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

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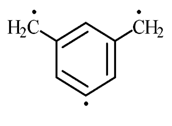
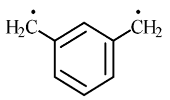
The electronic structure of dehydro-*m*-xylylene anion (**DMX**$^-$) has been investigated by using chemical reactivity studies and electronic structure calculations. **DMX**$^-$ has been generated in the gas phase via the sequential reaction of trimethyl-3,5-bis(trimethylsilylmethyl)phenylsilane with F^- and two molecules of F_2. 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.

Distonic 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 zwitterion[1] leading to ion radicals,[2,3] distonic ions are now generally considered to include ions with separated charge and radical centers, and examples of gaseous distonic ions that contain carbenes,[4−8] nitrenes,[6,9] and even biradicals[6,10−12] have been reported. Thus, distonic ions have been used to investigate the chemical reactivity of these types of moieties. However, because of their relationship to the neutral reactive intermediates, distonic ions also serve as convenient precursors for mass spectrometric[13−15] and spectroscopic[16] studies of the investigation of reactive intermediate thermochemistry. In addition to their utility in the investigation of neutral reactive intermediates, distonic ions are interesting species in their own right[17,18] and with unique reactivity and unusual electronic structures that result from ionization of complicated, open-shell wave functions.

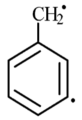
We recently reported the measurement of the bond dissociation energy at the 5-position of m-xylylene,[19] and its use for determining the heat of formation of the 5-dehydro-*m*-xylylene triradical (**DMX**). The **DMX** triradical has an unusual electronic structure with an unprecedented open-shell doublet ground state,[19] with three low-spin electrons in three, singly occupied molecular orbitals ($\sigma^1\pi^1\pi^1$). Ultimately, the measured thermochemical properties for **DMX** indicate little interaction between the unpaired σ- and π-electrons in the triradical.



DMX



MX



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 σ-orbital (Figure 1) leads to the formation of an ion consisting of a phenyl anion with a *m*-xylylene (**MX**) biradical moiety ($\sigma^2\pi_1{}^1\pi_2{}^1$) as represented by **1a**. However, it is also possible to add an

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[1] Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805−5808.

[2] Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649−1665.

[3] Smith, R. L.; Chou, P. K.; Kenttämaa, H. I. In *The Structure, Energetics and Dynamics of Organic Ions*; Baer, T., Ed.; John Wiley & Sons Ltd.: Chichester, U.K., 1997; pp 197−261.

[4] DePuy, C. H.; Van Doren, J. M.; Gronert, S.; Kass, S. R.; Motell, E. L.; Ellison, G. B.; Bierbaum, V. M. *J. Org. Chem.* **1989**, *54*, 1846−1850.

[5] Hu, J.; Hill, B. T.; Squires, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 11699−11700.

[6] Wenthold, P. G.; Hu, J.; Hill, B. T.; Squires, R. R. *Int. J. Mass Spectrom.* **1998**, *179/180*, 173−183.

[7] Seburg, R. A.; Hill, B. T.; Squires, R. R. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2249−2256.

[8] Hill, B. T.; Poutsma, J. C.; Chyall, L. J.; Hu, J.; Squires, R. R. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 896−906.

[9] Tichy, S. E.; Hill, B. T.; Campbell, J. L.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **2001**, *123*, 7923−7924.

[10] Thoen, K.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1997**, *119*, 3832−3833.

[11] Price, J. M.; Nizzi, K. E.; Campbell, J. L.; Kenttämaa, H. I.; Seierstad, M.; Cramer, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 131−140.

[12] Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 5816−5817.

[13] Reed, D. R.; Hare, M.; Kass, S. R. *J. Am. Chem. Soc.* **2000**, *122*, 10689−10696.

[14] Lee, J.; Grabowski, J. J. *Chem. Rev.* **1992**, *92*, 1611−1647.

[15] DePuy, C. H. *J. Org. Chem.* **2002**, *67*, 2393−2401.

[16] Wenthold, P. G.; Lineberger, W. C. *Acc. Chem. Res.* **1999**, *32*, 597−604.

[17] Rajca, S.; Rajca, A. *J. Am. Chem. Soc.* **1995**, *117*, 9172−9179.

[18] Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893.

[19] Slipchenko, L. V.; Munsch, T. E.; Wenthold, P. G.; Krylov, A. I. *Angew. Chem., Int. Ed. Eng.* **2004**, *43*, 742−745.

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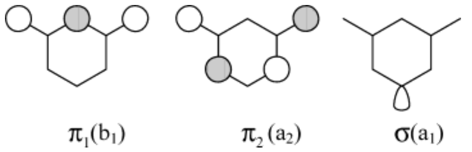
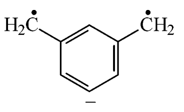
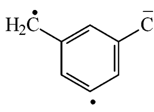


FIGURE 1. Nonbonding molecular orbitals 5-dehydro-*m*-xylylene (**DMX**). C_{2v} symmetry labels are shown in parentheses.

electron to one of the π-orbitals to create a *m*-xylylenyl anion with a phenyl radical, **1b** ($\sigma^1\pi_1{}^1\pi_2{}^2$ or $\sigma^1\pi_1{}^2\pi_2{}^1$),[20] where the biradical electronic structure resembles that of α,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*-xylylene (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*-xylylene biradical is a triplet, with a singlet−triplet energy difference (ΔE_{ST}) of 10.5 kcal/mol,[20] ion **1a** should have a triplet ground state. Similarly, α,3-dehydrotoluene is a ground-state singlet ($\Delta E_{ST} = 1{-}3$ kcal/mol),[21] 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,[23] 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 (**MX**) and nonoverlapping (**DHT**) electronic densities of biradical orbitals.[24,25] However, these predictions ignore any potential interactions between the σ- and π-systems or any effects that the charge site has on the electronic structure of the biradical.


1a


1b

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 allenic 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 Albrecht 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 tribromide. Treatment of 1-bromo-3,5-bis(bromomethyl)benzene[28] with excess LiCl (10 equiv) in DMF at room temperature for 12 h under nitrogen leads to chlorination at the α- and α′-positions.[29,30] Diethyl ether was added, and the mixture was washed with H_2O 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)benzene[29] 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. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, $C_8H_7{}^-$, 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 $F_2{}^{-\bullet}$ 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

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[20] Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 1354−1359.

[21] Wenthold, P. G.; Wiershke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 7378−7392.

[22] Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Linenberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601−620.

[23] Levchenko, S. V.; Krylov, A. I. unpublished results.

[24] Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587−4594.

[25] Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2002**, *117*, 4694−4708.

[26] Marinelli, P. J.; Paulino, J. A.; Sunderlin, L. S.; Wenthold, P. G.; Poutsma, J. C.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1994**, *130*, 89−105.

[27] Albrecht, M.; Kocks, B. M.; Spek, A. L.; Van Koten, G. *J. Organmet. Chem.* **2001**, *624*, 271−286.

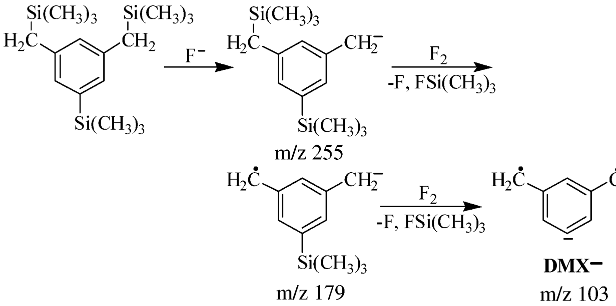
[28] Högberg, H.-E.; Wennerström, O. *Acta Chem. Scand., Ser. B* **1982**, *36*, 661−667.

[29] Tashiro, M.; Yamato, T.; Kobayashi, K.; Arimura, T. *J. Org. Chem.* **1987**, *52*, 3196−3199.

[30] Harvey, S.; Junk, P. C.; Raston, C. L.; Salem, G. *J. Org. Chem.* **1998**, *53*, 3134−3140.

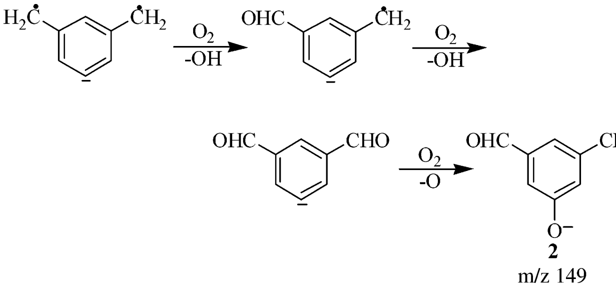
[31] Wrobel, D.; Wannagat, U. *J. Organmet. Chem.* **1982**, *225*, 203−210.

with HF impurity in the fluorine mixture.[6] 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.



(1)

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.[12] Similarly, the phenyl anion reacts with O_2 to form phenoxide and other products.[32] 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,[33] the barrier in the gas-phase reaction can be overcome by the ion/neutral complexation energy.[15] 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,[27] 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.



(2)

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,[12] but radical addition has been observed for open-shell carboxylates, including those derived from benzyne ions,[34] 1,3,5-trimethylenebenzene anion[12], and *m*-xylylene anion.[35] 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.[34] This reactivity is consistent with that expected for either ion **1a** or **1b**, as they are both open-shell biradicals.

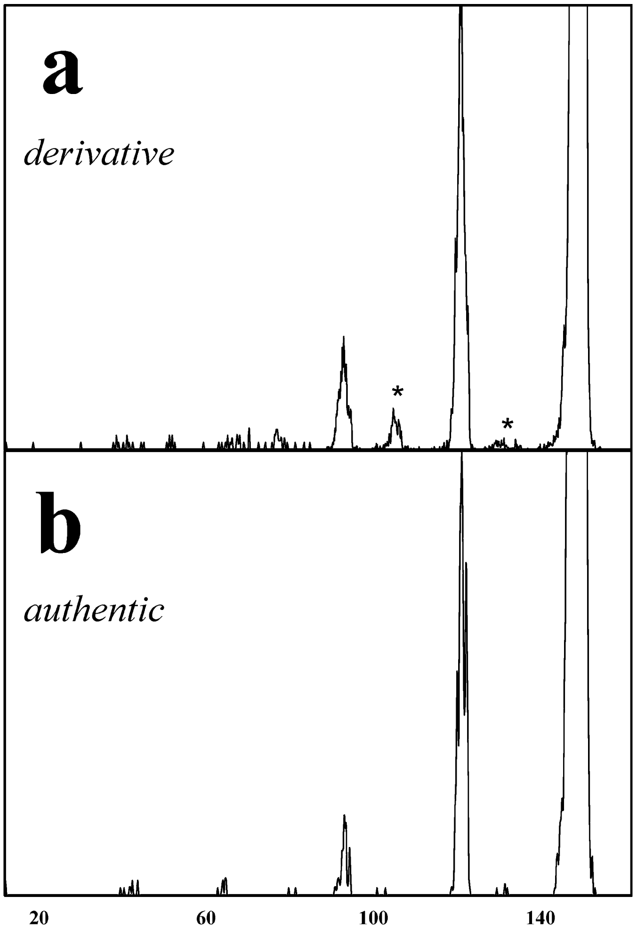


FIGURE 2. Collision-induced dissociation spectra for *m*/*z* 149, generated by the reaction of *m*/*z* 103 with oxygen (a) and from fluoride induced desilylation of 1-*tert*-butyldimethylsilyloxy-3,5-bis-formylbenzene (b). The starred peaks in the spectrum (b) indicate products attributable to *m*/*z* 149 arising from reaction of O_2 with *m*/*z* 104.

The question of the phenyl versus the benzyl anion has been addressed by using reactions with N_2O 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_2O (eq 3b).[36] As expected, the

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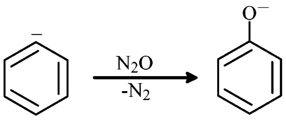
(32) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Mass Spectrom.* **1998**, *33*, 796−802.

(33) Lin, C. Y.; Lin, M. C. *Chem. Phys. Processes Comb.* **1987**, 7/1−7/4.

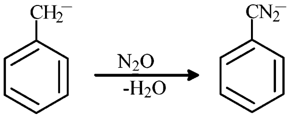
(34) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 11865−11871.

(35) Hammad, L. A.; Wenthold, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 11203−11211.

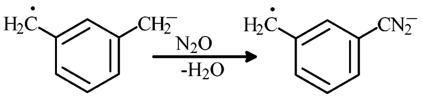
reaction shown in eq 3b also occurs with *m*-xylylene anion (eq 3c), formed by the reaction of *m*-xylylene with $O^{-}\bullet$.[20,35] Given the similarity between the electronic structure of **1b** and the *m*-xylylene anion, it is reasonably expected that the reaction shown in eqs 3b and 3c should occur with ion **1b** as well. However, the reaction of **DMX**⁻ with N_2O proceeds to give oxygen atom transfer (eq 4a), whereas the addition and loss of H_2O product (eq 4b) is not observed at all. On the basis of this observation, we conclude that the **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 N_2O. Benzylic radicals in the gas phase are essentially unreactive with N_2O.[12]



(3a)

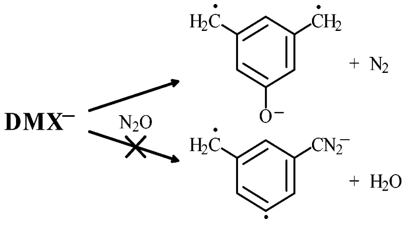


(3b)



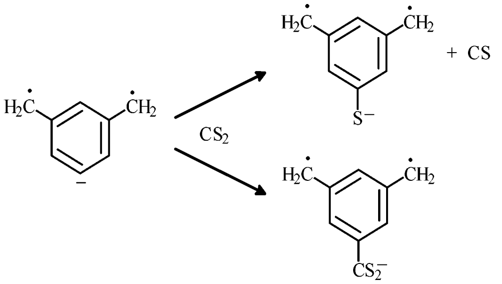
(3c)

The reaction with CS_2 is also consistent with a phenyl anion electronic structure. The reaction proceeds by sulfur atom transfer (25%), and CS_2 addition (75%) is formed. It is well-recognized that sulfur atom transfer occurs in the reaction of CS_2 with highly basic ions. For example, the reaction of CS_2 with phenyl anion has been measured in this work to proceed by 94% sulfur atom transfer and 6% CS_2 addition (eq 5), whereas the reaction of CS_2 with benzylic anions, including *m*-xylylene anion, proceeds only by CS_2 addition.[35] Thus, the observation of sulfur atom abstraction with CS_2 suggests a phenyl anion in **DMX**⁻. Generally, sulfur abstraction from CS_2 by a phenyl radical to form a phenylthiolate radical is endothermic by ca. 10 kcal/mol[37,38] 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 CS_2 is consistent with the phenyl anion assignment, it does not rule out structure **1b**.



(4a)
(4b)

The thermochemical properties measured for **DMX**⁻ are also consistent with the assignment of a phenyl anion/*m*-xylylene biradical electronic structure. For example, the electron binding energy in **DMX**⁻ (the EA of **DMX**) was measured to be 24.9 ± 2.0 kcal/mol.[19] This value is similar to the EA of phenyl radical, 25.3 ± 0.1 kcal/mol,[22] but is much higher than the EA of *m*-xylylene, 21.19 ± 0.18 kcal/mol.[39] Similarly, the proton affinity of the ion is measured to be 401 ± 3 kcal/mol,[19] nearly the same as that for phenyl anion, but much higher than that for the benzyl anion (~380 kcal/mol).[38] Thus, the reactivity and thermochemical properties of **DMX**⁻ are all consistent with an electronic structure with a phenyl anion and triplet *m*-xylylene biradical (**1a**), as predicted by simple EA considerations.



(5)

Theoretical Results

From the electronic structure point of view, adding an extra electron into the three-electrons-on-three-orbitals system of the **DMX** triradical leads to the four-electrons-in-three-orbitals pattern in **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.[40] The traditional method, EOM-EE-CCSD,[41] was used for states that can be described as single excitations from a

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(36) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849−2852.

(37) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, March 2003; pp 20899.

(38) Bartmess, J. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, March 2003; pp 20899.

(39) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401.

(40) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(41) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029−7039.

closed-shell reference. Its spin−flip counterpart, EOM-SF-CCSD,[25,42−44] was used for biradical states. Some states (e.g., triplets and closed-shell singlets) were accessible by traditional single-reference techniques, such as CCSD(T)[45] or density functional theory (DFT).[46]

Equilibrium geometries of all the triplet ($\sigma^2\pi_1{}^1\pi_2{}^1$, $\sigma^1\pi_1{}^2\pi_2{}^1$, $\sigma^1\pi_1{}^1\pi_2{}^2$) and closed-shell singlet ($\sigma^2\pi_1{}^2\pi_2{}^0$) states of **DMX**$^-$ were optimized at the B3LYP/6-311+G*[47,48,49] level of theory. The structures of the $^1B_1$ ($^1A''$) and $^1A_2$ open-shell singlet states ($\sigma^1\pi_1{}^1\pi_2{}^2$ and $\sigma^1\pi_1{}^2\pi_2{}^1$) were optimized at the EOM-CCSD/6-31+G*[49,50] level from the $\sigma^2\pi_1{}^0\pi_2{}^2$ and $\sigma^0\pi_1{}^2\pi_2{}^2$ references, respectively. Adiabatic excitation energies between the states that are well-described by single-reference methods[51] were calculated by the B3LYP, CCSD, and CCSD(T) methods. The energy differences between the two-configurational $^1B_1$/$^1A_2$ open-shell singlets and the corresponding $^3B_1$/$^3A_2$ triplet states were calculated by EOM-EE-CCSD and EOM-SF-CCSD. Calculations were performed by using the Q-CHEM[52] and ACES II[53] 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_{2v} 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 **1a**, with a phenyl anion and *m*-xylylene biradical moiety. Electronic states with labels to the right correspond to an electronic structure like that in **1b**. At the planar geometry, the ground state of the system is predicted to be the $^3B_2$ state, the triplet state of **1a**. The lowest energy state of **1b** is the $^1B_1$ singlet state and is 4.1 kcal/mol higher in energy than the ground state. The lowest energy triplet state of planar **1b** is the $^3B_1$ state, calculated to be 4.9 kcal/mol above the ground state, such that **1b** has a singlet−triplet energy splitting of 0.8 kcal/mol. A second triplet state in **1b,** the $^3A_2$ state, lies 8.2 kcal/mol higher than the ground state. The corresponding singlet−triplet energy splitting is 1.2 kcal/mol. The calculated singlet−triplet splitting of planar **1a** is 13.1 kcal/mol in favor of the triplet. These values are similar to the corresponding singlet−triplet splittings in α,3-dehydrotoluene[21] 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.

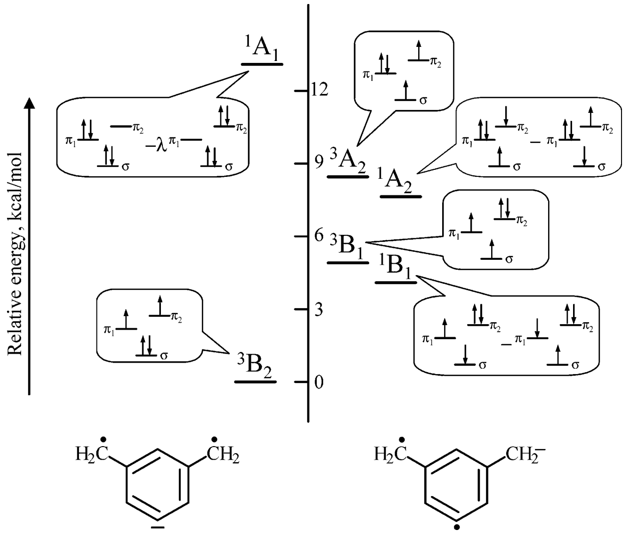

FIGURE 3. Relative energies of planar **DMX**$^-$ for phenyl anion/*m*-xylylene biradical states (left) and phenyl radical/*m*-xylylenyl anion states (right). Adiabatic energies (no ZPE included) were calculated by B3LYP/6-311+G*, EOM-CCSD/6-31+G* ($^1A_2$), and SF-EOM-CCSD/6-31+G* ($^1B_1$) (see text).

Surprisingly, only one of the planar states described previously, the $^1A_2$ 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 $^3B_2$, $^3B_1$, and $^1A_1$ states, the normal coordinate for the imaginary frequency distorts the molecule to C_2 symmetry. In the $^3A_2$ and $^1B_1$ states, the distortion leads to a planar C_s structure. Thus, the DFT calculations predict that many of the stable states of **DMX**$^-$ have non-C_{2v} structures, and as described next, are nonplanar. This is particularly striking since out-of-plane distortions perturb conjugation in the π-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_s allows mixing of the a_1 and b_2 orbitals (as a′) and of the a_2 and b_1 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_s are shown in Figure 4.

In the $^3B_2$ triplet state, charge delocalization can be enhanced by mixing the a_1 and a_2 orbitals, which requires

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(42) Krylov, A. I. *Chem. Phys. Lett.* **2001**, *338*, 375−384.

(43) Levchenko, S. V.; Krylov, A. I. *J. Chem. Phys.* **2004**, *120*, 175−185.

(44) Krylov, A. I.; Sherrill, C. D. *J. Chem. Phys.* **2002**, *116*, 3194−3203.

(45) Piecuch, P.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1999**, *110*, 6103−6122.

(46) Parr, R. G.; Yang, W. *Density-functional theory of atoms and molecules*; Oxford University Press: New York, 1989.

(47) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(48) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654.

(49) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. *J. Comput. Chem.* **1983**, *4*, 294−301.

(50) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(51) In the C_{2v} symmetry group, these are the $^3B_2$, $^3B_1$, and $^3A_2$ triplets and the $^1A_1$ singlet. Their electronic configurations are $\sigma^2\pi_1{}^1\pi_2{}^1$, $\sigma^1\pi_1{}^1\pi_2{}^2$, $\sigma^1\pi_1{}^2\pi_2{}^1$, and $\sigma^2\pi_1{}^2\pi_2{}^\circ$, respectively, and their wave functions are single-configurational. In the C_2 group, these electronic states mix with each other, and only ^3B and ^1A can be described by single-reference wave functions.

(52) Kong, J.; White, C. A.; Krylov, A. I.; Sherrill, D.; Adamson, R. D.; Furlani, T. R.; Lee, M. S.; Lee, A. M.; Gwaltney, S. R.; Adams, T. R.; Ochsenfeld, C.; Gilbert, A. T. B.; Kedziora, G. S.; Rassolov, V. A.; Maurice, D. R.; Nair, N.; Shao, Y. H.; Besley, N. A.; Maslen, P. E.; Dombroski, J. P.; Daschel, H.; Zhang, W. M.; Korambath, P. P.; Baker, J.; Byrd, E. F. C.; Van Voorhis, T.; Oumi, M.; Hirata, S.; Hsu, C. P.; Ishikawa, N.; Florian, J.; Warshel, A.; Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. *J. Comput. Chem.* **2000**, *21*, 1532−1548.

(53) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem.* **1992**, 879−894.

(54) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *Theoretical Chemistry Institute*; University of Wisconsin, Madison, WI, 1996.

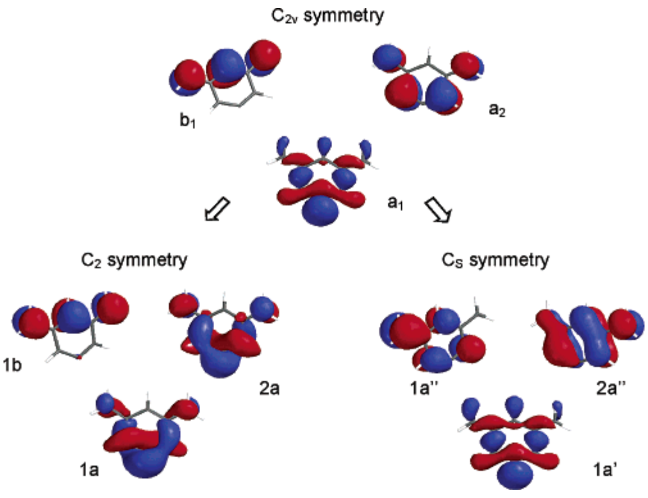

FIGURE 4. Effects of symmetry reduction on the nonbonding molecular oribtals in DMX$^-$.

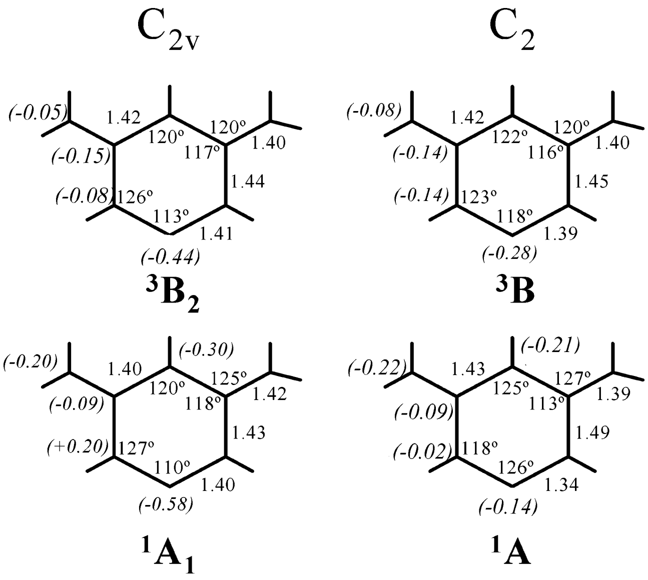

FIGURE 5. Geometries of the C_{2v} (planar) and C_2 (nonplanar) triplet and singlet states of **DMX**$^-$ calculated at the B3LYP/6-311+G* level of theory. Out-of-plane distortions of the C_2 structures are described in the text. The atomic charges calculated by using the NBO approach are shown in italics.

lowering the symmetry from C_{2v} to C_2. Because the energy gain due to the more extensive delocalization is more significant than the energy penalty for the breaking of the conjugation in the π-system, the nonplanar geometry is preferred at the B3LYP/6-311+G* level of theory. From the electronic structure point of view, this results in a mixing of the ^3B configurations that lowers the energy due to a configuration interaction. The increased charge delocalization is reflected in the calculated changes in natural charges (Figure 5).[55] At the C_{2v} geometry, the charge distribution for the most part reflects the a_1 orbital, with almost half the charge at the 5-position, and the remainder is distributed through the 1-, 3-, 4-, and 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−methylene 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 ^1A ($^1A_1$) states. The C−C bonds in the planar $^1A_1$ 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 ^1A ion suggest a valence structure like that shown

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(55) The C_{2v} structures of the $^3B_2$ and $^1A_1$ states and the C_2 structure of ^1A 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.

(56) Joireman, P. W.; Kroemer, R. T.; Pratt, D. W.; Simons, J. P. *J. Chem. Phys.* **1996**, *105*, 6075−6077.

(57) Borst, D. R.; Joireman, P. W.; Pratt, D. W.; Robertson, E. G.; Simons, J. P. *J. Chem. Phys.* **2002**, *116*, 7057−7064.

(58) Panja, S. S.; Chakraborty, T. *J. Chem. Phys.* **2003**, *119*, 9486−9490.

(59) Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783−4790.

(60) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2003**, *118*, 9614−9622.

(61) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2003**, *118*, 6874−6883.

(62) Davico, G. E.; Schwartz, R. L.; Ramond, T. M.; Lineberger, W. C. *J. Am. Chem. Soc.* **1999**, *121*, 6047−6054.

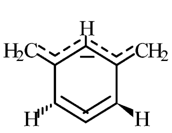
(63) Nicolaides, A.; Smith, D. M.; Jensen, F.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 8083−8088.

TABLE 1. Relative Energies of the Stable States of DMX$^-$ Calculated by Different DFT and CC Methods[a,b]

electronic state	DFT scheme[c]	CCSD scheme[d]	CCSD(T) scheme[e]
^{3}B[f]	0.0	0.0	0.0
^{1}A[f]	4.8	5.9	0.6
^{1}A[g]	5.1	7.6	7.7
^{1}A$_2$[h]	7.6	11.1	10.0

[a] Values in kcal/mol; ZPE corrections are not included. [b] The adiabatic energy differences between the triplet ^{3}B and the closed-shell singlet ^{1}A were calculated as differences between the total DFT or CC energies. The adiabatic energy differences between the ^{3}B and the open-shell ^{1}A″ (^{1}B$_1$)/^{1}A$_2$ states were computed in a two-step procedure: (i) the energy difference between ^{3}B and ^{3}B$_1$/^{3}A$_2$ was calculated at the DFT or CC levels, respectively and (ii) the ^{3}B$_1$−^{1}B$_1$/^{3}A$_2$−^{1}A$_2$ energy separation was calculated by EOM-CCSD/6-31+G*. [c] B3LYP/6-311+G* was used for ^{3}B and ^{1}A and B3LYP/6-311+G* and EOM-CCSD/6-31+G* for ^{1}A″ and ^{1}A$_2$ (see footnote *b*). [d] CCSD/6-311+G* was used for ^{3}B and ^{1}A and CCSD/6-311+G* and EOM-CCSD/6-31+G* for ^{1}A″ and ^{1}A$_2$ (see footnote b). [e] CCSD(T)/6-311+G* was used for ^{3}B and ^{1}A and CCSD(T)/6-311+G* and EOM-CCSD/6-31+G* for ^{1}A″ and ^{1}A$_2$ (see footnote b). [f] C_2 equilibrium geometries optimized at the B3LYP/6-311+G* level were used. [g] C_{2v} geometry optimized at the EOM-CCSD/6-31+G* level was used. The equilibrium geometry of this open-shell singlet is of C_s 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 ^{1}A$_2$ (^{1}A″ in C$_s$) state. [h] Calculated at the C_{2v} equilibrium geometry optimized at the EOM-CCSD/6-31+G* level.

as **3**, consisting of a pentadienyl (π) anion with an allene moiety. The bonding shown in **3**, confirmed by NBO,[64] is only possible in the lower symmetry geometry, and is surprisingly reminiscent of that found for deprotonated cyclooctatetraene,[65] which also forms an allene and a delocalized anion, **4**.



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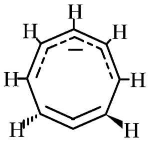

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The relative energies of the stable states of **DMX$^-$**, calculated at various levels of theory, are shown Table 1. At all the levels of theory employed in this work, the ^{3}B state is the ground state of the system. However, the energies of the 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 ^{1}A 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 ^{1}B$_1$ and ^{1}A$_2$ states, only 0.6 kcal/mol higher in energy than the ^{3}B ground state. Although the conservative estimate of an energy error bar of the employed computational scheme exceeds 0.6 kcal/mol, we believe that the calculated energy gap between the ^{3}B and the ^{1}A states is reliable due to the error cancellation, which is supported by the amplitude analysis of the CC wave function. Thus, the theoretical calculations predict the ground state of the system to be the triplet but find that the singlet is slightly higher in energy.

This state ordering is in agreement with the reactivity studies of **DMX$^-$**. As noted in the preceding section, the reactivity of ion **1** with NO and N$_2$O suggests open-shell character but argues against a benzylic structure. This would then seem to be evidence against the possibility of the ^{1}A state being the reactive state of the ion. Although the singlet ion, **3**, is more of a pentadienyl anion than benzylic, the reaction of N$_2$O with pentadienyl anion is also found to proceed by addition and loss of water,[66] and this reaction 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, ^{3}B, consisting of a phenyl anion and a *m*-xylylene biradical. The benzylic ion, electronically similar to the dehydrotoluene biradical, is calculated to lie 4−5 kcal/mol higher in energy than the ground state. Triplet carbanions are rare but have been found for other reduced triradicals[12,17] or for carbyne anions.[67] This ion is unique among the known hydrocarbon distonic biradical anions in that the charge is nominally separated from the biradical moiety. The lowest energy singlet is not the biradical but is an allenic structure with a pentadienyl anion and is calculated to be slightly higher in energy than the triplet state. Atomic charges calculated for the singlet ion indicate significant charge density at the 2-position, suggesting that it may be possible to modify the ground-state electronic structure by using substituents at that position. Indeed, preliminary calculations suggest that a cyano substituent at the 2-position of the ion preferentially stabilizes the singlet state with respect to the triplet, resulting in a singlet ground state. Experimental studies to test this possibility are currently underway.

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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.

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(64) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

(65) Kato, S.; Lee, H. S.; Gareyev, R.; Wenthold, P. G.; Lineberger, W. C.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1997**, *119*, 7863−7864.

(66) Munsch, T. E.; Wenthold, P. G., unpublished results.

(67) Seburg, R. A.; Hill, B. T.; Jesinger, R. A.; Squires, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 6310−6311.