5816 *J. Am. Chem. Soc.* **1996,** *118,* 5816−5817

Distonic Biradical Anions. Synthesis and Characterization of the 3,5-Dehydrophenyl and 1,3,5-Trimethylenebenzene Negative Ions

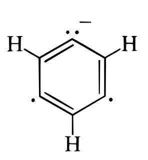
Jun Hu and Robert R. Squires*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

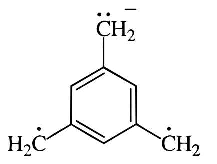
Received March 8, 1996

We recently described a new method for producing intense beams of structurally-defined biradical negative ions ("distonic radical anions") in the gas phase based on reactions between trimethylsilyl-substituted carbanions and molecular fluorine.[1] This synthetic procedure has been used to generate, *inter alia*, trimethylenemethane anion and *m*- and *p*-benzyne anions for use in negative ion photoelectron spectroscopic measurements of the singlet-triplet splittings in the corresponding neutral biradicals.[2] We now wish to report the extension of this procedure to the rational synthesis of negative ions of *triradicals*, i.e., "distonic biradical anions". The significance of these species is manifold. Polyradicals and their associated ions are the central focus of current efforts to produce synthetic organic ferromagnets.[3,4] Although triradical negative ions have been prepared in solution and in frozen matrices,[5] they are unprecedented in the gas phase. Just as distonic *radical* ions are useful surrogates for mass spectrometric studies of free radical chemistry,[6,7] so distonic *biradical* ions can also provide a means to examine the properties and reactivity of biradicals using gas-phase ion techniques. From a theoretical perspective, triradical ions represent important paradigms for computational studies of ferromagnetic coupling, Jahn−Teller effects, and electron delocalization in open-shell organic molecules.[3,5,8] Perhaps the most compelling aspect of these ions is that they are the essential precursors for negative ion photoelectron measurements of doublet−quartet splittings in hydrocarbon triradicals. These important physical quantities are unknown at present.

In this report, we describe the gas-phase synthesis and characterization of 3,5-dehydrophenyl anion, **1**, and 1,3,5-trimethylenebenzene negative ion, **2**. Ion **1** corresponds to the negative ion of the (σ,σ,σ) triradical 1,3,5-benzenetriyl, and it can also be viewed as a deprotonated *m*-benzyne. The fascinating orbital topology of the 3,5-dehydrophenyl *cation* was recognized more than 17 years ago by Schleyer *et al.*,[9] who coined the term "double aromaticity" to indicate the aromatic cyclopropenyl cation-like array of three σ orbitals imbedded within the aromatic π-system. Occupation of these σ orbitals by four electrons gives rise to the interesting possibility for this carbanion to exhibit low-lying singlet and triplet spin states, with the latter form constituting a novel example of an "antiaromatic" σ-system. Ion **2** is the negative ion of the all-π triradical α,α',α''-mesitylenetriyl,[10] and it can also be thought of as an ionic derivative of *m*-xylylene.[11] As in **1**, occupation of the three valence π orbitals in **2** with four electrons also necessarily leads to low-lying singlet and triplet states. Indeed, the valence orbital symmetries and energy level pattern, and the overall electronic state symmetries of **2** are essentially the same as those of the archetypal non-Kekule biradical trimethylenemethane.[12] Thus, an obvious challenge in characterizing **1** and **2** is the assignment of their ground-state multiplicities. In this work we demonstrate that the gas-phase reactivities of these species are consistent with a singlet ground state for **1** and a triplet ground state for **2**.

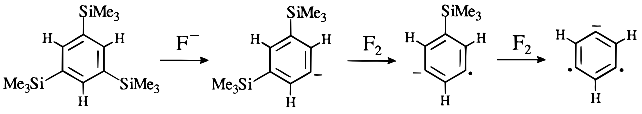


1



2

Scheme 1



1

All experiments were carried out at room temperature in a flowing afterglow triple-quadrupole apparatus.[13] The gas-phase syntheses of **1** and **2** involve sequential desilylation of the corresponding *tris*-trimethylsilyl-substituted hydrocarbons. Thus, reaction between F$^-$ and 1,3,5-*tris*(trimethylsilyl)benzene produces *bis*(trimethylsilyl)phenyl anion as a major ionic product (Scheme 1). Further reaction of this ion with F_2 (added as a 5% mixture in helium) yields the monosilylated (*meta*) benzyne radical anion and the fully-desilylated $C_6H_3^-$ ion, along with several ionic side products.[14] As discussed in previous reports,[1,15,16] the F_2-induced desilylations are believed to involve electron transfer from the silylated carbanion intermediates to F_2 ($EA = 3.01 \pm 0.07$ eV[17]) within the initial collision complex, followed by desilylation of the resulting (bi)radical by either $F_2^{-\bullet}$ or F$^-$. The regiospecificity of this synthetic procedure was demonstrated previously by the formation of *m*- and *p*-benzyne anions as distinct, non-interconverting species.[1,16]

Ion **1** is, predictably, the least stable of three possible cyclic $C_6H_3^-$ isomers. The properties and reactivity of the 2,3-dehydrophenyl anion, **3**, formed by collision-induced dissociation of *o*-fluorophenide, have been described by Gronert and DePuy.[18] This ion can also be formed as a side product of the reaction between F_2 and *m*-(trimethylsilyl)phenyl anion.[1,16] The 3,4-dehydrophenyl anion is unknown; in fact this ion may be

---

(1) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6961.

(2) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475.

(3) Rajca, A. *Chem. Rev.* **1994**, *94*, 871 and references therein.

(4) (a) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179. Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346. (b) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88. (c) West, A. P.; Silverman, S. K.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 1452.

(5) Rajca, A.; Rajca, A. *J. Am. Chem. Soc.* **1995**, *117*, 9172 and references therein.

(6) (a) Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649. (b) Kenttämaa, H. I. *Org. Mass Spectrom.* **1994**, *29*, 1.

(7) (a) Smith, R.; Chyall, L. J.; Stirk, K. M.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1993**, *28*, 1623. (b) Smith, R.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1995**, *117*, 1393.

(8) (a) Borden, W. T. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195. (b) Gordon, M. S.; Kass, S. R. *J. Phys. Chem.* **1995**, *99*, 6548.

(9) (a) Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 3707. (b) Schleyer, P. v. R.; Jiao, H.; Glukhovtsev, M. N. *J. Am. Chem. Soc.* **1994**, *116*, 10129.

(10) (a) Yoshizawa, K.; Hatanaka, M.; Matsuzaki, Y.; Tanaka, K.; Yamabe, T. *J. Chem. Phys.* **1994**, *100*, 4453. (b) Yoshizawa, K.; Hatanaka, M.; Ito, A.; Tanaka, K.; Yamabe, T. *Chem. Phys. Lett.* **1993**, *202*, 483. (c) Li, S.; Ma, J.; Jiang, Y. *J. Phys. Chem.* **1996**, *100*, 4775.

(11) (a) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Academic Press: New York, 1982; Chapter 5. (b) Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1988; Vol. II, Chapter 10. (c) Fort, R. C.; Getty, S. J.; Hrovat, D. A.; Lahti, P. M.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 7549. (d) Gajewski, J. J.; Paul, G. C.; Chang, M. J.; Gortva, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 5150.

(12) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; Chapter 1.

(13) 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. Standard operating conditions: P (He) = 0.4 Torr; flow (He) = 190 STP cm^3/s.

(14) Ionic side products formed in significant amounts include $C_6H_4^{-\bullet}$ and $C_6H_5^-$, which result from reactions of the silylated intermediates with HF impurity in the F_2 gas mixture, along with $Me_2SiFCH_2^-$, and various HF and F$^-$ containing cluster ions.

(15) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 11890.

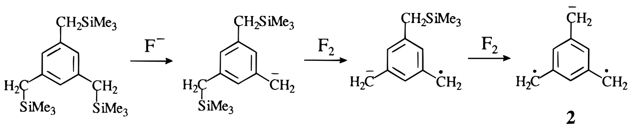
(16) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* In press.

(17) Wenthold, P. G.; Squires, R. R. *J. Phys. Chem.* **1995**, *99*, 2002.

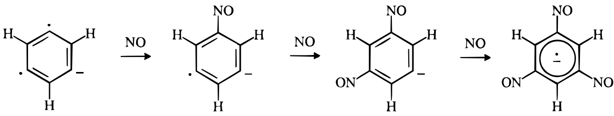
(18) Gronert, S.; DePuy, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 9253.

S0002-7863(96)00756-1 CCC: $12.00

Scheme 2

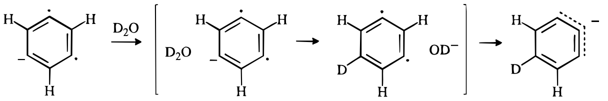


unstable with respect to ring opening.[19] The reactivity of **1** clearly distinguishes it from **3**. For instance, **1** undergoes sequential addition of up to three NO molecules (eq 1), whereas



(1)

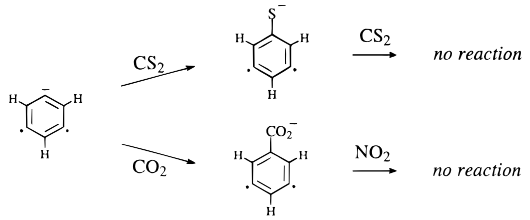
ion **3** reacts mainly by associative electron detachment (signal loss) and produces only traces of a single NO addition product. For comparison, *m*- and *p*-benzyne anions exhibit sequential addition of two NO molecules, while the *o*-isomer and phenyl anion react with NO mainly by associative detachment.[1,16] Ion **1** undergoes a single H/D exchange with D_2O and ND_3, while **3** does not react at all with these reagents (ΔH_{acid}[*o*-benzyne, C-3] = 382 kcal/mol[18]). The occurrence of only a single exchange by **1** is taken as evidence for its acid-catalyzed isomerization to the more stable 2,3-dehydrophenyl anion isomer, **3**, (eq 2). This can occur by D^+ transfer from D_2O or ND_3 to the phenyl anion site of **1** within the initial collision complex, followed by reabstraction of H^+ from the strongly acidic 2-position of the nascent *m*-benzyne (ΔH_{acid}[*m*-benzyne, C-2] = 366 kcal/mol[20]).



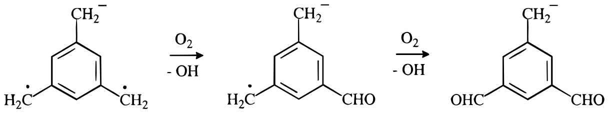
(2)

Radical-type reactivity for **1** could be construed as evidence for a triplet state.[21] However, as was observed previously with *m*- and *p*-benzyne anions,[1,16] the strongly basic and nucleophilic phenyl anion character of **1** dominates its reactivity with typical "radical-probes" such as dimethyldisulfide,[22] allyl iodide,[7] and 1,4-cyclohexadiene.[23] That is, atom or group abstractions characteristic of a radical are not observed in reactions of **1** with these reagents: only elimination and proton transfer. However, the reactivity of certain derivatives of **1** provides indirect indications of the spin state (Scheme 3). For example, while *m*- and *p*-benzyne anions react with CS_2 by sequential abstraction of *two* sulfur atoms,[1,16] ion **1** yields only a *single* sulfur abstraction product that does not react further. Moreover, *o*-, *m*-, and *p*-benzyne anions all undergo addition of CO_2 to yield dehydrobenzoate anions that readily couple with added NO_2 to produce the three isomeric nitrobenzoate derivatives.[1,16] In contrast, carboxylation of **1** yields a didehydrobenzoate anion that *does not react at all* with either NO_2, NO, or any of the other radical probes mentioned above. The nonreactivity of the thiophenolate and the benzoate derivatives of **1** evinces kinetic reaction barriers, which is interpreted to mean that the *m*-benzyne moieties in these ions are in singlet spin-states.[21] This, in turn, suggests (but does not necessarily require) that ion **1** is also a singlet, since the derivatization reactions shown in Scheme 3 are relatively fast, efficient processes that occur without apparent barriers or dynamical impediments, i.e., they appear to be spin-conserving reactions.[24]

Scheme 3



The behavior of **2** provides an instructive counterpoint. This ion is formed in abundance from sequential reactions of F^- and F_2 with 1,3,5-*tris*(trimethylsilylmethyl)benzene (Scheme 2).[25] All six methylene hydrogens in **2** are rapidly exchanged in reactions with D_2O and CH_3OD, which indicates that the three methylene groups are chemically equivalent. Ion **2** undergoes sequential addition of two NO molecules and reacts with O_2 by oxidation of two methylene groups to aldehyde groups (eq 3).[26] This latter reaction is characteristic of neutral primary alkyl radicals,[27] and it has been observed in our laboratory with several distonic *radical* anions possessing primary allylic and benzylic radical sites.[28] Moreover, the CO_2 adduct of **2** also displays (bi)radical-type reactivity, i.e., it undergoes sequential addition of two NO or two NO_2 molecules and reacts with O_2 by (bis)-methylene oxidation. The behavior of **2** and [**2** + CO_2] clearly contrasts that of **1** and [**1** + CO_2], which is interpreted as evidence for triplet biradical spin states for ion **2** and its carboxylated derivative.[21]



(3)

The above inferences regarding the spin states of **1** and **2** are supported by *ab initio* molecular orbital calculations,[29] which find the Jahn–Teller distorted C_{2v} $^1A_1$ state of **1** to be lower in energy than the D_{3h} $^3A_1'$ state and the C_{2v} $^3B_2$ state of **2** to be lower in energy than any of the possible singlet states. Further details concerning the reactivity, electronic structures, and, ultimately, the photoelectron spectroscopy of **1** and **2** will be published.

Acknowledgment. This work was supported by the National Science Foundation and the Department of Energy, Office of Basic Energy Sciences.

JA960756R

---

[19] At the TCSCF/6-31G* level of theory, the planar $^1A'$ state of 3,4-dehydrophenyl anion is a minimum lying 9 kcal/mol above *Z*-3-hexen-1,5-diyn-1-yl anion. The height of the ring-opening barrier is unknown.

[20] Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401.

[21] For examples of spin-state specific reactivity differences for biradicals, see: (a) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; Chapter 4. (b) Inglin, T. A.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 3394. (c) Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3659. (d) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. (e) Adam, W.; Finzel, R. *J. Am. Chem. Soc.* **1992**, *114*, 4563. For precautionary comments, see: (f) Heath, R. B.; Bush, L. C.; Fang, X.-W.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Phys. Chem.* **1993**, *97*, 13355. (g) Gajewski, J. J. *et al.*, ref 11(d).

[22] Stirk, K. M.; Orlowski, J. C.; Leeck, D. T.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 8604.

[23] Chyall, L. J.; Byrd, M. H. C.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1994**, *116*, 10767.

[24] Ion **1** reacts with CS_2 at about 10% of the ion/molecule collision rate and displays a maximal cross-section of about 5 Å^2 at 0.1 eV (center-of-mass). The saturated termolecular reaction of **1** with CO_2 at 0.45 Torr in the flowing afterglow occurs at about 20% of the collision rate.

[25] Variable yields (20–60%) of methyl-*m*-xylylene anion ($CH_3C_6H_3(CH_2)_2^{-\bullet}$) and mesityl anion ($(CH_3)_2C_6H_3CH_2^-$) are also formed as a result of the HF impurity in the F_2.

[26] The occurrence of two NO additions and two methylene oxidations (as opposed to three) is expected since benzyl anions do not react in this way with NO and O_2.

[27] (a) Kopczynski, S. L. *Int. J. Air Wat. Poll.* **1964**, *8*, 107. (b) Benson, S. W. *J. Am. Chem. Soc.* **1965**, *87*, 972. (c) Ebata, T.; Obi, K.; Tanaka, I. *Chem. Phys. Lett.* **1981**, *77*, 480. (d) Atkinson, R. *Atmos. Environ.* **1990**, *24A*, 1.

[28] Hu, J.; Hill, B. T.; Squires, R. R. Unpublished results.

[29] Preliminary calculations carried out at the ROHF/6-31G* level for triplet states and at the TCSCF/6-31G* level for the singlet states find ΔE_{ST} ($E_{\mathrm{singlet}} - E_{\mathrm{triplet}}$) = −12 kcal/mol for **1** and +1.5 kcal/mol for **2**. Higher level calculations are in progress.