The electronic structure of dehydro-m-xylylene anion (DMX⁻) has been investigated by using chemical reactivity studies and electronic structure calculations. DMX⁻ has been generated in the gas phase via the sequential reaction of trimethyl-3,5-bis(trimethylsilylmethyl)phenylsilane with F₂ and two molecules of F₂. Reactivity and thermochemical properties of the ion indicate a phenyl-like anion (1a), consistent with theoretical predictions. Density functional calculations predict a nonplanar triplet anion, with an allenic singlet anion slightly higher in energy. The driving force for the out-of-plane distortion is more efficient charge delocalization that is achieved at lower symmetry.

Distant ions provide a very useful means for investigating the properties of organic radicals in the gas phase. Originally defined as the ions that result from ionization of a biradical or zwitterion¹ leading to ion radicals,²³ distant ions are now generally considered to include ions with separated charge and radical centers, and examples of gaseous distant ions that contain carbenes,⁴ with separated charge and radical centers, and examples of gaseous distant ions with separated charge and radical centers, and examples of gaseous distant ions containing carbenes. Thus, distant ions have been used to investigate the chemical reactivity of these types of moieties. However, because of their relationship to the neutral reactive intermediates, distant ions also serve as convenient precursors for mass spectrometric¹³–¹⁵ and spectroscopic¹⁶ studies of the investigation of reactive intermediate thermochromies. In addition to their utility in the investigation of neutral reactive intermediates, distant ions are interesting species in their own right¹⁷,¹⁸ and with unique reactivity and unusual electronic structures that result from ionization of complicated, open-shell wave functions.

We recently reported the measurement of the bond dissociation energy at the 5-position of m-xylylene,¹⁹ and its use for determining the heat of formation of the dehydro-m-xylylene triradical (DMX). The DMX triradical has an unusual electronic structure with an unprecedented open-shell doublet ground state,¹⁹ with three low-spin electrons in three, singly occupied molecular orbitals (ο²ο²ο²). Ultimately, the measured thermochemical properties for DMX indicate little interaction between the unpaired ο and σ-electrons in the triradical.

\[
\text{DMX} \quad \text{MX} \quad \text{DHT}
\]

The C–H bond dissociation energy in m-xylylene was measured by using thermochemical studies involving the triradical negative ion, DMX⁻. Whereas the original study focused on the thermochemical properties of neutral triradical, DMX, the structure of DMX⁻ is also an interesting question. Addition of an electron to the singly occupied phenyl ο-orbital (Figure 1) leads to the formation of an ion consisting of a phenyl anion with a m-xylylene (MX) biradical moiety (ο²ο²ο²) as represented by 1a. However, it is also possible to add an

electron to one of the $\pi$-orbitals to create a m-xylenic anion with a phenyl radical, $1b$ ($\alpha^{3} \pi_{a}^{2} \pi_{b}^{2}$ or $\alpha^{2} \pi_{a}^{2} \pi_{b}^{2}$), where the biradical electronic structure resembles that of $\alpha,3$-dehydrotoluene (DHT).21 Advantages of either structure can be envisioned, as $1a$ has localized charge but a delocalized biradical, whereas $1b$ has a delocalized (benzylic) charge but a localized phenyl radical. To a first approximation, structure $1a$ would be expected to be lower in energy because the electron affinity (EA) of the phenyl radical (1.096 eV)22 is greater than that for a benzyl radical (0.912 eV)22 or m-xylene (0.907 eV).20

Because ions $1a$ and $1b$ are biradical in nature, there should be several low-lying excited states of different multiplicities. Given the similarities between the systems, it may be expected that the properties and energy separations between states of $1a$ would be similar to those of the MX biradical, whereas the states of $1b$ would be similar to the states of the DHT biradical. For example, because the ground state of m-xylene biradical is a triplet, with a singlet–triplet energy difference ($\Delta E_{ST}$) of 10.5 kcal/mol,20 ion $1a$ should have a triplet ground state. Similarly, $\alpha,3$-dehydrotoluene is a ground-state singlet ($\Delta E_{ST} = 1.3$ kcal/mol),23 such that $1b$ is also expected to have a singlet ground state. Other biradical states (i.e., open-shell singlet of MX and closed-shell singlet of DHT) are considerably higher in energy (28 and 62 kcal/mol,24 respectively). The state orderings in the MX and DHT biradicals (triplet, closed-shell singlet, open-shell singlet for MX and open-shell singlet, triplet for DHT) are typical for biradicals with overlapping electronic densities of biradical orbitals.24 However, these predictions ignore any potential interactions between the $\sigma$- and $\pi$-systems or any effects that the charge site has on the electronic structure of the biradical.

In this paper, we investigate the electronic structure of DMX by using chemical reactivity studies and electronic structure calculations. We show that the reactivity and thermochemical properties of the ion indicate a phenyl-like anion ($1a$), consistent with theoretical predictions. Calculations indicate a triplet anion, with an allene singlet anion slightly higher in energy.

**Experimental Procedures**

All experiments were carried out at room temperature in a flowing afterglow triple-quadrupole apparatus described elsewhere.26 Fluoride ion was generated by electron ionization of $F_{2}$ (5% in helium). Collision-induced dissociation (CID) experiments are carried out by selecting the ions with the desired mass-to-charge ratio using the first quadrupole (Q1) and then injecting them into the second quadrupole (Q2, radio frequency only), where they undergo collision with argon gas. The reactant and product ions are analyzed with the third quadrupole (Q3) and are detected with an electron multiplier.

**Materials.** Gas purities were as follows: He (99.995%) and $F_{2}$ (5% in He). Authentic 3,5-bis-formylphenoxide ion was generated from 1-tert-butyldimethylsilyloxy-3,5-bis-formylbenzene, prepared by using the procedures described by Allbrecht et al.27 All other reagents were obtained from commercial sources and were used as supplied.

Trimethyl-3,5-bis(trimethylsilylmethyl)phenylsilane was prepared starting from the triisobutylborane. Treatment of 1-bromo-3,5-bis(bromomethyl)benzene28 with excess LiCl (10 equiv) in DMF at room temperature for 12 h under nitrogen leads to chlorination at the $\alpha$- and $\alpha'$-positions.29,30 Diethyl ether was added, and the mixture was washed with $H_{2}O$ to remove DMF. The organic layer was dried over MgSO$_{4}$ and the solvent was removed in vacuo. The crude 1-bromo-3,5-bis(chloromethyl)-benzene29 was dissolved in anhydrous THF and added dropwise to a refluxing mixture of 12 equiv of Mg turnings at room temperature for 12 h under nitrogen leads to chlorination at the $\alpha$- and $\alpha'$-positions.29,30 Diethyl ether was added, and the mixture was washed with $H_{2}O$ to remove DMF. The organic layer was dried over MgSO$_{4}$ and the solvent was removed in vacuo. The crude 1-bromo-3,5-bis(chloromethyl)-benzene29 was dissolved in anhydrous THF and added dropwise to a refluxing mixture of 12 equiv of trimethylsilyl chloride and 2.6 equiv of Mg turnings in anhydrous THF.31 The mixture was refluxed for 5 h under nitrogen. Hexane was added, the mixture was filtered and dried over MgSO$_{4}$ and the solvent was removed in vacuo. The yellow residue was purified by column chromatography with hexane to afford trimethyl-3,5-bis(trimethylsilylmethyl)phenylsilane as a colorless oil.1H NMR (300 MHz, CDCl$_{3}$): 6.85 (s, 2H), 6.64 (s, 1H), 2.03 (s, 4H), 0.23 (s, 9H), 0.02 (s, 18H).

**Experimental Results**

The gas-phase synthesis of DMX involves sequential reaction of trimethyl-3,5-bis(trimethylsilylmethyl)phenylsilane with F$^{-}$ and two molecules of $F_{2}$ resulting in formation of an ion with m/z 103, $C_{14}H_{4}F_{3}$, which is deduced on the basis of reactivity studies to be DMX$^{-}$ (eq 1). As has been discussed previously,6 the mechanism of $F_{2}$-induced desilylation is believed to occur via electron transfer from silylated carbanions within a collision complex, followed by desilylation of the radical by either $F_{2}^{-}$ or $F^{-}$. Other products observed in the flow reactor include the intermediate ions shown in eq 1, m/z 255 and m/z 179, and their fluoride adducts. In addition, we also observe smaller amounts of ions at m/z 180, m/z 104, and m/z 105, which result from reaction of the silylated anions.


5736 J. Org. Chem., Vol. 69, No. 17, 2004
with HF impurity in the fluorine mixture. Although the reaction scheme shown in eq 1 implies initial formation of a silylated m-xylylenyl anion, which then reacts to give DMX, the silylated dehydrotoluene anion is also a possible intermediate. The exact sequence of reactions is not known but is not important.

\[ \text{Si(CH}_3\text{)}_3\text{Si(CH}_3\text{)}_3 \xrightarrow{\text{O}_2} \text{Si(CH}_3\text{)}_3\text{Si(CH}_3\text{)}_3^{-} \xrightarrow{\text{F}_2, \text{FSi(CH}_3\text{)}_3} \text{DMX}^{-} \]

Absolute confirmation of the structure of DMX was achieved by using the reaction with O\(_2\), which leads to a product that has the same mass-to-charge ratio as 3,5-bis-formylphenoxide ion (2). The formation of the phenoxide ion can be attributed to oxygen atom abstraction from O\(_2\) by DMX and sequential oxidation of the benzylic radicals as shown in eq 2. Oxidation of benzylic radicals in distonic biradical anions with O\(_2\) has been observed previously by Hu and Squires. Similarly, the phenyl anion reacts with O\(_2\) to form phenoxide and other products. However, the phenyl radical can also react with O\(_2\) by oxygen atom abstraction. Although it is inefficient for neutral phenyl radical because it has a barrier of 6–7 kcal/mol, the barrier in the gas-phase reaction can be overcome by the ion/neutral complexation energy. Therefore, formation of 2 would be expected regardless of the electronic structure of the ion. The CID spectra of 2, prepared by derivatization of DMX, and of authentic bis(formyl)phenoxide ion, prepared from 1-tert-butyldimethylsilyloxy-3,5-bis-formylbenzene, are shown in Figure 2a–b, respectively. The major ionic fragments are m/z 121 and 92 with measured yields of 5/1 for both reactant ions. Because of impurities arising from mass overlap in the spectrum of the derivative, it is not possible to compare the absolute cross-sections for the two ions. The excellent agreement between the CID spectra of the authentic phenoxide and derivative 2 confirms the 5-dehydro-m-xylylene structure of the anion but does not provide insight into the electronic structure.

\[ \text{H}_2\text{C} = \text{C} \text{CH}_2 \xrightarrow{\text{O}_2} \text{OHC} - \text{C} \text{CH}_2 \xrightarrow{\text{O}_2} \text{OHC} - \text{C} \text{CHO} \xrightarrow{\text{O}_2} \text{CHO} \xrightarrow{\text{O}_2} \text{m/z 149} \]

The electronic structure of DMX was characterized by using chemical reactivity. For example, DMX reacts with CO\(_2\) molecules by condensation to form a carboxylate ion, and the reactivity of the carboxylates reflects the ion structure. Carboxylates formed from closed-shell anions are typically not found to undergo addition with NO or NO\(_2\), but radical addition has been observed for open-shell carboxylates, including those derived from benzene ions, 1,3,5-trimethylenebenzene anion, and m-xylylene anion. The CO\(_2\) adduct of DMX undergoes sequential addition of two NO or NO\(_2\) molecules, indicating biradical character in the carboxylate. The DMX ion itself is also found to undergo addition of up to three NO molecules. Sequential addition of NO has been observed with other open-shell systems. This reactivity is consistent with that expected for either ion 1a or 1b, as they are both open-shell biradicals.

The question of the phenyl versus the benzyl anion has been addressed by using reactions with N\(_2\)O and CS\(_2\). Nitrous oxide reacts with phenyl anion by oxygen atom transfer (eq 3a) but reacts with benzyl anions by the addition and loss of H\(_2\)O (eq 3b). As expected, the

\[ \text{H}_2\text{C} = \text{C} \text{CH}_2 \xrightarrow{\text{N}_2\text{O}} \text{OHC} - \text{C} \text{CH}_2 \xrightarrow{\text{N}_2\text{O}} \text{OHC} - \text{C} \text{CHO} \xrightarrow{\text{N}_2\text{O}} \text{CHO} \xrightarrow{\text{N}_2\text{O}} \text{m/z 149} \]

\[ \text{H}_2\text{C} = \text{C} \text{CH}_2 \xrightarrow{\text{CS}_2} \text{OHC} - \text{C} \text{CH}_2 \xrightarrow{\text{CS}_2} \text{OHC} - \text{C} \text{CHO} \xrightarrow{\text{CS}_2} \text{CHO} \xrightarrow{\text{CS}_2} \text{m/z 149} \]

\[ \text{H}_2\text{C} = \text{C} \text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{OHC} - \text{C} \text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{OHC} - \text{C} \text{CHO} \xrightarrow{\text{H}_2\text{O}} \text{CHO} \xrightarrow{\text{H}_2\text{O}} \text{m/z 149} \]

\[ \text{H}_2\text{C} = \text{C} \text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{OHC} - \text{C} \text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{OHC} - \text{C} \text{CHO} \xrightarrow{\text{H}_2\text{O}} \text{CHO} \xrightarrow{\text{H}_2\text{O}} \text{m/z 149} \]

---

reaction shown in eq 3b also occurs with m-xylylene anion (eq 3c), formed by the reaction of m-xylylene with $\text{O}_2$.

Given the similarity between the electronic structure of 1b and the m-xylylene anion, it is reasonably expected that the reaction shown in eqs 3b and 3c should occur with ion 1b as well. However, the reaction of $\text{DMX}^-$ with $\text{N}_2\text{O}$ proceeds to give oxygen atom transfer (eq 4a), whereas the addition of $\text{CS}_2$ to $\text{DMX}^-$ (eq 4b) is not observed at all. On the basis of this observation, we conclude that the $\text{DMX}^-$ signal consists of a single ion structure and that it is a phenyl anion with a triplet m-xylylene biradical moiety. The presence of 1b, either in whole or as part of a mixture, would be expected to be indicated by the reaction with $\text{N}_2\text{O}$. Benzyl radical in the gas phase are essentially unreactive with $\text{N}_2\text{O}$.

$\text{H}_2\text{C}^\cdot \text{CH}^\cdot \text{CH}_2^\cdot \text{O}^- + \text{N}_2\text{O} \rightarrow \text{H}_2\text{C}^\cdot \text{CH}^\cdot \text{CH}_2 \cdot \text{O}^- + \text{N}_2$

The reaction with $\text{CS}_2$ is also consistent with a phenyl anion electronic structure. The reaction proceeds by sulfur atom transfer (25%), and $\text{CS}_2$ addition (75%) is formed. It is well-recognized that sulfur atom transfer occurs in the reaction of $\text{CS}_2$ with highly basic ions. For example, the reaction of $\text{CS}_2$ with benzyl anions, including m-xylylene anion, proceeds only by $\text{CS}_2$ addition.

Thus, the observation of sulfur atom abstraction with $\text{CS}_2$ suggests a phenyl anion in $\text{DMX}^-$. Generally, sulfur abstraction from $\text{CS}_2$ by a phenyl radical to form a phenylthiolate radical is endothermic by ca. 10 kcal/mol and therefore would not be expected for ion 1b. However, in this case, the product would likely be the thiolate anion, which would be more favorable, and therefore, while the reaction with $\text{CS}_2$ is consistent with the phenyl anion assignment, it does not rule out structure 1b.

The thermochemical properties measured for $\text{DMX}^-$ are also consistent with the assignment of a phenyl anion.

Theoretical Results

From the electronic structure point of view, adding an extra electron into the three-electrons-on-three-orbitals system of the $\text{DMX}^-$ triradical leads to the four-electrons-in-three-orbitals pattern in $\text{DMX}^-$. This leads to many near-degenerate arrangements resulting in multiconfigurational wave functions. However, if the interaction between a doubly occupied orbital and two others is weak due to the symmetry/nodal considerations or spatial separation, then the system can be more simply described as an anion and a biradical, and the wave functions can be described within the traditional two-electrons-in-two-orbitals biradical model. Because of the extensive electronic near-degeneracies, the choice of an electronic structure method is extremely important. An accurate model needs to provide a qualitatively correct description of an electronic wave function and also needs to include dynamical correlation, crucial for quantitative accuracy in anions. Moreover, to maintain a balanced description of several states of interest, multistate methods are preferred to state-to-state approaches.

In this paper, we have used the equation-of-motion approach, which describes excited states as single and double excitations from the reference state CCSD (coupled-cluster with singles and doubles model) wave function. The traditional method, EOM-EE-CCSD, was used for states that can be described as single excitations from a m-xylylene biradical electronic structure. For example, the electron binding energy in $\text{DMX}^-$ (the EA of $\text{DMX}^-$) was measured to be 24.9 ± 2.0 kcal/mol. This value is similar to the EA of phenyl radical, 25.3 ± 0.1 kcal/mol, but is much higher than the EA of m-xylylene, 21.19 ± 0.18 kcal/mol. Similarly, the proton affinity of the ion is measured to be 401 ± 3 kcal/mol nearly the same as that for phenyl anion, but much higher than that for the benzyl anion (~380 kcal/mol). Thus, the reactivity and thermochemical properties of $\text{DMX}^-$ are all consistent with an electronic structure with a phenyl anion and triplet m-xylylene biradical (1a), as predicted by simple EA considerations.

\(\text{H}_2\text{C}^\cdot \text{CH}_2^\cdot \text{O}^- + \text{N}_2\text{O} \rightarrow \text{H}_2\text{C}^\cdot \text{CH}_2 \cdot \text{O}^- + \text{N}_2\)

\(\text{H}_2\text{C}^\cdot \text{CH}_2^\cdot \text{O}^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C}^\cdot \text{CH}_2 \cdot \text{O}^- + \text{H}_2\text{O}\)

\(\text{H}_2\text{C}^\cdot \text{CH}_2^\cdot \text{O}^- + \text{CS}_2 \rightarrow \text{H}_2\text{C}^\cdot \text{CH}_2 \cdot \text{O}^- + \text{CS}_2\)

\(\text{H}_2\text{C}^\cdot \text{CH}_2^\cdot \text{O}^- + \text{CS}_2 \rightarrow \text{H}_2\text{C}^\cdot \text{CH}_2 \cdot \text{O}^- + \text{CS}_2\)

\(\text{H}_2\text{C}^\cdot \text{CH}_2^\cdot \text{O}^- + \text{CS}_2 \rightarrow \text{H}_2\text{C}^\cdot \text{CH}_2 \cdot \text{O}^- + \text{CS}_2\)

dihedral reference. Its spin–flip counterpart, EOM-SF-CCSD,
was used for biradical states. Some states (e.g., triplets and
doubly occupied orbitals) are accessible by traditional single-reference techniques, such as
CCSD(T)46 or density functional theory (DFT).46

Equilibrium geometries of all the triplet (\(\sigma^2\pi^2\sqrt{2}\)) and
doubly occupied singlet (\(\sigma^2\pi^2\sqrt{2}\)) states of DMX
were optimized at the B3LYP/6-311+G*47,48,49 level of theory. The structures of the \(1\text{B}_1\)
(\(1\text{A}^\prime\)) and \(1\text{A}_2\) open-shell singlet states (\(\sigma^2\pi^2\sqrt{2}\)) were optimized at the
EOM-CCSD/6-31+G*49,50 level from the \(\sigma^2\pi^2\sqrt{2}\) and \(\sigma^2\pi^2\sqrt{2}\) references, respectively.
Adiabatic excitation energies between the states
that are well-described by single-reference methods51
were calculated by the B3LYP, CCSD, and CCSD(T) methods. The energy differences between the
two-configurational \(1B^\prime\)/\(1A_2\) open-shell singlets and the corresponding \(1B^\prime\)/\(1A_2\) triplet states were calculated by EOM-
EE-CCSD and EOM-SF-CCSD. Calculations were performed
by using the Q-CHEM52 and ACES II53 electronic structure
packages. Molecular orbitals were visualized by
using Spartan. Natural atomic charges are calculated by
using the Natural Bond Orbital (NBO 4.0) program,54
which is interfaced to Q-CHEM.

The electronic configurations and relative adiabatic energies of the low-lying states of planar DMX
are summarized in Figure 3. At the planar \(C_2\) geometries, the correlation between the electronic states of DMX
and those of MX and DHT is obvious. Electronic states indicated to the left correspond to an electronic structure
such as that in \(1\text{a}\), with a phenyl anion and m-xylylene biradical moiety. Electronic states with labels to the right
correspond to an electronic structure like that in \(1\text{b}\). At
the planar geometry, the ground state of the system is
predicted to be the \(1\text{B}_2\) state, the triplet state of \(1\text{a}\).

The lowest energy state of \(1\text{b}\) is the \(1\text{B}_1\) singlet state and is
4.1 kcal/mol higher in energy than the ground state. The lowest energy triplet state of planar \(1\text{b}\) is the \(1\text{B}_2\) state,
calculated to be 4.9 kcal/mol above the ground state, such that
\(1\text{b}\) has a singlet–triplet energy splitting of 0.8 kcal/
mol. A second triplet state in \(1\text{b}\), the \(1\text{A}_2\) state, lies 8.2
cal/mol higher than the ground state. The corresponding
singlet–triplet energy splitting is 1.2 kcal/mol. The calculated
singlet–triplet splitting of planar \(1\text{a}\) is 13.1 kcal/mol in favor of the triplet. These values are similar to the corresponding singlet–triplet splittings in \(a_3\), 3-dehydrotoluene21 and m-xylylene,20 respectively. Ultimately,
the calculated energy ordering for the planar ion
is essentially what would be predicted based on the
electron affinities of phenyl and benzyl anions and the
singlet–triplet splittings in the model biradicals.

Surprisingly, only one of the planar states described
previously, the \(1\text{A}_2\) state, has been found to be a true
minimum with the B3LYP approach, as each of the
others has a single imaginary frequency. For the \(1\text{B}_2\), \(1\text{B}_1\),
and \(1\text{A}_2\) states, the normal coordinate for the imaginary
frequency distorts the molecule to \(C_2\) symmetry. In the
\(1\text{A}_2\) and \(1\text{B}_1\) states, the distortion leads to a planar C2
structure. Thus, the DFT calculations predict that many of the stable states of DMX
have non-\(C_2\) structures, and as described next, are nonplanar. This is particularly striking since out-of-plane distortions perturb conjugation in the \(\pi\)-system, thus destabilizing it.

The driving force for the nonplanarity of DMX has
been found to be more efficient charge delocalization that is achieved at twisted geometries due to the lifting
of symmetry-imposed constraints. When the symmetry lowers from \(C_{2v}\) to \(C_2\), the \(a_1\) and \(a_2\) orbitals are able to mix
as a-type orbitals, whereas the \(b_1\) and \(b_2\) orbitals can mix as b-type orbitals. Similarly, lowering the symmetry
from \(C_{2v}\) to planar \(C_2\) allows mixing of the \(a_1\) and \(a_2\) orbitals as (a') and of the \(b_1\) and \(b_2\) orbitals as (a'). The pair of a’
orbitals that results is essentially the GVB orbitals in
the m-xylylene biradicals.20 The orbitals that result from
the mixing upon distorting to \(C_2\) and \(C_3\) are shown in
Figure 4.

In the \(1\text{B}_2\) triplet state, charge delocalization can be enhanced by mixing the \(a_1\) and \(a_2\) orbitals, which requires

---

FIGURE 3. Relative energies of planar DMX for phenyl anion/m-xylylene biradical states (left) and phenyl radical/m-
xylylene anion states (right). Adiabatic energies (no ZPE in
duced) were calculated by B3LYP/6-311+G*, EOM-CCSD/6-
31+G* \((1\text{A}_2)\), and SF-EOM-CCSD/6-31+G* \((1\text{B}_1)\) (see text).

---


(51) In the \(C_2\) symmetry group, these are the \(1\text{B}_2\), \(1\text{A}_1\), and \(1\text{A}_2\) triplets and the \(1\text{A}_1\) singlet. Their electronic configurations are \(\sigma^2\pi^2\sqrt{2}\), \(\sigma^2\pi^2\sqrt{2}\), \(\sigma^2\pi^2\sqrt{2}\), and \(\sigma^2\pi^2\sqrt{2}\), respectively, and their wave functions are
single-configurational. In the \(C_2\) group, these electronic states mix with each other, and only \(1\text{B}_2\) and \(1\text{A}_2\) states
are single-reference wave functions.


(54) Glendenning, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Theoretical Chemistry Institute of the University of Wisconsin, Madison, WI, 1996.)
6-positions. However, in the C$_2$ geometry, an additional charge is delocalized from the 5-position to the methylene groups, thereby reducing the energy penalty due to charge localization. It should be noted that the overall energy of the triplet is lowered by only 0.3 kcal/mol as a result of symmetry lowering, and that the preference for the non-planar geometry is not found using MP2 or coupled-cluster theory.

Reduction of symmetry can have dramatic effects of spectroscopic observables and electronic structure of the excited states. For example, in substituted benzenes, small conformational changes in the substituent produce very large changes the direction of electronic transition dipole moment (e.g., 50° and more) due to the mixing of excited nearly degenerate states that are not interacting in the symmetric nonsubstituted benzene.56–58 Symmetry can also have a pronounced effect on the bonding and equilibrium structures of the Jahn–Teller and pseudo-Jahn–Teller molecules.59–61 The DMX$^-$ anion, however, is an example where low-symmetry equilibrium structures are preferred because of more efficient charge delocalization that is not possible at higher symmetry. This type of behavior has been observed previously for deprotonated benzoquinone, which, like DMX$^-$, adopts a nonplanar structure to delocalize the charge into the π-system.62

The out-of-plane distortion of the carbon framework in the triplet ground state is not large. For example, the C1–C2–C3–C4 dihedral angle is only 5.5° (Figure 5). A larger out-of-plane distortion is found for the hydrogen atoms bonded to C4 and C6, which are approximately 10° out of the plane of the aromatic ring. Moreover, the out-of-plane distortion mainly occurs in the C4–C5–C6 portion of the ring, as the methylene–C1–C2–C3–methylenes portion is essentially planar. As shown in Figure 5, there is little difference between bond angles and bond lengths in the C$_{2v}$ and C$_2$ geometries of the triplet. Much larger differences are observed between the C$_{2v}$ and C$_2$ geometries and charge distributions of the 1$^A$ (1$^A_1$) states. The C–C bonds in the planar 1$^A_1$ state are all essentially 1.40–1.43 Å, with little bond length alternation, and the bond angles resemble those for phenyl anion.63 with a C4–C5–C6 angle of 110°. In the C$_2$ geometry, however, the C4–C5–C6 angle is 126°. The carbon–carbon bonds to C5 are only 1.34 Å, 0.06 Å shorter than those in the planar ion, whereas the C3–C4 and C1–C6 bonds are 0.06 Å longer in the nonplanar structure. Correspondingly, there is less charge at C5 and more at the methylene positions and C2 (Figure 5) in the C$_2$ distorted ion. The geometry and charge distributions of the 1$^A$ ion suggest a valence structure like that shown

(55) The C$_{2v}$ structures of the 3$^B_2$ and 1$^A_1$ states and the C$_2$ structure of 1$^A$ were also optimized at the MP2/6-311+G* level. The resulting geometries were very similar to those obtained at the B3LYP level of theory, differences not exceeding 0.01 Å and 1°–2° for bond lengths and bond angles, respectively.

Reactivity and Structure of 5-Dehydro-m-xylylene Anion

As noted in the preceding section, the reactivity of ion 1 with NO and N₂O suggests open-shell character but argues against a benzylic structure. This would then seem to be evidence against the possibility of an electronic excited state of the anion. Although the singlet ion, 3, is more of a pentadienyl anion than benzylic, the reaction of N₂O with pentadienyl anion is also found to proceed by addition and loss of water, which is not observed for 1.

**Conclusion**

Chemical and theoretical studies indicate that the ground state of the dehydro-m-xylylene anion is a ground-state triplet. This work was supported by the National Science Foundation (P.G.W.: CHE-0317627 and A.I.K.: CHE-0094116), by the Alfred P. Sloan Foundation, and the donors of the Petroleum Research Fund administered by the American Chemical Society (PRF-AC) to A.I.K.

**Supporting Information Available**: Cartesian coordinates for optimized geometries and absolute energies used in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

### Table 1. Relative Energies of the Stable States of DMX^− Calculated by Different DFT and CC Methods

<table>
<thead>
<tr>
<th>electronic state</th>
<th>DFT scheme</th>
<th>CCSD scheme</th>
<th>CCSD(T) scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>3B⁠¹</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1A⁠²</td>
<td>4.8</td>
<td>5.9</td>
<td>0.6</td>
</tr>
<tr>
<td>1A⁠³</td>
<td>5.1</td>
<td>7.6</td>
<td>7.7</td>
</tr>
<tr>
<td>1A²⁠⁴</td>
<td>7.6</td>
<td>11.1</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Values in kcal/mol; ZPE corrections are not included. The adiabatic energy differences between the 3B and the closed-shell singlet 1A were calculated as differences between the total DFT or CC energies. The adiabatic energy differences between the 3B and the open-shell 1A' (1B/1A2) states were computed in a two-step procedure: (i) the energy difference between 3B and 1B/1A2 was calculated at the DFT or CC levels, respectively and (ii) the 1B/1A2 energy separation was calculated by EOM-CCSD/6-311+G*. B3LYP/6-311+G* was used for 3B and 1A and B3LYP/6-311+G* and EOM-CCSD/6-311+G* for 1A' and 1A2. EOM-CCSD/6-311+G* was used for 3B and 1A and CCSD/6-311+G* and EOM-CCSD/6-311+G* for 1A' and 1A2. CCSD(T)/6-311+G* was used for 3B and 1A and CCSD(T)/6-311+G* and EOM-CCSD(T)/6-311+G* for 1A' and 1A2. Calculated at the energy level optimized at the EOM-CCSD/6-311+G* level was used. The equilibrium geometry of this open-shell singlet is of C₅ symmetry. However, we were not able to obtain fully optimized geometry due to the instabilities caused by the strong mixing between this state and the closely lying 1A2 (1A' in C₅) state. Calculated at the C₂ equilibrium geometry optimized at the EOM-CCSD/6-311+G* level.

The relative energies of the stable states of DMX^−, calculated at various levels of theory, are shown in Table 1. At all the levels of theory employed in this work, the 3B state is the ground state of the system. However, the energies of the singlet states are found to be slightly higher in energy and depend strongly on the level of theory. Because of the extensive difference in charge delocalization, the relative energy of the 1A state at nonplanar geometries is significantly lower than that of the planar ion, and is, at the CCSD(T)/6-311+G* level of theory, lower in energy than the 3B and 1A2 states, only 0.6 kcal/mol higher in energy than the 3B ground state. Although the conservative estimate of an energy

---
