from MX, i.e., 2- and 5-dehydro-*meta*-xylylenes (2-DMX and 5-DMX). 5-DMX is the first example of a hydrocarbon with an *open-shell doublet* ground state [8], due to the σ–π character of frontier MOs. In agreement with spin-polarization model, the ground state of 2-DMX is quartet. We compare the electronic structure of the 5-DMX and 2-DMX triradicals, and consider the substituents that we

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found to have a considerable effect on the state ordering in MX [2].

The structure of the Letter is as follows. Section 2 briefly describes electronic structure of triradicals, methodology, and computation details. Section 3 presents the results and discussion. Conclusions are given in Section 4.

2. Theory and computational details

Extending the Salem's definition of diradicals [9], triradicals [10] can be defined as molecules with three unpaired electrons distributed in three nearly degenerate orbitals. This gives rise to several low-lying electronic states and multi-configurational wave functions, which can be accurately and efficiently described by the spin-flip (SF) method [11,10]. Electronic structure of triradicals and the relevant methodology issues are discussed in details in Refs. [10,11].

The SF method describes low-spin states as spin-flip excitations from a well-behaved high-spin reference state:

$$\Psi_{M_s=1/2}^{d,q} = \widehat{R}_{M_s=-1} \widetilde{\Psi}_{M_s=3/2}^{q} \qquad (1)$$

where $\Psi_{M_s=1/2}^{d,q}$ are target low-spin quartet and doublet states, $\widetilde{\Psi}_{M_s=3/2}^{q}$ is a high-spin reference state, i.e. $\alpha\alpha\alpha$ component of the quartet state, and $\widehat{R}_{M_s=-1}$ is an excitation operator that flips the spin of an electron. Thus, all the determinants present in the multi-determinantal doublets and low-spin quartet state can be obtained by single spin-flipping excitations of an electron from high-spin $\alpha\alpha\alpha$ component of the quartet state, and therefore are treated in a balanced way. By increasing the accuracy of the reference state description, accuracy of the target states can be systematically improved [12–19,11]. This study employs EOM-SF-CCSD method [18] in which the reference is described by coupled-cluster method with single and double substitutions (CCSD) [20], and the target states are described by the equation-of-motion (EOM) theory [21]. Thus, in EOM-SF-CCSD, the operator $\widehat{R}$ includes single and double excitations that flip the spin of an electron. This method has been used to study structures, thermochemistry, excited states and singlet–triplet gaps in diradicals [15,22–24,2] and triradicals [25,8,26,10]. Equilibrium geometries were determined by using analytic gradients that we developed and implemented for CCSD and EOM-CCSD wave functions [17]. The CCSD and EOM-SF-CCSD analytic gradients enable quantitatively accurate and computationally affordable optimization of triradicals' geometries in the ground and low-lying excited states.

Calculations were performed using the *Q-Chem* electronic structure package [27]. The equilibrium structures of high-spin quartet states were optimized by the CCSD method with the UHF reference and the 6-31G* basis set [28], and used to calculate vertical energy gaps. Other states were optimized at the EOM-SF-CCD/6-31G* level using the UHF reference. The vertical and adiabatic energy gaps were evaluated by EOM-SF-CCSD with the ROHF reference and the 6-31G* basis set [28].

3. Results and discussion

5-DMX, 2-DMX and their derivatives studied in this work are shown in Fig. 1. MOs of 5-DMX (molecule I) and 2-DMX (molecule IV), which host the unpaired electrons, are shown in Fig. 2. The frontier MOs of their substituted derivatives are very similar. These triradicals are of a σ–π type. Two π MOs are nearly degenerate and have different nodal structure. At the C2 position, the b_1 orbital has considerable density, whereas the a_2 orbital has a node. Likewise, at the C4 and C6 positions, the a_2 orbital has considerable density, whereas the b_1 orbital has a node. Therefore, stabilizing or destabilizing substituents in these positions may affect the energy gap between these two orbitals, subsequently changing the ordering of excited states. However, as found in the recent study of MX [2], only charged substituents and N-oxidation have considerable effect on the states ordering. Following these ideas, we introduced positive and negative charges in molecules II and V. Molecules III and VI feature NO group, which was found to have strong stabilizing effect on low-spin open-shell states [2].

Fig. 3 and Table 1 summarize optimized geometries for the ground and excited states of the triradicals. The
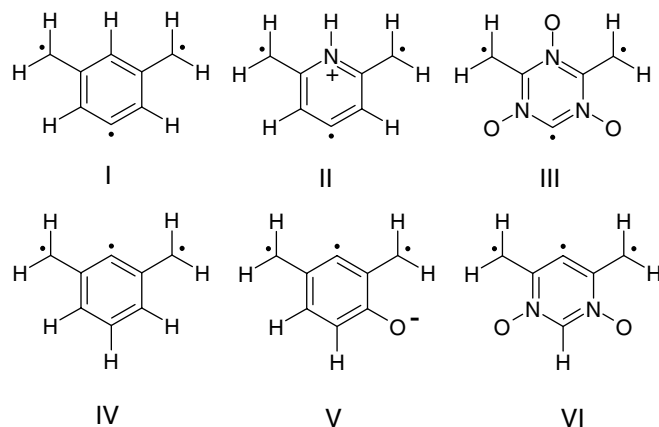

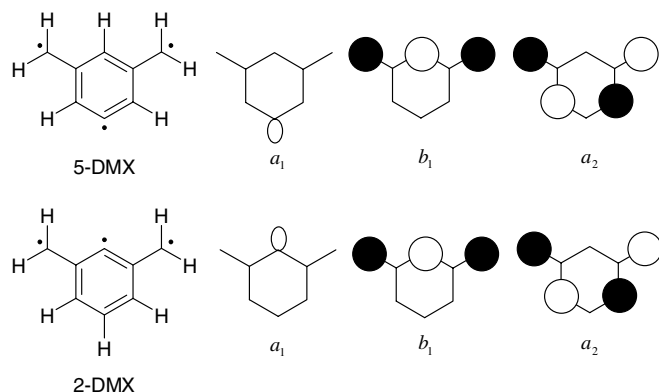Fig. 1. 5-DMX, 2-DMX and their derivatives.

Fig. 2. Frontier molecular orbitals of 5-DMX (I) and 2-DMX (IV).

geometries of the quartet states were used to calculate vertical excitation energies for the six lowest states, which are presented in Table 2 and Figs. 4, 5. Selected adiabatic excitation energies are also given in Table 2.
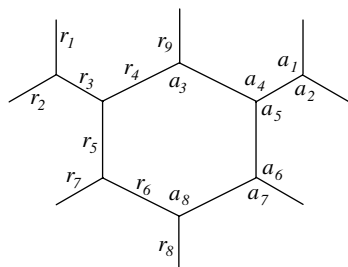

Fig. 3. The definition of the geometrical parameters summarized in Table 1.

The σ–π character of the DMX isomers results in an unusual ordering of the electronic states [8,10]. For example, closed-shell doublets, $^2B_1$ and $^2A_2$ states, in which the lowest frontier orbital (σ) is doubly occupied are 1.6–3.4 eV above the quartet and open-shell doublet states in both I and IV. This violation of the aufbau principle occurs because placing two electrons on the σ-orbital results in charge separation between the σ and π systems, which is energetically unfavorable in the gas phase. Interestingly, the relative ordering of these two states in 5-DMX and 2-DMX is different. In 5-DMX, the $^2A_2$ state in which the third electron occupies higher of the two π orbitals higher in energy than $^2B_1$, in agreement with aufbau considerations. In 2-DMX, however, the vertical energy of this state drops by about 1 eV below $^2B_1$! This can be explained by the nodal structure of MOs and the electrostatic repulsion

Table 1

The equilibrium geometries of the 1^4B_2, 1^2B_2, and 1^2A_1 states used in the vertical and adiabatic excitation energy calculations

Parameter	I (1^4B_2)	II (1^4B_2)	III (1^4B_2)	IV (1^4B_2)	V (1^4B_2)	VI (1^4B_2)
r_1	1.087	1.087	1.082	1.086	1.087	1.084
r_2	1.087	1.084	1.082	1.087	1.089	1.083
r_3	1.402	1.409	1.341	1.397	1.400	1.368
r_4	1.419	1.371	1.415	1.408	1.415	1.400
r_5	1.441	1.421	1.435	1.441	1.437	1.442
r_6	1.374	1.375	1.330	1.394	1.388	1.354
r_7	1.088	1.086	1.281	1.089	1.267	1.278
r_8				1.089	1.091	1.080
r_9	1.090	1.020	1.277			
a_1	121.2	122.0	119.6	121.2	121.6	119.8
a_2	121.3	120.0	118.9	121.0	119.0	120.0
a_3	122.9	126.0	124.2	127.2	128.4	128.6
a_4	121.4	118.2	123.4	123.1	123.8	128.1
a_5	120.8	124.4	121.1	122.2	119.3	118.7
a_6	120.1	120.2	119.1	118.8	120.6	119.7
a_7	122.5	123.5	122.0	120.4	124.7	119.9
a_8	126.6	126.8	127.0	121.8	124.6	124.3
E_{tot}	−307.938393	−324.328562	−580.904181	−307.944907	−382.414178	−489.936199
E_n	310.414416	327.034675	602.879812	308.822007	377.442850	493.572563

Parameter	I (1^2B_2)	II (1^2B_2)	II (1^2A_1)	III (1^2B_2)	V (1^2A_1)
r_1	1.087	1.087	1.086	1.082	1.087
r_2	1.087	1.085	1.084	1.082	1.088
r_3	1.399	1.404	1.405	1.343	1.399
r_4	1.423	1.373	1.375	1.415	1.387
r_5	1.442	1.427	1.403	1.432	1.462
r_6	1.379	1.378	1.373	1.344	1.347
r_7	1.088	1.086	1.087	1.278	1.236
r_8					1.090
r_9	1.090	1.021	1.016	1.278	
a_1	121.2	122.0	122.2	119.6	121.2
a_2	121.3	120.0	119.7	118.9	120.0
a_3	123.0	126.4	125.1	124.2	130.0
a_4	121.4	118.1	122.1	123.1	128.1
a_5	120.9	124.9	120.4	121.2	116.6
a_6	120.0	119.9	120.1	119.2	124.1
a_7	122.5	123.6	122.5	121.5	119.4
a_8	126.4	126.5	125.4	125.7	122.2
E_{tot}	−307.945084	−324.331665	−324.330836	−580.915902	−382.415560
E_n	310.053496	326.606071	327.727909	602.350319	378.759802

Bond lengths are in angstrom, angles are in degrees. The corresponding total and the nuclear repulsion energies (hartrees) are also given.

Table 2
Total (hartree), vertical and adiabatic excitation energies (eV) relative to the $^4B_2$ state

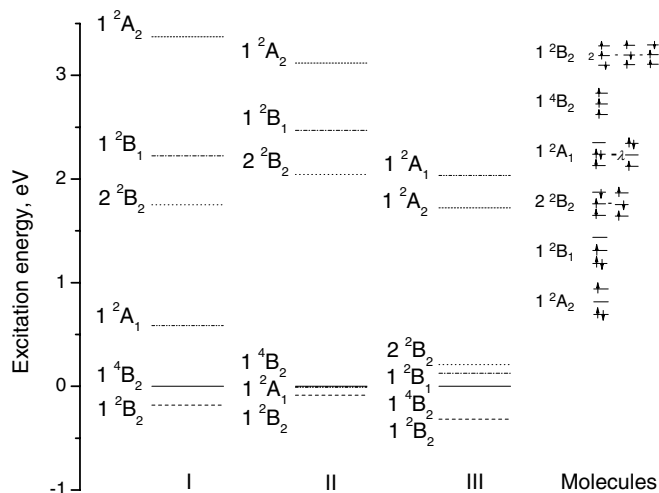| Molecule	1^4B_2	1^2B_2	2^2B_2	1^2B_1	1^2A_1	1^2A_2	$1^2B_2^{adiab}$	$1^2A_1^{adiab}$
I	−307.938393	−0.182	1.752	2.223	0.587	3.373	−0.182	
II	−324.328562	−0.085	2.045	2.470	−0.010	3.118	−0.085	−0.062
III	−580.904181	−0.317	0.211	0.127	2.034	1.722	−0.319	
IV	−307.944907	0.460	1.967	2.681	0.799	1.565		
V	−382.414178	0.415	1.541	0.718	0.152	1.566		−0.0376
VI	−489.936200	1.060	0.426	2.019	1.508	0.803		

Fig. 4. Vertical state ordering in 5-DMX and its derivatives calculated at the ROHF-EOM-SF-CCSD/6-31G* level at the UHF-CCSD/6-31G* optimized geometry of the $^4B_2$ state.
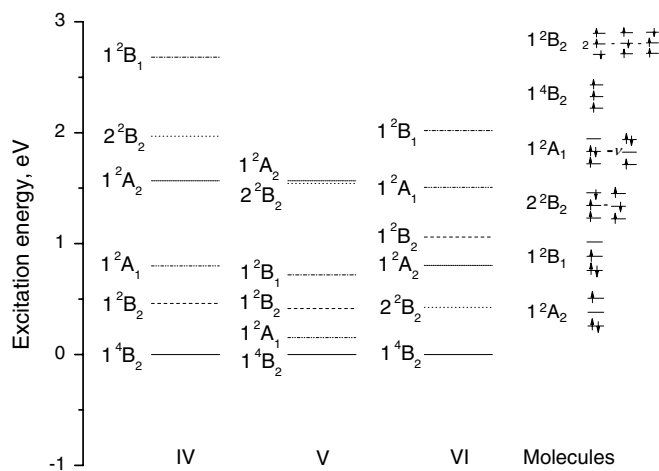

Fig. 5. Vertical state ordering in 2-DMX and its derivatives calculated at the ROHF-EOM-SF-CCSD/6-31G* level at the UHF-CCSD/6-31G* optimized geometry of the $^4B_2$ state.

between σ and π electrons – the lower π orbital has some density on σ radical center in 2-DMX, but not in 5-DMX. Finally, the lowest closed-shell doublet state in both isomers is the $^2A_1$ state with the singly occupied σ-orbital, and in which stabilization is achieved through the interaction of two configurations with doubly occupied π orbitals.

The two lowest states in DMXs are those in which all three triradical orbitals are singly occupied, i.e., quartet $^4B_2$ and open-shell doublet $^2B_2$. These states have the lowest energy because these electronic arrangements correspond to the covalent configuration and does not involve charge separation. The relative ordering of these states and, therefore, the multiplicity of the ground state is different: in 2-DMX, the quartet is 0.46 eV lower than the doublet, whereas in 5-DMX, the doublet is 0.18 eV below the quartet. This can be explained by spin-polarization model [29] or by disjoint/non-disjoint MO analysis [30]. In 5-DMX, the σ-orbital does not overlap with the π-orbital and, therefore, Coulomb repulsion between the σ and π electrons is small both for the same and different spin electrons. However, the interactions between the electrons in these orbital with the core electrons preferentially stabilize an open-shell doublet. In 2-DMX, the doublet is de-stabilized due to the Coulomb repulsion between the same-spin σ and π electrons. As expected [8], the optimized geometry of the $^2B_2$ state in 5-DMX is very similar to that of the quartet, and the corresponding adiabatic energy is the same as vertical.

As follows from Table 2 and Figs. 4, 5, the vertical (and adiabatic) energy gap between the open-shell doublet and the quartet states is not very sensitive to the charged substituents (molecules II and V), however, the energy of the 1^2A_1 state is, in agreement with the MX results, where the corresponding singlet state becomes the ground state upon the substitution. In molecule II, a derivative of 5-DMX with a positive charge introduced at the C2 position, the vertical energy of the closed-shell doublet 1^2A_1 state drops below the quartet. Adiabatic results show that 1^2A_1 becomes nearly degenerate with the open-shell doublet, $^2B_2$.

Likewise, in molecule V with a negative charge introduced at the position where the a_2 orbital of 2-DMX has considerable density and the b_1 orbital has a node, both 1^2A_1 and 1^2B_1 are stabilized, the latter dropping below 1^2A_2. Adiabatically, the 1^2A_1 state is 0.04 eV below 1^4B_2. Such a small energy gap (less than 1 kcal/mol) cannot be resolved without higher level calculations, however, the present result suggests that the character of the ground state in 2-DMX may be altered by charged substituents. The relative stabilization of 1^2B_1 occurs due to the destabilization of the a_2 orbital, which has the considerable density at C4.

In molecules III and VI, N-oxidized derivatives, the 1^2B_1 and 1^2A_2 states become lower, whereas the 1^2A_1 state goes up, due to the stabilization of the doubly occupied σ orbital by the two neighboring NO groups bearing partial positive charges on nitrogens. Similarly to MX, the NO substitution stabilizes the open-shell doublet ($^2B_2$) in molecule III, increasing the doublet–quartet gap from 0.18 to 0.32 eV, however, in molecule V the doublet actually becomes higher.

4. Conclusions

The EOM-SF-CCSD method is employed to describe the ground and low-lying excited states of the 5-DMX and 2-DMX triradicals, as well as their derivatives. The effect of substituents in the C2, C4, and C6 positions on electronic states ordering is also investigated. Calculations demonstrate that in the 5-DMX, which has the 1^2B_2 ground state, charged substituents at C2 stabilize the closed-shell 1^2A_1 state, whereas the NO substituent lowers the 1^2A_2 and 1^2B_1 states. In the 2-DMX, which has the 1^4B_2 ground state, the charged substituent also significantly stabilizes the 1^2B_1 state. The results suggest that the closed-shell 1^2A_1 state may, in fact, become the ground state. The observed effects are explained by the nodal structure of the π orbitals and charge localization in the σ radical center.

Acknowledgments

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