

The effect of substituents on electronic states' ordering in *meta*-xylylene diradicals: Qualitative insights from quantitative studies

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Equation-of-motion spin-flip coupled-cluster method with single and double substitutions (EOM-SF-CCSD) is employed to study how substituents affect the electronic states' ordering in *meta*-xylylene diradicals. The electronegativity of substituents and the incorporation of a heteroatom are found to have a negligible effect. The effect of charges on energy gaps is much more pronounced, in agreement with the proposal of Dougherty and co-workers [J. Am. Chem. Soc. **118**, 1452 (1996)]. Resonance structure theory and molecular orbital analysis are employed to explain this phenomenon. The changes in the exocyclic C–C bond length in substituted *meta*-xylylenes, derived from equilibrium structures calculated by using analytic gradients for the EOM-SF-CCSD method, support the original resonance theory explanation by West *et al.* However, a similar resonance-theory-based reasoning fails to explain the quantitative difference between positively and negatively charged systems as well as the observed strong stabilization of an open-shell singlet state in the N-oxidized pyridinium analog of *meta*-xylylene. © 2005 American Institute of Physics. [DOI: 10.1063/1.2018645]

I. INTRODUCTION

Molecules with one or more unpaired electrons attract considerable attention as prospective building blocks in plastic magnetic materials.¹ However, for successful applications many fundamental issues have to be resolved. For example, the stabilization of radical centers and the control of the multiplicity of the ground state of a single polyradical building block are important for practical design. Both properties can be controlled by strategically placed substituents. Qualitative structure-property relationships and simple electronegativity and molecular orbital (MO) considerations provide useful guidelines for this approach. Since electron density varies strongly as a function of an electronic state, energy gaps between electronic states can be tuned up by differential stabilization or destabilization of the states involved. In systems with closely lying electronic states, substituents can change the excited-state ordering and even flip the ground and excited states, thus altering the chemical identity of a molecule. As far as the design of molecular magnets is concerned, the key properties are the multiplicity of the ground state and the energy gap between the ground and the lowest excited states.

While the ground-state multiplicity can often be predicted by using simple orbital occupancy guidelines such as the Aufbau principle, Hund's rule, and their generalizations to molecular systems (e.g., spin-polarization model,² /non* or topology rule,³ disjoint/nondisjoint MO analysis,⁴ and more⁵), the effect of substituents is more difficult to predict (see, for example, the recent study of Clark and Davidson⁶ where the anticipated substituent effect was not achieved due to the rehybridization of radical centers). Charged systems are even more challenging—it was demonstrated by Dough-

erty and co-workers⁷ that, whereas replacing benzene by pyridinium in a *m*-xylylene diradical does not affect the energy separation between the ground triplet and excited singlet states, protonation of the pyridinium unit reverses the state ordering!

The effect of substituents on the singlet-triplet gaps in diradicals has been studied by many theoretical and experimental groups.^{6–14} For example, for a 1,4-didehydrobenzene diradical, Clark and Davidson⁶ found that substituents, which strongly interact with the benzyne π system, do not interact with the σ space, and are only weakly electronegative, should yield the smallest singlet-triplet energy differences and might lead to the triplet ground state. Berson and co-workers^{8,9} reported that electron-withdrawing substituents modulate the singlet-triplet gaps of the singlet tetramethyleneethane-type diradical. Ito *et al.*¹⁰ reported examples of π -conjugated trianthrene systems showing the reverse spin-state preferences depending on the substitution patterns. Geise and Hadad¹¹ found that for *ortho*-, *meta*-, and *para*-substituted phenylcarbenes aromatic ring substituents have a large effect on the singlet-triplet splitting. Shultz *et al.*¹² experimented on the modulation of a singlet-triplet gap in triplet ground-state diradicals. *Ab initio* calculations on pyridine and pyridinium analogs of *m*-xylylene by Dougherty and co-workers⁷ demonstrated that the neutral heterocycle is essentially equivalent to benzene as a ferromagnetic coupling unit, whereas the cationic pyridiniums behave quite differently. Reactivity studies by Kentamaa and co-workers^{13,14} verified that a cationic 2,6-dimethylenepyridinium has a singlet ground state.

In this study, we investigate the effects of substituents on the state ordering in *meta*-xylylenes. We choose this diradical as a prototype¹⁵ because its coupling scheme, *meta* through benzene, has been extensively explored in theory and

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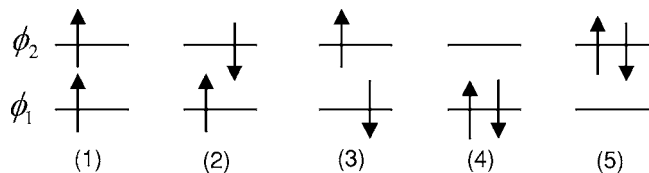


FIG. 1. In diradicals two electrons are distributed in two nearly degenerate orbitals, which results in the following Slater determinants with positive- or zero-spin projection.

experiments.¹⁶ We go beyond considering the two lowest states, i.e., the lowest singlet and triplet states, and investigate several low-lying states by employing accurate electronic structure methods. The focus of this study is on the understanding of the mechanism by which substituents affect the electronic states' ordering. For example, does the electron withdrawal by substituents affect singlet-triplet gaps? How does the charge of substituents influence energy separations? Section II describes electronic structures of diradicals, methodology, and computation details. Section III presents the results and discussion. Conclusions are given in Sec. IV. Additional details are provided as an EPAPS document.¹⁷

II. THEORETICAL METHODS

A. Diradicals

Salem and Rowland¹⁸ define diradicals as molecules with two electrons distributed in two nearly degenerate orbitals. The resulting Slater determinants that have positive- or zero-spin projection are shown in Fig. 1. In all five determinants, the open-shell determinants (2) and (3) are not eigenfunctions of \hat{S}^2 , but the open-shell determinant (1) and the closed-shell determinants (4) and (5) are. As shown in Fig. 2, one can construct valid wave functions that are eigenfunctions of both \hat{S}^2 and \hat{S}_z by taking a linear combination of these determinants. From an electronic structure point of view, wave functions (1) and (2) from Fig. 2 describe high-spin and low-spin triplets, respectively, wave function (3) corresponds to an open-shell singlet, and wave functions (4) and (5) are those of closed-shell singlet states. The coefficient λ from Fig. 2 depends on the energy separation between the two diradical orbitals; e.g., when the orbitals are exactly degenerate, $\lambda=1$. Thus, from a methodological perspective, except for wave function (1), all the others are two configurational. This is why the bulk of the previous studies of diradicals employed multireference methods. Alternatively, these states can accurately be described by the efficient and robust single-reference spin-flip (SF) approach,^{19–26} which is presented in Sec. II B.

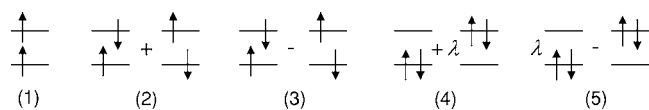


FIG. 2. Diradical wave functions that are eigenfunctions of both \hat{S}^2 and \hat{S}_z .

B. Spin-flip method

The SF method describes low-spin states as spin-flip excitations from a high-spin reference state for which nondynamical and dynamical correlation effects are smaller than those for the corresponding low-spin states,¹⁹

$$\Psi_{M_s=0}^{s,t} = \hat{R}_{M_s=-1} \tilde{\Psi}_{M_s=1}^t, \quad (1)$$

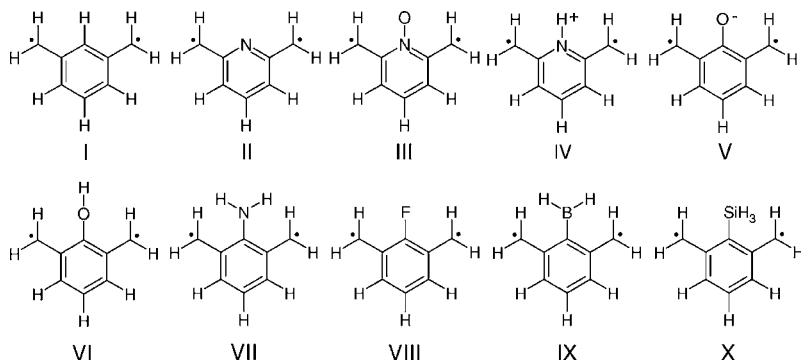
where $\Psi_{M_s=0}^{s,t}$ are target singlet and triplet states, i.e., wave functions (2)–(5) in Fig. 2, $\tilde{\Psi}_{M_s=1}^t$ is a high-spin reference state, i.e., wave function (1) in Fig. 2, and $\hat{R}_{M_s=-1}$ is an excitation operator that flips the spin of an electron. Thus, all the determinants present in multiconfigurational wave functions (2)–(5) from Fig. 2 can be obtained by single spin-flipping excitations of an electron from the high-spin determinant (1) and are therefore treated in a balanced way. This is how these multiconfigurational states can be described by the SF method within a single-reference formalism. By increasing the accuracy of the reference state description, the accuracy of the target state can be systematically improved. For example, one can combine the SF approach with perturbation or density-functional theory to derive the SF-MP2 (Ref. 20) or spin-flip density-functional theory²⁶ (SF-DFT) models, respectively. In this paper, the coupled-cluster method with single and double substitutions²⁷ (CCSD) is employed to describe the reference state, and the target states are described by the equation-of-motion²⁸ (EOM) theory, EOM-SF-CCSD (Ref. 25). In EOM-SF-CCSD, the operator \hat{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^{22,29} and triradicals.^{30–33} To characterize equilibrium geometries, we employ analytic gradients for the EOM-SF-CCSD model, which we recently developed.²⁴ The EOM-SF-CCSD analytic gradients enable quantitatively accurate and computationally affordable optimization of diradical geometries in the ground and low-lying excited states.

C. Computational details

Calculations are performed using the Q-CHEM electronic structure package.³⁴ The equilibrium structures of triplet states are calculated by the CCSD method with the UHF reference and the 6-31G* basis set.³⁵ These geometries are used to calculate vertical state ordering. The adiabatic energy differences are calculated by using the above triplet geometries and the singlet state geometries optimized by the EOM-SF-CCSD method with the UHF reference and the 6-31G* basis set. Optimized geometries and total energies are provided as an EPAPS document.¹⁷ Energy gaps are evaluated by EOM-SF-CCSD with the restricted open-shell Hartree-Fock (ROHF) reference and the mixed 6-311G(2d)/6-31G* basis set,^{35,36} i.e., 6-311G(2d) on second- and third-row atoms and 6-31G* on hydrogen.

III. RESULTS AND DISCUSSION

The *meta*-xylylene (MX) diradical and its derivatives studied in this work are shown in Fig. 3. The prototype sys-

FIG. 3. The *meta*-xylylene diradical (I) and its analogs.

tem, the *m*-xylylene (I), has a high-spin triplet ground state. Figure 4 shows nearly degenerate molecular orbitals that host the unpaired electrons. As dictated by symmetry, the two MOs have different nodal structures. For example, at the *ortho* position (relative to the CH₂ groups), the *b*₁ orbital has considerable density, whereas the *a*₂ orbital has a node. Thus, the energy gap between these two orbitals may be affected by substituents at the *ortho* (C₃) position.⁷ Preferential stabilization of the *b*₁ orbital will increase the energy gap and may result in a singlet ground state. In order to study the effect of electronegativity and donor-acceptor properties of substituents, we considered the following groups: OH, NH₂, F, BH₂, and SiH₃ (molecules VI–X, respectively). The former three groups are π donors and σ acceptors. BH₂ is a π acceptor.³⁷ A large SiH₃ group is a σ donor. Molecules IV (the original Dougherty system) and V are introduced to investigate the effect of charge. Molecule II is a heteroatom analog of MX. Molecule III can be considered as an electro-neutral analog of IV.³⁸

Table I and Fig. 5 present vertical energy differences between the three lowest states: 3B_2 , 1B_2 , and 1A_1 , which correspond to wave functions (2), (3), and (4) from Fig. 2, respectively. Adiabatic energy gaps are also given in Table I. Table I and Fig. 5 demonstrate quite unexpectedly that, apart from charged systems IV and V, all other molecules maintain a triplet ground state. Moreover, the corresponding singlet-triplet gap is surprisingly insensitive to the wide spectrum of substituents considered in this study. Charged systems IV and V have a singlet 1A_1 ground state, whereas molecule III,

despite its similarity to IV, exhibits a larger gap between the 3B_2 and 1A_1 states. Moreover, the open-shell singlet state 1B_2 drops in III by more than 1 eV (vertically) relative to II and IV.

There are several simple rules that govern ground-state multiplicity in open-shell species. The spin preference of an alternant planar π system can be evaluated by a simple $(n^* - n)/2$ formula³ (also known as the topology rule), where n^* and n are the numbers of starred and nonstarred carbons, respectively. This rule, which can be derived from the Hückel model, predicts a triplet ground state for all molecules from Fig. 3. Alternatively, one can attempt to determine the spin preference from the molecular-orbital considerations. If the orbitals that host unpaired electrons are nearly degenerate and overlap in space (i.e., are nondisjoint⁴), the high-spin coupling, which minimizes the electron repulsion, would be preferred, as summarized in Hund's rule. Otherwise, the low-spin coupling may win^{4,39} due to the stabilizing interactions between the opposite spin unpaired electrons and the electrons from doubly occupied lower-energy orbitals (spin-polarization effect). As the two MOs of MX and its derivatives (Fig. 4) overlap at the radical centers, this generalization of Hund's rule predicts a triplet ground state for all the molecules from Fig. 3. Thus, the charged systems IV and V, which have singlet ground states, violate both of the above rules! The original explanation of this phenomenon suggested by Dougherty and co-workers,⁷ which employs the resonance theory, is presented below. By analyzing the changes in the corresponding equilibrium geometries we

TABLE I. Vertical and adiabatic state ordering (eV) in *meta*-xylylene diradicals. Energies are calculated by the EOM-SF-CCSD method with the ROHF reference and the 6-311G(2d)/6-31G* basis set. Vertical excitation energies are calculated at the 3B_2 equilibrium geometry optimized by the CCSD method with the UHF reference and the 6-31G* basis set. Adiabatic energy gaps are calculated using the 1A_1 and 1B_2 geometries optimized by the EOM-SF-CCSD method with the UHF reference and the 6-31G* basis set.

Molecule	3B_2	1B_2	$^1A_1^{\text{vert}}$	$^1A_1^{\text{adiab}}$	$^1B_2^{\text{adiab}}$
I	-308.732 558	1.726	0.599	0.490	1.193
II	-324.761 202	1.882	0.476	0.387	1.443
III	-399.806 886	0.568	1.277	0.800	0.478
IV	-325.132 139	1.979	-0.045	-0.127	1.616
V	-383.260 157	1.456	-0.189	-0.381	1.103
VI	-383.769 508	1.603	0.604	0.499	1.071
VII	-363.959 386	1.473	0.573		
VIII	-407.836 446	1.723	0.601		
IX	-334.077 387	1.511	0.490		
X	-598.808 406	1.666	0.597		

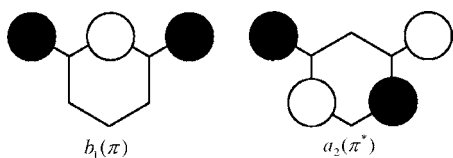


FIG. 4. Molecular orbitals of *meta*-xylylene (I) and its analogs from Fig. 3 that host the unpaired electrons. In the Huckel model, these orbitals assume the following form: $b_1=0.58(p_1+p_5-p_3)$ and $a_2=0.5(p_1-p_5+p_6-p_8)$, where carbons are numbered clockwise starting from the left methylene group.

were able to justify the validity of the resonance theory explanation. However, further analysis reveals limitations and inconsistencies of the resonance theory, especially when other excited states are concerned.

Figure 6 shows the leading resonance structures for molecules I, III, IV, and V. All five resonance structures of molecule I (Ref. 40) correspond to the covalent configurations with two radical centers. At least one of the unpaired electrons is localized on a methylene group. The ionic resonance structures, in which one p orbital is doubly occupied and another is empty, have higher energies due to the charge separation and are therefore less important. The covalent structures with two unpaired electrons can contribute into both singlet and triplet wave functions, although their relative importance may be different, as shown below. The leading resonance structures for all other molecules (except III, IV, and V) are identical.

Molecules IV and V include several additional resonance structures. In two of these (second rows in Fig. 6) all electrons are paired. Thus, these resonance structures may only be present in the singlet wave functions. This preferential resonance stabilization of the singlet states explains the changes in the ground-state multiplicity in molecules IV (Ref. 7) and V. As will be shown below, the resonance theory explanation is supported by the observed contraction of the exocyclic C–C bond in the singlet 1A_1 state. Unlike the original Dougherty system, molecule V has five additional resonance structures (third row), which all have two radical centers and can therefore appear in both singlet and triplet wave functions. However, no additional contraction in the triplet state of V relative to IV (due to these five additional struc-

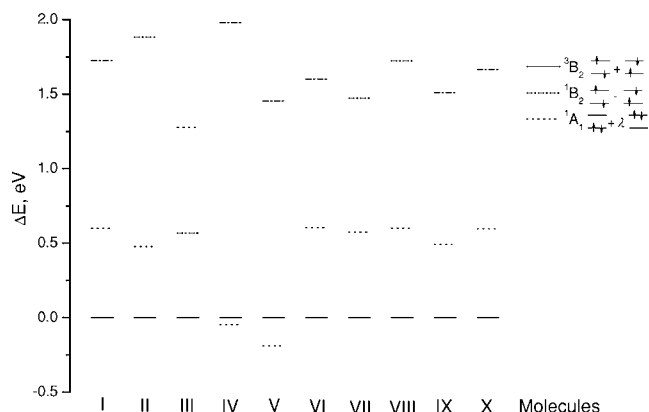


FIG. 5. Vertical state ordering calculated at the ROHF-EOM-SF-CCSD/6-311G(2d)/6-31G* level at the UHF-CCSD/6-31G* optimized geometry of the 3B_2 state.

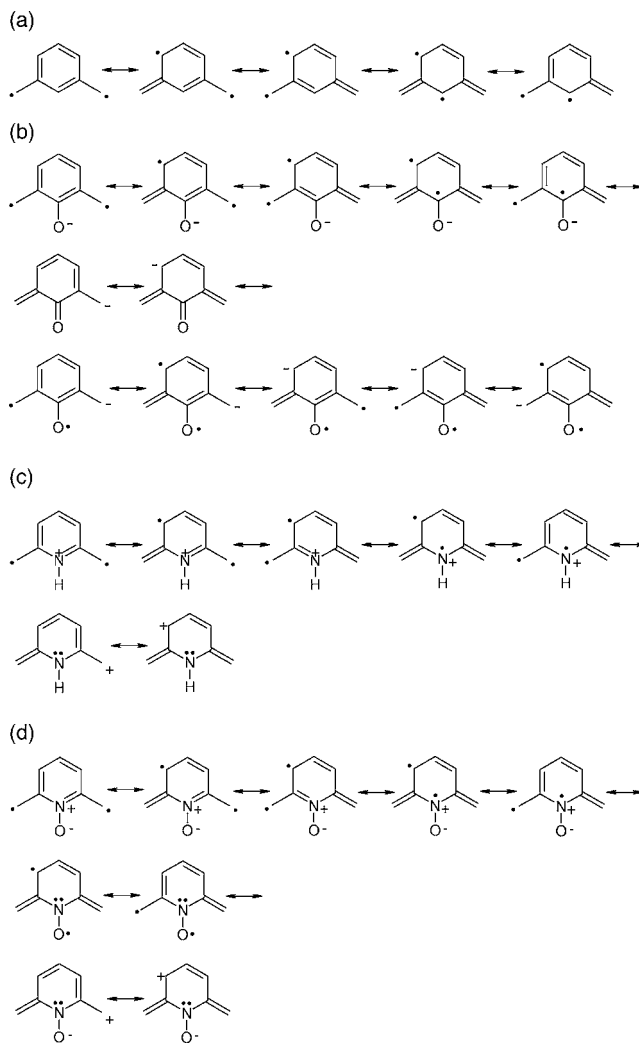


FIG. 6. Leading resonance structures for molecules I, III, IV, and V. Only C_{2v} unique structures are shown.

tures) was observed. Moreover, applying electronegativity considerations to explain a quantitative difference between IV and V reveals more inconsistencies in the resonance theory explanation. The closed-shell structures for IV which have positively charged carbons should be more energetically preferable than the closed-shell structures of V with negatively charged carbons. Therefore, one may expect a stronger stabilization of the singlet state in IV, but the reverse is true.

Because of the coordinate-covalent character of the N–O bond, molecule III also includes additional resonance structures; e.g., it has two additional closed-shell structures (third row), as well as two additional open-shell ones (second row). Thus, one may expect both the stabilization of the singlet states and the stabilization of the triplet state. Since the additional open-shell structures are covalent and do not involve charge separation, one may expect that their contributions will be more significant than those of the ionic structures from the third row, which explains why the closed-shell singlet state is not preferentially stabilized in III. The observed strong stabilization of the open-shell singlet state cannot be explained by considering principal resonance structures alone. One possible and highly speculative explanation is

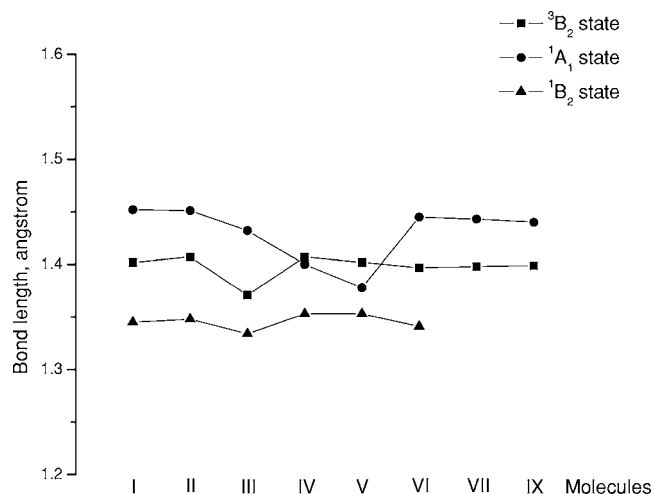


FIG. 7. The exocyclic C–C bond length in the 3B_2 , 1A_1 , and 1B_2 states.

based on the spin-polarization model, which predicts a singlet coupling between the radical centers in additional open-shell resonance structures of III. Thus, one may expect that they have larger relative weights in the open-shell singlet wave function relative to the triplet one. However, applying the spin-polarization model to the additional open-shell structures of V would also predict the strong stabilization of the open-shell singlet state, but only a minor stabilization was observed. Finally, we would like to note that the changes in the frontier MOs (Ref. 17) upon the N–O substitution do not explain the observed small energy gap between the open-shell singlet and the triplet state: although the observed changes in the state ordering suggest that the MOs become more disjoint,³⁷ the Hartree-Fock MOs in III appear to be very similar to those in I and II, apart from the additional density on oxygen.

The relevance of additional resonance structures can be verified by analyzing the changes in equilibrium geometries of the 3B_2 and the 1A_1 states. Figure 7 shows the exocyclic C–C bond length in the 3B_2 , 1A_1 , and 1B_2 states for selected molecules from Fig. 3. Apart from III, IV, and V, all other molecules have very similar bond lengths in the triplet and 1A_1 states. In IV and V, the 3B_2 state bond length is close to that of other molecules; however, the 1A_1 state bond length is considerably shorter, which is consistent with additional singlet resonance structures with double exocyclic C–C bonds. For III, both the 3B_2 and 1A_1 bonds contract because of the additional resonance structures with double exocyclic C–C bonds that stabilize both singlet and triplet states. Despite the additional open-shell resonance structures in V, no additional bond contraction in the 3B_2 state was observed. There are no significant changes in the exocyclic C–C bond length in the 1B_2 state, including III. Thus, although the equilibrium structures of *meta*-xylylenes are consistent with the resonance theory description of the corresponding wave functions, some inconsistencies remain.

Finally, we combine the Huckel model and a simple 2×2 configuration-interaction (CI) model to analyze bonding patterns in *meta*-xylylenes,^{15,40} and to establish a relationship with resonance structures. We begin with a simple wave-function analysis of the characters of the states concerned.¹⁸

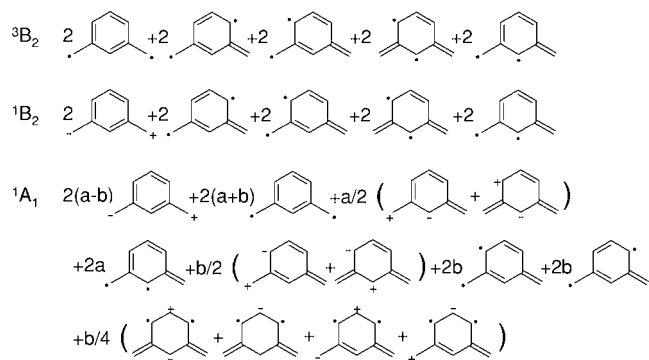


FIG. 8. Characters of the *meta*-xylylene wave functions in the Huckel model. Only C_{2v} unique configurations are shown. The coefficients a and b are equal to 0.58^2 and $0.5^2\lambda^2$, respectively.

The Huckel MO coefficients^{15,40} are given in Fig. 4. The corresponding (non-normalized) diradical wave functions (Fig. 2) are:

$$^3B_1 = [b_1(1)a_2(2) - a_2(1)b_1(2)] \times [\alpha(1)\beta(2) + \beta(1)\alpha(2)], \quad (2)$$

$$^1B_1 = [b_1(1)a_2(2) + a_2(1)b_1(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)], \quad (3)$$

$$^1A_1 = [b_1(1)b_1(2) - \lambda a_2(1)a_2(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]. \quad (4)$$

By expanding the spatial parts of the above wave functions, one arrives at the configurations summarized in Fig. 8. Consistent with the resonance theory, the triplet wave function is a combination of all possible covalent structures with two radical centers. This relationship between the Huckel model and the resonance theory was pointed out by Longuet-Higgins.⁴⁰ The open-shell singlet wave function consists of all the above configurations, except for the one in which both radical centers are on methylene groups. In addition, it includes two ionic configurations in which both electrons occupy one of the methylene orbitals, whereas the second methylene group hosts the positive charge. As pointed out by Kato *et al.*,¹⁵ these structures are inconsistent with the bonding pattern in the open-shell singlet state derived from *ab initio* calculations, which reveals the limitations of such a simple model. Finally, the closed-shell singlet wave function includes all of the above, plus a number of additional ionic configurations with charges in the benzene ring. One can see that the positive charge on C_3 (as in IV) will stabilize the 1A_1 state. The additional singlet resonance structures of IV would annihilate the negative charge on methylene or on C_6 and C_8 positions and therefore stabilize the 1A_1 wave function. However, the same resonance structures would also stabilize 1B_1 . Similar reasoning explains the stabilization in V; however, we cannot offer a consistent explanation of the open-shell singlet stabilization in III. Thus, the Huckel bonding picture in *meta*-xylylene only partially explains the observed substituent effect.

IV. CONCLUSIONS

The effect of substituents on the electronic states' ordering in *m*-xylylene diradicals are studied by the EOM-SF-CCSD method. Calculations demonstrate that the effect on the singlet-triplet gap of different substituents in the *ortho* position including electronegative and electropositive groups, as well as π donors/acceptors on singlet-triplet gaps, is negligible. However, if charges are introduced, the state ordering is reversed and the singlet ground states are produced. The N-oxidized pyridinium exhibits a strong stabilization of the open-shell singlet state. Resonance structures show that, when charge is introduced, the contribution of closed-shell configurations to the singlet wave function increases, which preferentially stabilizes the singlet ground state. The original resonance explanation⁷ is supported by the observed changes in the exocyclic C–C bond lengths. However, a similar resonance-theory-based reasoning fails to explain the strong stabilization of the open-shell singlet state in the N-oxide, as well as quantitative differences between negative and positive charges. Thus, accurate and reliable calculations are essential for predicting substituent effects on the state ordering in diradicals and triradicals.

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