Radicals

5-Dehydro-1,3-quinodimethane: A Hydrocarbon with an Open-Shell Doublet Ground State[**]

Lyudmila V. Slipchenko, Tamara E. Munsch, Paul G. Wenthold,[*] and Anna I. Krylov[*]

We report experimental and theoretical studies of the organic triradical, 5-dehydro-1,3-quinodimethane (5-dehydro-*m*-xylylene, DMX, Figure 1), a hydrocarbon with an unprecedented electronic ground state of three low-spin coupled unpaired electrons, that is, an "open-shell doublet." Although low-spin, open-shell states occur in molecules containing transition metals, the ground states of organic molecules are rarely of this type. Organic biradicals can have open-shell singlet ground states, depending on the orbital structure,[1] but DMX is the first example of an organic triradical with an open-shell doublet ground state.

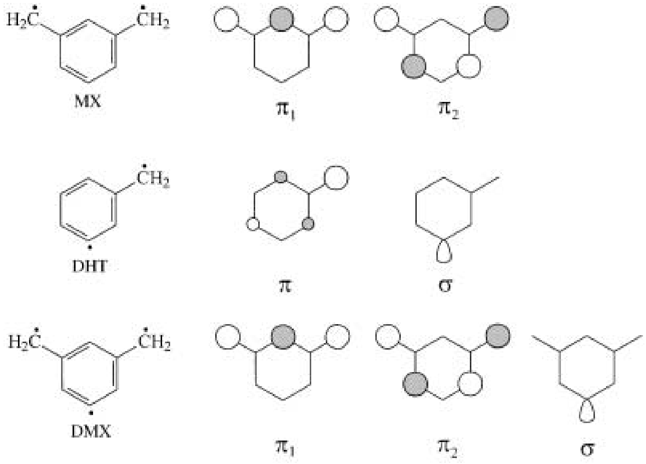


Figure 1. Nonbonding molecular orbitals in MX, DHT, and DMX.

Qualitatively, the preference for the open-shell doublet ground state in DMX can be understood by considering the electronic structures in *m*-xylylene (MX) and α,3-dehydrotoluene (DHT). The MX biradical has a triplet ground state[2–4] with two ferromagnetically coupled electrons in two π molecular orbitals (Figure 1). DHT, also shown in Figure 1, is a $\sigma^1\pi^1$ biradical[5] with singlet-coupled unpaired electrons, a result of spin polarization that favors antiferromagnetic coupling.[5,6] The features responsible for the MX and DHT ground state multiplicities are also present in DMX. The π system is similar to that of MX, such that it should contain two ferromagnetically coupled electrons. Likewise, the interaction between the σ and π systems resembles that in DHT, and should therefore have a preference for antiferromagnetic coupling. The net result is a hydrocarbon with a $\sigma^1\pi^1\pi^1$, open-shell doublet, ground state configuration (Figure 1).

More rigorously, the electronic structure of triradicals is described by the three-electrons-in-three-orbitals model.[7] Different occupations of three nearly degenerate triradical orbitals result in one quartet and eight doublet low-lying states.[7] The eight lowest energy electronic states of DMX are shown in Figure 2. Orbital near-degeneracies in the triradical result in multiconfigurational wave functions for most of the

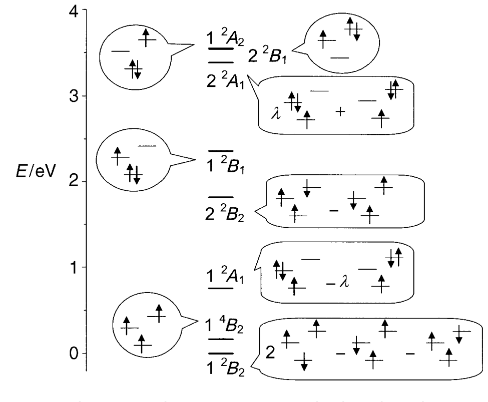


Figure 2. Vertical state ordering in DMX calculated at the SF-CCSD/6-311G** level at the equilibrium geometry of the ground $X\,^2B_2$ state. The orbital ordering is as follows: the lowest orbital is σ, the middle one is π_1, and the upper one is π_2 orbital from Figure 1.

---

[*] T. E. Munsch, Prof. P. G. Wenthold
Department of Chemistry
Purdue University
560 Oval Drive, West Lafayette, IN 47907-2084 (USA)
Fax: (+1) 765-494-0239
E-mail: pgw@purdue.edu
L. V. Slipchenko, Prof. A. I. Krylov
Department of Chemistry
University of Southern California
3620 McClintock Avenue, Los Angeles, CA 90089-0482 (USA)
Fax: (+1) 213-740-3972
E-mail: krylov@usc.edu

[**] This work was funded by the National Science Foundation (P.G.W.: CHE-0137627; A.I.K.: CAREER CHE-0094116). Additional support was provided by the Petroleum Research Fund, administered by the American Chemical Society (P.G.W. and A.I.K.), and the Camille and Henry Dreyfus New Faculty Awards and Alfred P. Sloan Programs (A.I.K.).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200352990

low-lying electronic states, which greatly complicates electronic structure calculations. Fortunately, the recently introduced spin–flip (SF) approach,[8–10] wherein the target electronic states are described as spin–flipping excitations from a high-spin reference state, is well-suited for these calculations. Unlike low-spin states, the high-spin states are not affected by orbital degeneracies and can be accurately described by a single-reference method. In the case of triradicals we employ the high-spin component of the quartet state as a reference and describe the doublets and the low-spin component of the quartet as "excited" states in the space of the single spin–flipping excitations as shown in Equation (1), in which

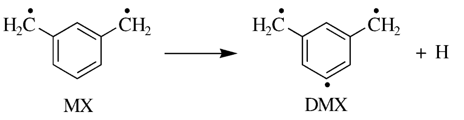
$$\Psi^{d,q}_{M_S=1/2} = \hat{R}_{M_S=-1}\tilde{\Psi}^{q}_{M_S=3/2} \tag{1}$$

M_S is the projection of the total spin, $\tilde{\Psi}^{q}_{M_S=3/2}$ is the $\alpha\alpha\alpha$ component of the quartet reference state, $\Psi^{d,q}_{M_S=1/2}$ represents the wave functions of the final doublet and quartet states, and $\hat{R}_{M_S=-1}$ is an excitation operator that flips the spin of one electron.

Because all the Slater determinants present in triradical wave functions from Figure 2 are formally single spin–flipping excitations, a balanced and accurate description of all the triradical states can be obtained within the SF scheme,[7,11] similar to the way that problematic singlet states of biradicals can be well-described as spin–flipping excitations from the high-spin triplet reference. As demonstrated in the comprehensive benchmark study of 15 biradicals, the SF models describe open-shell systems with an accuracy comparable to that achieved by traditional single reference methods in the case of well-behaved closed-shell molecules.[11] Most of the results presented in this work are obtained by the SF model in which the reference state is described by the coupled-cluster method with single and double substitutions (CCSD), and the excitation operator $\hat{R}$ consisting of single- and double-excitation operators involving the flip of the spin of one electron (SF-CCSD). For this method, the typical errors in the singlet–triplet gaps in biradicals are about 1 kcal mol^{-1}.[11] All SF calculations were performed by using the Q-CHEM 2.1 electronic structure package.[12]

The multistate nature of the SF approach allows the calculation of an entire manifold of low-lying electronic states of DMX. In agreement with the qualitative, spin-polarization-based predictions, the ground state of DMX is the open-shell doublet 1^2B_2 state (Figure 2). The counterpart of the 1^2B_2 state, the 1^4B_2 quartet, is 0.16 eV higher in energy. Equilibrium geometries of these two states are similar. Interestingly, the 1^2B_1 state that results from sequential electron addition (an "aufbau" approach) is more than 2 eV higher in energy than the open-shell 1^2B_2, as transferring an electron between spatially separated π and σ systems leads to an anionic state with negative charge at the C5 position. Similar considerations also explain the high excitation energy of the 2^2A_1 state. The lowest energy closed-shell type doublet (i.e., doublet with one of the triradical orbitals being occupied by a pair of electrons) is the 1^2A_1 state, which resembles the lowest-energy singlet in MX.[4] The net conclusion is that state-of-the-art calculations carried out by using the SF approach confirm the prediction of the open-shell doublet ground state for DMX.

We have carried out an experimental determination of the heat of formation of the DMX triradical by measuring the bond dissociation enthalpy, DH_{298}, at the C5 position of MX, as shown in Equation (2). The value of DH_{298} was obtained



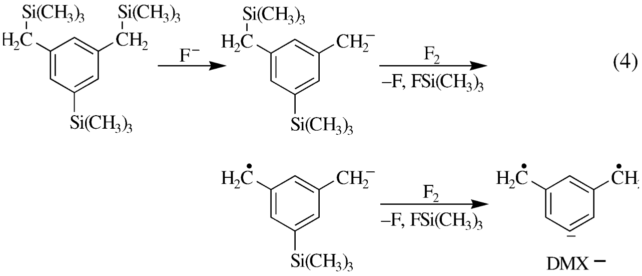
(2)

from the gas-phase acidity of the C5 position of MX ($\Delta_{\text{acid}}H_{298}$(5-MX)), the electron affinity (EA) of DMX, and the ionization energy (IE) of the hydrogen atom according to the relationship shown in Equation (3). The gas-phase acidity

$$DH_{298}(\text{MX}) = \text{EA}(\text{DMX}) + \Delta_{\text{acid}}H_{298}(\text{MX}) - \text{IE}(\text{H}) \tag{3}$$

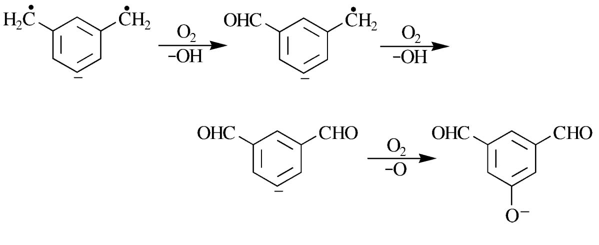
and electron affinity values were obtained from studies of DMX$^-$ anion.[13]

The synthesis of DMX$^-$ involves sequential reaction of 5,α,α′-*tris*-trimethylsilyl-*m*-xylene with F$^-$ and two equivalents of F_2 [Eq. (4)] results in formation of an ion with *m*/*z* 103, $C_8H_7^-$, which is deduced on the basis of reactivity studies



(4)

to be DMX$^-$. Reaction of the ion with O_2 leads to a product that has the same mass-to-charge ratio and collision-induced dissociation spectrum as 3,5-*bis*-formylphenoxide ion [Eq. (5)]. The formation of the phenoxide ion can be



(5)

attributed to oxygen atom abstraction from O_2 by DMX$^-$ and sequential oxidation of the benzylic radicals. Oxidation of benzylic radicals in distonic biradical anions with O_2 has been observed previously by Hu and Squires.[14] The formation of the phenoxide from reaction of DMX$^-$ with oxygen confirms the dehydro-*m*-xylylene structure of the ion.

The gas-phase acidity at the C5 position in MX was determined by bracketing the proton affinity of DMX$^-$.

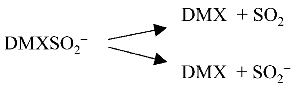
Proton transfer bracketing results,[15] summarized in Table 1, indicate a proton affinity very close to that of phenyl anion, and we assign a value of 392 ± 3 kcal mol^{-1} for $\Delta_{\text{acid}}G_{298}$ of the C5 position of MX. The quantity $\Delta_{\text{acid}}H_{298}$ is calculated from the measured $\Delta_{\text{acid}}G_{298}$ by using $\Delta H = \Delta G + T\Delta S$. The value of $\Delta_{\text{acid}}\Delta S_{298}$ is calculated from the B3LYP/6-311+G* frequencies for DMX$^-$ and MX to be 29.0 cal mol^{-1} K^{-1}, giving a value of 401 ± 3 kcal mol^{-1} for the 298 K acidity of the C5 position of MX.

Table 1: Proton transfer bracketing results for DMX$^-$.

Reference acid	$\Delta_{298}G_{\text{acid}}$[a]	Is proton transfer observed?[b]
*i*PrNH$_2$	389.9 ± 3.0	Yes
*n*PrNH$_2$	391.0 ± 3.0	Yes
EtNH$_2$	391.7 ± 0.7	No
DMF	392.0 ± 4.0	No
C_6H_6	392.3 ± 0.1	Yes
MeNH$_2$	395.7 ± 0.7	No
NH$_3$	396.0 ± 0.2	No

[a] Acidity values taken from reference [15], in kcal mol^{-1}. [b] A "Yes" indicates that proton transfer is observed with this acid, and "No" indicates that proton transfer is not observed.

The EA of DMX was determined by using the kinetic method developed by Cooks, and co-workers.[16] The experiment involves the measurement of the branching ratio for collision-induced dissociation of the SO$_2$ adducts of DMX$^-$ [Eq. (6)][17] prepared by direct addition of DMX$^-$ with SO$_2$. In

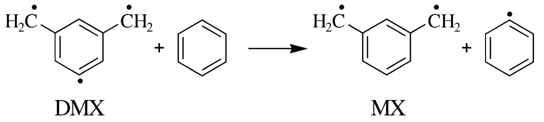


$$\mathrm{DMXSO_2^-} \begin{array}{l} \rightarrow \mathrm{DMX^-} + \mathrm{SO_2} \\ \rightarrow \mathrm{DMX} + \mathrm{SO_2^-} \end{array} \qquad (6)$$

this work, we have used the extended form of the kinetic method that incorporates the entropy differences in the competing dissociation channels.[17,18] The experimental procedures and representative data plots are provided in the Supporting Information. From our measurements, we obtain EA(DMX) = 24.9 ± 2.0 kcal mol^{-1}, similar to that for phenyl radical, 25.3 ± 0.1 kcal mol^{-1}.[19] Combination of the measured EA and $\Delta_{\text{acid}}H_{298}$ values according to Equation (3) gives a C–H DH_{298} of 112 ± 4 kcal mol^{-1}, indistinguishable from the DH_{298} of benzene, 112.9 ± 0.5 kcal mol^{-1}.[20] By using the measured DH_{298} along with the previously reported heat of formation of MX, 80.8 ± 2.4 kcal mol^{-1},[21] the heat of formation of DMX is found to be 141 ± 5 kcal mol^{-1}.

We have previously described the "triradical stabilization energy" (TSE)[22] as the energy required to separate a radical into radical and biradical components. The TSE for DMX corresponds to the energy change for the reaction shown in Equation (7), where DMX and MX are in their ground doublet and triplet states, respectively. From the experimental results, the TSE of DMX is calculated to be 1 ± 4 kcal mol^{-1}, thus indicating little measurable interaction between the σ and π electrons in this open-shell doublet triradical.

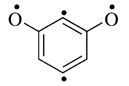
The experimentally determined TSE can be compared to that obtained from ab initio calculations. To achieve a balanced description of all species involved in Equation (7),



(7)

we first calculate the TSE for the quartet state (TSE$_Q$) at the CCSD with perturbative triples corrections [CCSD(T)] level. Since all species involved in the high-spin reaction are well described by single-reference methods, the calculated TSE$_Q$ is expected to be very accurate (within 1 kcal mol^{-1}). The TSE for the doublet state is obtained by adding the quartet-doublet energy difference ΔE_{QD}, calculated at the SF-CCSD level, to TSE$_Q$. Basis set effects were estimated by calculating the difference in ΔE_{QD} in double- and triple-ζ basis sets at the lower level of theory as described previously.[11] Our best estimate for TSE$_Q$ is 0.35 kcal mol^{-1}, which, when combined with $\Delta E_{\text{QD}} = 2.54$ kcal mol^{-1} for DMX, gives TSE = 2.89 kcal mol^{-1} for the ground state triradical. Thus, the calculated TSE indicates a weak but stabilizing interaction between σ and π radical centers in DMX, in agreement with the experimental result.

The presence of a weak electronic interaction between the σ and π electrons in DMX is consistent what has been found previously in other organic systems such as the dehydrotoluenes[5] and the dehydrophenylnitrenes.[23] On the other hand, recently reported computational studies by Clark and Davidson[24] suggest a strong interaction between the σ and π systems in 2,6-dehydro-*m*-quinone (DMQ), somewhat surprising for electrons in formally orthogonal regions of space. These results indicate a myriad of mechanisms for the interactions between electrons in open-shell systems, a factor that will become more important as their size continues to grow.[25]



DMQ

Received: October 1, 2003 [Z52990]

Keywords: ab initio calculations · radicals · spin–flip method · thermochemistry · triradicals

---

[1] L. Salem, C. Rowland, *Angew. Chem.* **1972**, *84*, 86; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 92.
[2] G. Kothe, K. H. Denkel, W. Summermann, *Angew. Chem.* **1970**, *82*, 935; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 906.
[3] G. R. Luckhurst, G. F. Pedulli, *J. Chem. Soc. B* **1971**, 329.
[4] P. G. Wenthold, J. B. Kim, W. C. Lineberger, *J. Am. Chem. Soc.* **1997**, *119*, 1354.
[5] P. G. Wenthold, S. G. Wiershke, J. J. Nash, R. R. Squires, *J. Am. Chem. Soc.* **1994**, *116*, 7378.
[6] W. T. Borden, E. R. Davidson, *J. Am. Chem. Soc.* **1977**, *99*, 4587.
[7] L. V. Slipchenko, A. I. Krylov, *J. Chem. Phys.* **2003**, *118*, 9614.
[8] A. I. Krylov, *Chem. Phys. Lett.* **2001**, *338*, 375.
[9] A. I. Krylov, C. D. Sherrill, *J. Chem. Phys.* **2002**, *116*, 3194.
[10] Y. Shao, M. Head-Gordon, A. I. Krylov, *J. Chem. Phys.* **2003**, *118*, 4791.
[11] L. V. Slipchenko, A. I. Krylov, *J. Chem. Phys.* **2002**, *117*, 4694.
[12] J. Kong, C. A. White, A. I. Krylov, D. Sherrill, R. D. Adamson, T. R. Furlani, M. S. Lee, A. M. Lee, S. R. Gwaltney, T. R. Adams, C. Ochsenfeld, A. T. B. Gilbert, G. S. Kedziora, V. A. Rassolov,

D. R. Maurice, N. Nair, Y. Shao, N. A. Besley, P. E. Maslen, J. P. Dombroski, H. Daschel, W. Zhang, P. P. Korambath, J. Baker, E. F. C. Byrd, T. V. Voorhis, M. Oumi, S. Hirata, C.-P. Hsu, N. Ishikawa, J. Florian, A. Warshel, B. G. Johnson, P. M. W. Gill, M. Head-Gordon, J. A. Pople, *J. Comput. Chem.* **2000**, *21*, 1532.

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

[14] J. Hu, R. R. Squires, *J. Am. Chem. Soc.* **1996**, *118*, 5816.

[15] J. E. Bartmess in *NIST Chemistry WebBook*, *NIST Standard Reference Database Number 69*, March 2003 ed. (Eds.: W. G. Mallard, P. J. Linstrom), National Institute of Standards and Technology, Gaithersburg, MD, 20899, **March 2003**.

[16] R. G. Cooks, P. S. H. Wong, *Acc. Chem. Res.* **1998**, *31*, 379.

[17] H. A. Lardin, R. R. Squires, P. G. Wenthold, *J. Mass Spectrom.* **2001**, *36*, 607.

[18] P. B. Armentrout, *J. Am. Soc. Mass Spectrom.* **2000**, *11*, 371.

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

[20] K. M. Ervin, V. F. DeTuri, *J. Phys. Chem. A* **2002**, *106*, 9947.

[21] L. A. Hammad, P. G. Wenthold, *J. Am. Chem. Soc.* **2000**, *122*, 11203.

[22] H. A. Lardin, J. J. Nash, P. G. Wenthold, *J. Am. Chem. Soc.* **2002**, *124*, 12612.

[23] H. F. Bettinger, W. Sander, *J. Am. Chem. Soc.* **2003**, *125*, 9726.

[24] A. E. Clark, E. R. Davidson, *J. Org. Chem.* **2003**, *68*, 3387.

[25] A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* **2001**, *294*, 1503.