J. Am. Chem. Soc. **2000,** *122,* 10689−10696

Formation of Gas-Phase Dianions and Distonic Ions as a General Method for the Synthesis of Protected Reactive Intermediates. Energetics of 2,3- and 2,6-Dehydronaphthalene

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Received June 29, 2000

Abstract: New methods for the regioselective formation of radical anions are described. Dicarboxylates are generated by electrospray ionization mass spectrometry and lose carbon dioxide and an electron upon collision-induced dissociation to afford distonic ions. These radical anions also can be synthesized via laser desorption, chemical ionization, and electron ionization of dibenzyl esters. Subsequent fragmentation of the remaining CO_2 affords new radical anions corresponding to neutral reactive intermediates. By measuring the proton affinities and electron binding energies of these species, quantitative energetic information on carbenes, biradicals, and other transient molecules can be obtained. This approach is demonstrated by measuring the heats of formation of 2,3- and 2,6-dehydronaphthalene, ancillary thermochemical data also are derived, and the results are compared to either *o*- or *p*-benzyne.

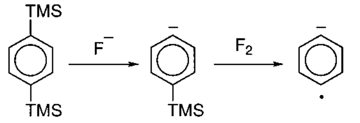
Introduction

One of the major successes of gas-phase ion chemistry has been the determination of a wide variety of thermochemical data.[1] Anions are useful in this regard for probing neutral molecules including reactive intermediates because they often are easier to generate and less prone toward rearrangements and/or fragmentations than their uncharged counterparts. In other words, *an electron can serve as a protecting group*! The energetics of free radicals can be obtained from carbanions while bond energies and heats of formation of carbenes, alkenes, alkynes, biradicals, and many other species can be derived from radical anions. One way to accomplish this is by measuring an ion's proton affinity (PA) and electron binding energy (EBE) and applying these data in a thermodynamic cycle (eq 1).

$$\begin{array}{lll}
\mathrm{HA} \rightarrow \mathrm{H}^+ + \mathrm{A}^- & \Delta H^\circ = \mathrm{PA}(\mathrm{A}^-) & \text{(1a)} \\
\mathrm{A}^- \rightarrow \mathrm{A}^\bullet + \mathrm{e}^- & \Delta H^\circ = \mathrm{EBE}(\mathrm{A}^-) & \text{(1b)} \\
\underline{\mathrm{H}^+ + \mathrm{e}^- \rightarrow \mathrm{H}^\bullet} & \underline{\Delta H^\circ = -\mathrm{IP}(\mathrm{H}^\bullet)} & \text{(1c)} \\
\mathrm{HA} \rightarrow \mathrm{H}^\bullet + \mathrm{A}^\bullet & \Delta H^\circ = \mathrm{PA}(\mathrm{A}^-) + \mathrm{EBE}(\mathrm{A}^-) - \mathrm{IP}(\mathrm{H}^\bullet) & \text{(1d)}
\end{array}$$

This general approach is applicable to all anions, in principle, and has been used to measure the energetics of a number of transient species (e.g., *o*-benzyne, bicyclo[1.1.0]but-1(3)-ene, cubene, cubyl radical, dichlorocarbene, phenyl radical, and vinyl radical).[2−8]

The key to broadly applying a thermodynamic cycle as shown in eq 1 is the preparation of the required starting ions. Unfortunately, there are few systematic and predictable methods for synthesizing radical anions, even though they can serve as precursors to many different classes of compounds. Of the available procedures, the atomic oxygen ion ($O^{\bullet -}$) has been employed in a number of instances but its reactivity is capricious and its selectivity cannot be controlled.[9] The only other broadly applicable approach for producing radical anions was developed by Squires and co-workers and involves the reaction of a trimethylsilyl-containing carbanion with molecular fluorine.[10−12] For example, the radical anion of *p*-benzyne can be generated first by reacting *p*-bis(trimethylsilyl)benzene with fluoride ion and then allowing the resulting *p*-(trimethylsilyl)phenyl anion to interact with F_2 (eq 2). This methodology is extremely powerful and has been elegantly applied in a number of instances,[13−19] but it does have several significant drawbacks:



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10.1021/ja002351j CCC: $19.00

(1) Molecular fluorine must be used! (F_2 is highly toxic and corrosive, and is harsh on vacuum systems.) (2) The reaction is rarely clean and leads to many side products, in part, because the product ions are unstable with respect to F_2. (3) F^- is not reactive enough to afford basic anions (PA > ~400 kcal/mol) at room temperature. (4) The requisite bis(trimethylsilyl) precursors must be synthesized. In this paper, we describe a versatile and general alternative for the selective formation of radical anions. Electrospray ionization (ESI) of dicarboxylic acids affords dianions that can be collisionally fragmented in a synthetically useful manner to afford odd electron species in violation of the "even-electron rule".[20] Likewise, laser desorption ionization (LDI), electron impact (EI), and chemical ionization (CI) of bisesters leads to the formation of monoester carboxylates which also can be broken apart to radical anions corresponding to reactive intermediates. To demonstrate the utility of this approach, the heats of formation of 2,3- and 2,6-dehydronaphthalene were measured, ancillary thermochemical data are derived, and the results are compared to either *o*- or *p*-benzyne.

Experimental Section

Synthesis. Dibenzyl esters were prepared using a slightly modified literature procedure.[21] The dicarboxylic acid of interest was dissolved in water containing 2 equiv of sodium hydroxide. The resulting solution was pumped dry under vacuum at 0.1 Torr and 60 °C. Ether was added to the remaining salt along with 0.2 equiv of tetra-*n*-butylammonium bromide and 2.2 equiv of benzyl bromide. After the heterogeneous mixture was stirred for 24 h at room temperature, water was added and the organic layer concentrated via rotary evaporation. The crude product was purified by recrystallization from methanol or a hexanes/ethyl acetate mixture and, in some cases, a subsequent vacuum sublimation (150 °C at ~0.01 Torr).

Gas-Phase Experiments. All experiments were carried out with a Finnigan model 2001 Fourier transform mass spectrometer (FTMS) equipped with a Sun workstation running the Odyssey Software 4.2 package. This instrument is outfitted with a 3.0-T superconducting magnet and a differentially pumped dual cell. A base pressure of less than 2×10^{-9} Torr was maintained in each cell by two Edwards model 160M Diffstak diffusion pumps, each of which is backed by an Alcatel model 2015 mechanical pump. The two cubic 2-in. cells are separated by a common wall (or conductance limit) with a 1-mm opening so that ions can be passed from one cell to the other at designated times and a differential pressure of ~2 orders of magnitude can be maintained between the cells. Trapping potentials of −1 to −2.5 V were employed except when ions were being transferred from one cell to the other and the conductance limit was grounded for 50−150 μs, depending upon the mass-to-charge ratio of the ions being transferred. Neutral compounds were introduced into the instrument through a variety of inlets including a heated solids probe, a batch inlet system, a Granville-Phillips series 203 variable leak valve, or any of three independent General Valve dual-solenoid pulsed valves. The FTMS also is equipped with a N_2 laser which emits 337-nm light with a 3-ns pulse width and a power of 6 mW for laser desorption/ionization (LDI) experiments.

For ESI, an API custom-built source from Analytica was interfaced to an Ultrasource electrostatic ion guide. This external source is equipped with an adjustable-amplitude fixed-frequency (5.2 MHz) hexapole ion guide for external trapping of ions prior to injection into the magnetic field. We have found that lowering the rf amplitude from the standard 600 V_{p-p} to between 50 and 250 V_{p-p} substantially improves performance for low-mass (<200 Da) ions.

Aryne Radical Anion Generation By ESI. Lithium, sodium, potassium, or cesium salts of *o*-, *m*-, and *p*-benzenedicarboxylic acids and 2,3- and 2,6-naphthalenedicarboxylic acids were dissolved in 3:1 (v/v) H_2O/MeOH to a concentration of 1 mM. These solutions were investigated, and diluted further, to find optimal conditions for the production of the dicarboxylate dianion signals. In general, 750 μM solutions injected at a rate of 3 μL/min were used since they gave the most intense signals of the dianions. In these experiments, the ions were focused through the analyzer cell using the analyzer trap plate and conductance limit as lenses into the source cell where they were trapped. This was advantageous because the amount of background water from the external source is less in the source cell than in the analyzer cell. Isolation of the dianions was carried out using a broad-band chirp excitation,[22] and then they were subjected to collision-activated dissociation. In all cases, low-energy (0.5−1.0 eV lab) sustained off-resonance irradiation (SORI)[23] was found to be the best method for cleaving the first molecule of carbon dioxide. The second CO_2 also was removed by SORI except in the case of 2,3-naphthalenedicarboxylate, where on-resonance collision-induced dissociation (CID) (~10 eV lab) was used. In this instance, on-resonance CID was used to suppress an undesired fragmentation pathway involving the loss of carbon monoxide. After the aryne radical anions were formed, they were cooled with an argon pulse ($\geq 1 \times 10^{-4}$ Torr) and carefully isolated by a combination of a broad-band chirp excitation and SWIFT waveform.[24]

Aryne Radical Anion Generation By EI, CI, or LDI. Large amounts of hydroxide were generated by pulsed valve addition of a ~1:1 N_2O/CH_4 mixture up to a pressure of 2×10^{-5} Torr followed by electron ionization at 3 eV for 100−150 ms. These ions rapidly reacted with the dibenzyl esters, which were introduced into the FTMS via a solids probe inlet heated to 170 °C. The resulting monoester monocarboxylate ions also could be prepared by EI or LDI of the dibenzyl esters. In the former (CI) case, they were transferred to the second (analyzer) cell and fragmented by an on-resonance excitation (~20 eV lab) in the presence of a high pressure (2×10^{-5} Torr) of argon; these conditions were found to be optimal for the loss of one CO_2 and one benzyl radical. The resulting distonic ion (a dehydrocarboxylate) was isolated using a broad-band chirp excitation and SWIFT waveform and decarboxylated using SORI under high-pressure conditions ($\geq 10^{-5}$ Torr Ar). The resulting benzyne or dehydronaphthalene radical anion was collisionally cooled with a high-pressure pulse of argon ($>10^{-4}$ Torr) followed by a 700-ms pump out delay and careful isolation to avoid any re-excitation. Subsequent reactions with a variety of probe reagents were monitored as a function of time.

2,6-Dehydronaphthalene Radical Anion (8) Derivatization. For the conversion of 2,6-dehydronaphthalene radical anion (**8**) to 2-naphthoxide (**13**), a static pressure of 3×10^{-8} Torr sulfur dioxide was admitted into the FTMS cell and an argon pulse for the SORI generation of **8** was carefully optimized. If the pressure is too low, not enough fragmentation takes place, and if the pressure is too high, the subsequent oxygen atom abstraction is largely replaced by adduct formation. Reaction of the resulting dehydronaphthoxide with a pulse of *t*-BuSH leads to hydrogen atom abstraction and the formation of 2-naphthoxide. The identity of this product was confirmed by comparison with authentic 1- and 2-naphthoxide via bracketing and collision-induced dissociation studies.

Computations. All calculations were performed using Gaussian 94 or 98[25,26] installed on IBM and SGI workstations. Geometry optimizations were carried out with the B3LYP functional and the 6-31+G(d)

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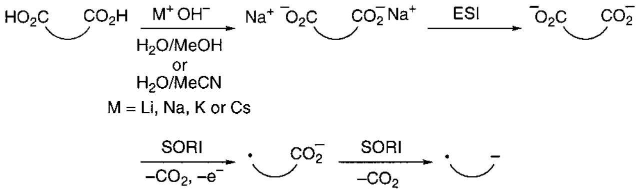
Scheme 1

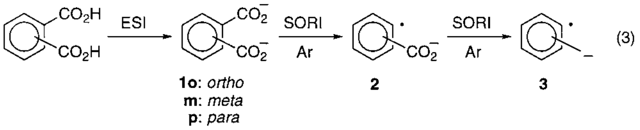


basis set. Unrestricted wave functions were used for open shell species. Vibrational frequencies were computed to ensure that each stationary point corresponds to an energy minimum and to provide zero-point energy and temperature corrections to 298 K. Computed proton affinities and reaction energies are given at 298 K while electron binding energies are reported at 0 K; temperature corrections typically amount to ≤ 0.2 kcal/mol in the case of electron binding energies.

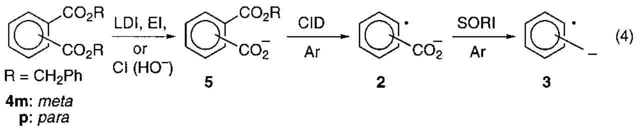
Results and Discussion

Multiply charged anions such as dicarboxylates can be produced in the gas phase via electrospray ionization.[27−34] These ions experience large Coulombic repulsions, especially when the two charges are close to each other. If one uses the dielectric constant for a vacuum ($\epsilon = 1$), Coulomb's law indicates that the interaction energy between two point charges is $332/d$ kcal/mol, where d is the distance between the charge centers in angstroms. One can exploit this situation for the synthesis of radical anions since fragmentation of a dicarboxylate should lead to the regiospecific loss of carbon dioxide and an electron (Scheme 1). Decarboxylation upon collision-induced dissociation is a well-known process,[35−37] and the accompanying loss of an electron in violation of the "even-electron rule" also has been observed in the analytical literature.[28,29] The formation of an odd-electron species occurs because the new charge center that would result holds on to an electron less tightly than a carboxylate ($\text{EA}(\text{RCO}_2^\bullet)$ ∼3.3 eV), and the diminished distance between the charges leads to an increase in the Coulomb repulsion.[38] The resulting distonic ion is interesting in its own right, but another collision-induced decarboxylation should lead to a new radical anion which can serve as a precursor to a variety of reactive intermediates.

***o*-, *m*-, and *p*-Benzyne Radical Anions.** To test this approach, *o*-, *m*-, and *p*-benzenedicarboxylic acids were dissolved in a 3:1 (v/v) water/methanol solution containing cesium hydroxide and were electrosprayed into the gas phase using an Analytica source interfaced to a Finnigan FTMS. In all three cases, the ESI mass spectra showed abundant signals for the dianions as previously observed by Siu et al.[28] Mass selection of the dianions **1** and collision-induced dissociation with argon via SORI[23] leads to **2**, which can be further fragmented to the known *o*- and *m*- and *p*-benzyne radical anions (**3**, eq 3).[2,10,14,16]



As an alternative to electrospray, we generated **3m** and **3p**, but not **3o**, via EI, CI, and LDI of their corresponding dibenzyl esters (Figure 1, eq 4). In particular, 337-nm irradiation of the bisesters **4**, direct electron ionization, or reaction with hydroxide ion affords the monocarboxylates **5**. Sequential fragmentation of these ions via on-resonance and then off-resonance irradiation first affords **2** and then **3**. This two-step sequence was employed rather than fragmenting **5** directly to **3** because the former route is more efficient, and the intermediate dehydrocarboxylates **2** are of interest and can be isolated even in the presence of a wide variety of reactive neutral reagents. The ortho isomers of **2** and **3** could not be generated in this fashion because fragmentation of **5o** leads to the loss of carbon monoxide rather than carbon dioxide and an alkyl radical. The effect of the ester's alkyl group on aryne formation also was briefly examined but was not optimized. Using EI or CI on the bismethyl esters leads to **5** where R = Me, but fragmentation of this species to **2** is less efficient. Ethyl and trimethylsilyl esters do not work at all because they donate a hydrogen atom upon dissociation to give benzoate anion.



The reactivity of the *m*- and *p*-benzyne radical anions has been characterized by Squires and co-workers[10,14,16] in a seminal series of investigations and the ortho isomer has been thoroughly explored by Guo and Grabowski[2] in an important flowing afterglow study. This enabled us to distinguish and confirm the identity of the three structures of **3** and thereby demonstrate that their preparation occurs without isomerization. For example, in accord with the literature, **3o** reacts with carbon disulfide and sulfur dioxide via electron transfer while **3m** and **3p** undergo sulfur atom abstraction with the former reagent[39] and somewhat different behavior from each other with the latter compound. **3m** affords electron and oxygen atom transfer products (∼15:

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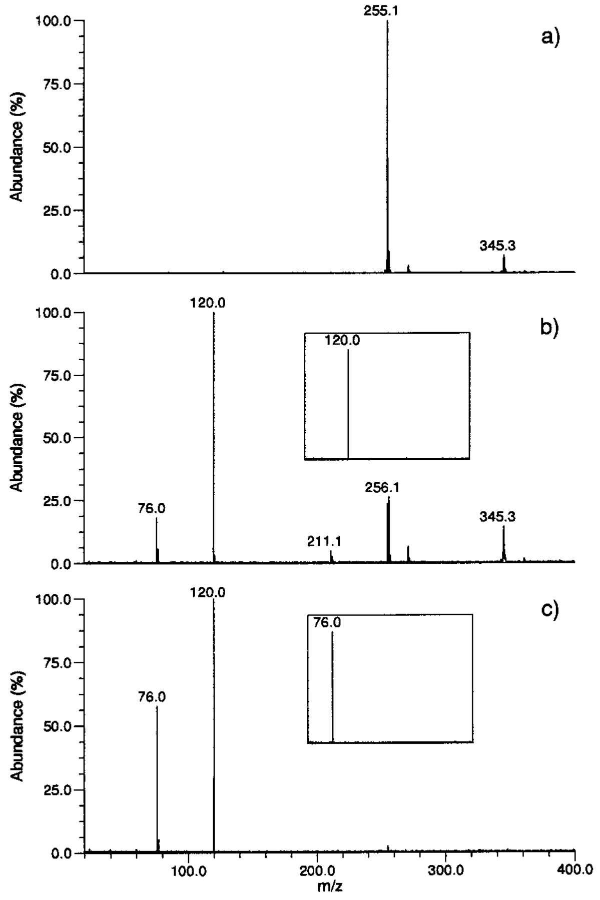
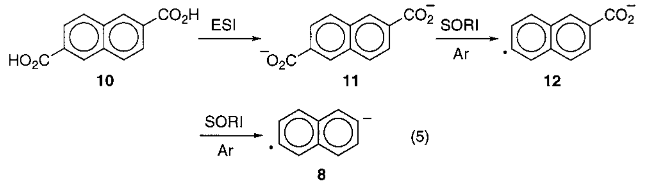


Figure 1. (a) Chemical Ionization (OH$^-$) mass spectrum of *p*-dibenzyl benzenedicarboxylate from *m*/*z* 18 to 400 (**5p**, *m*/*z* 255; (**4p**-H)$^-$, *m*/*z* 345). (b) Collision-induced dissociation of **5p** with argon plotted from *m*/*z* 18 to 400 (**5p**-^{13}C, *m*/*z* 256; (**5p**-CO$_2$)$^-$, *m*/*z* 211; **2p**, *m*/*z* 120; **3p**, *m*/*z* 76). Inset corresponds to the isolation of **2p**. (c) Sustained off-resonance irradiation of **2p** with argon shown from *m*/*z* 18 to 400 (**3p**, *m*/*z* 76). Inset corresponds to the isolation of **3p**.

1), and the latter slowly ($k_{\rm rel}$ = 1) undergoes a second oxygen atom abstraction, while **3p** reacts to a larger extent (~30%) via oxygen atom transfer, the second atom abstraction proceeds relatively quickly ($k_{\rm rel}$ = 40), and a significant amount (~25%) of adduct is observed.[40,41] In addition, the *m*- and *p*-benzyne radical anions can be isomerized to the more stable ortho isomer upon reaction with deuterium oxide, as previously described.[16]

2,6- and 2,3-Dehydronaphthalene Radical Anions. To demonstrate the utility of our methodology, we decided to measure the heats of formation of 2,6- and 2,3-dehydronaphthalene (**6** and **7**, respectively) as these species are of interest as reactive intermediates in synthetic transformations, combustion processes, and drug design.[42−47] This was accomplished by generating the 2,6- and 2,3-dehydronaphthalene radical anions (**8** and **9**, respectively), measuring their electron binding energies and proton affinities, and combining these data in a thermodynamic cycle as described below.

2,6-Dehydronaphthalene Radical Anion. Generation. Electrospray ionization of the lithium, sodium, potassium, or cesium salts of 2,6-naphthalenedicarboxylic acid (**10**) from water/methanol or water/acetonitrile solutions affords the dianion **11** as the base peak in the mass spectrum (Figure 2). Significant amounts of the monodeprotonated diacid (**10** − H$^+$, *m*/*z* 215) and the corresponding alkali metal salt of the dianion (**11** + M$^+$, where M = Li, Na, K, or Cs; *m*/*z* 253 when M = K) also are observed. After isolation of the dianion, collision-induced dissociation with argon via SORI cleanly affords 6-dehydro-2-naphthalenecarboxylate (**12**, eq 5). This distonic ion corresponds to the loss of carbon dioxide and an electron from **11**. Its subsequent fragmentation yields 2,6-dehydronaphthalene radical anion (**8**) in abundant quantities. This same ion also can be prepared starting from the dibenzyl ester of **10** via LDI, EI, or CI with OH$^-$ as described for **5m** and **5p**. In addition, a labeling experiment using ^{18}OH$^-$ was carried out. Oxygen-18 is incorporated into the carboxylate corresponding to **5**, and subsequent dissociation of this ion leads to the complete loss of the label (eq 6). This indicates that only the carboxylate is lost and that the CO$_2$ in the ester group is retained; the same result was found using **5m** with a ^{13}C-labeled carboxylate and R = Me and several other substrates,[48] we therefore believe that this is a general finding.



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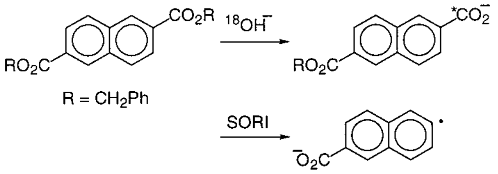
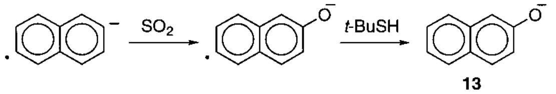


(6)

To confirm the structure of **8**, we examined its reactivity with several neutral probe reagents. Carbon disulfide and sulfur dioxide both react with **8** in a fashion analogous to **3p**. With CS$_2$, two sulfur atom abstractions take place in a sequential manner while the reaction with SO$_2$ leads to two sequential oxygen atom abstractions and adduct formation. The latter reagent also provided a means to derivatize **8** to a known species. In particular, the oxygen atom transfer product abstracts a hydrogen atom from 2-methyl-2-propanethiol (*t*-BuSH) to afford 2-naphthoxide (**13**, *m*/*z* 143, eq 7). Bracketing studies show that **13** has the same proton affinity (343.8 ± 2.1 kcal/mol) as authentic 2-naphthoxide (i.e., proton transfer is not observed with *t*-BuSH and acetic acid ($\Delta H°_{\rm acid}$ = 352.5 ± 2.2



(7)

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[39] We were able to observe a second sulfur atom abstraction with **3p**, as described in ref 16 and carried out in Q2 of a triple quadrupole mass analyzer, but not the analogous reaction with **3m**.

[40] The reactivity of SO$_2$ with **3p** (and **8**), but not **3m**, is pressure dependent. The low-pressure reactivity is cited in the text, but at high pressures (>10^{-5} Torr), the oxygen atom abstraction product is replaced by adduct formation. This pressure-dependent reactivity is also observed with phenyl anion and agrees well with reactions carried out under flowing afterglow conditions as described in ref 14.

[41] The relative rates for the second oxygen atom abstraction are in good agreement with experiments carried out on independently generated *m*- and *p*-dehydrophenoxide. Reed, D. R.; Kass, S. R., unpublished results.

[42] Bunnett, J. F.; Brotherton, T. K. *J. Am. Chem. Soc.* **1956**, *78*, 155−158.

[43] Roberts, J. D.; Semenow, D. A.; Simmons, H. E. Jr.; Carlsmith, L. A. *J. Am. Chem. Soc.* **1956**, *78*, 601−611.

[44] Weimer, H. A.; McFarland, B. J.; Li, S.; Weltner, W., Jr. *J. Phys. Chem.* **1995**, *99*, 1824−1825.

[45] Synder, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 7630−7632.

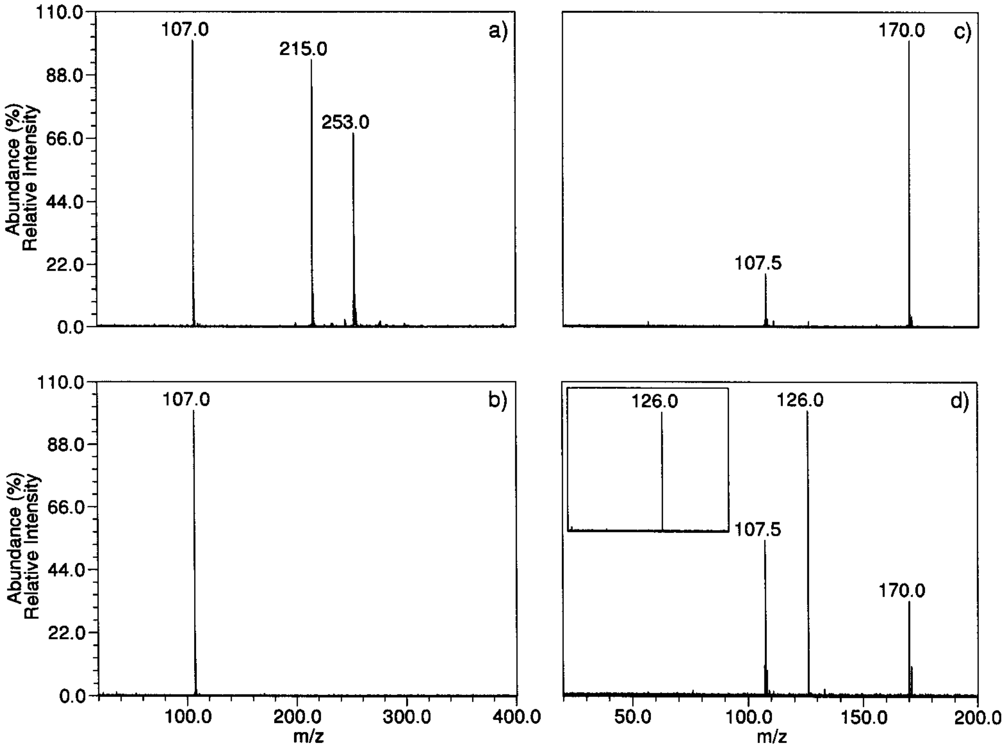
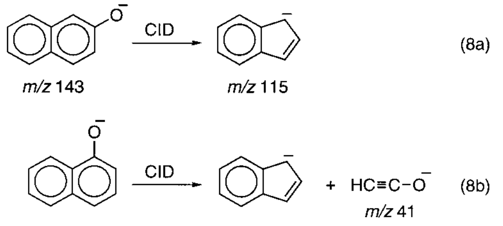


Figure 2. (a) Electrospray ionization mass spectrum of the potassium salt of 2,6-naphthalenedicarboxylic acid (**10**) in a 3:1 water/methanol solution from *m*/*z* 20 to 400 (**11**, *m*/*z* 107; (**10**−H)$^-$, *m*/*z* 215; (**10**-2H+K)$^-$, *m*/*z* 253). (b) Mass selection of 2,6-naphthalenedicarboxylate plotted from *m*/*z* 20 to 400 (**11**, *m*/*z* 107). (c) Sustained off-resonance irradiation of **11** with argon shown from *m*/*z* 20 to 200 (**12**, *m*/*z* 170; **11**-^{13}C, *m*/*z* 107.5). (d) Sustained off-resonance irradiation of **12** with argon plotted from *m*/*z* 20 to 200 (**8**, *m*/*z* 126). Inset (*m*/*z* 20 to 200) corresponds to the isolation of **8**.

and 348.1 ± 2.2 kcal/mol, respectively) but does take place with benzoic acid (ΔH°_{acid} = 340.1 ± 2.2 kcal/mol)), but this result is unlikely to differentiate between the 1- and 2-isomers.[49,50] Therefore, collision-induced dissociation studies were carried out. The *m*/*z* 143 ion produced from **8** and authentic 2-naphthoxide (generated by proton abstraction of 2-naphthol using F^-) give identical spectra in which CO is lost over a wide range of energies (eq 8). In contrast, 1-naphthoxide (generated by proton abstraction of 1-naphthol using F^-) exhibits an additional fragmentation pathway to afford ketene enolate, which becomes dominant with increasing collision energy.[51]



Thermochemistry. The proton affinity of **8** was examined by reacting it with a series of standard reference acids. 2,6-Dehydronaphthalene radical anion was found to deprotonate fluorobenzene and methanol-O*D* (ΔH°_{acid} = 387.2 ± 2.5 and 383.5 ± 0.7 kcal/mol, respectively) but not water (ΔH°_{acid} = 390.7 ± 0.1 kcal/mol) unless kinetic energy is provided. Upon reaction with deuterium oxide (ΔH°_{acid} = 392.9 ± 0.1 kcal/mol), a maximum of 3 H/D exchanges is observed and an acid-catalyzed isomerization to a more stable and less basic 1,2- and/or 2,3-dehydronaphthalene radical anion takes place.[52] The latter pathway is indicated by the lack of reactivity of the d_3 ion with additional D_2O and the failure to observe back-exchange with H_2O. Nevertheless, on the basis of these observations, we can reasonably assign PA(**8**) = 390 ± 4 kcal/mol.[53,54] This value is in good accord with the predicted B3LYP/6-31+G(d) result of 392.5 kcal/mol and is consistent with this hybrid functional's ability to reproduce the acidity (ΔH°_{acid}) of phenyl radical (381.2 (calcd), 377.4 ± 3.4,[18] and 379 ± 5[2] (expt) kcal/mol), benzene (399.9 (calcd), 401.7 ± 0.5 (expt) kcal/mol), and naphthalene (394.4 (calcd for the 2-position), 395.5 ± 1.3 (expt) kcal/mol).[55]

The electron binding energy of **8** also was examined by the bracketing method. Unfortunately, most of the reference compounds in the desired range are substituted aromatic compounds with acidic protons. These compounds (*m*-fluoromethylnitrobenzene, *o*-trifluoromethylnitrobenzene, and *m*-trifluoromethylnitrobenzene) react with **8** by proton transfer as well as isomer-

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(46) Thoen, K. K.; Thoen, J. C.; Uckun, F. M. *Tetrahedron Lett.* **2000**, *41*, 4019−4024.

(47) Cioslowski, J.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1998**, *120*, 1695−1700.

(48) Broadus, K. M.; Kass, S. R., unpublished results.

(49) All thermochemical data, unless otherwise noted, comes from ref 38.

(50) The proton affinity of 1-naphthoxide is unknown, but most likely is very similar to its 2-isomer.

(51) Since no 1-naphthoxide is observed upon derivatization of **8** and CID of its *m*/*z* 143 ion, 1,*n*-dehydronaphthalene radical anion structures for **8** are highly improbable. The only other possible structure that could not give 1-naphthoxide is 2,7-dehydronaphthalene radical anion, but an improbable hydrogen atom shift is required to form this species. Moreover, **8** reacts with SO_2 to give two sequential oxygen atom abstractions at roughly equal rates. This behavior parallels that of **3p**, but not **3m**, and is consistent with the fact that *p*-quinone and 2,6-naphthoquinone are stable closed-shell molecules whereas *m*-quinone and 2,7-naphthoquinone are not; they are non-Kekule molecules.

(52) B3LYP calculations indicate that the two isomers differ in energy by only 0.2 kcal/mol and that the 1,2-species is more stable.

(53) "[A] dual cell FTMS can be used to bracket lower acidity sites in multiple-acidic-site- molecules." See: Kurinovich, M. A.; Lee, J. K. *J. Am. Chem. Soc.* **2000**, *122*, 6258−6262.

Table 1. Summary of Energetic Data[a]

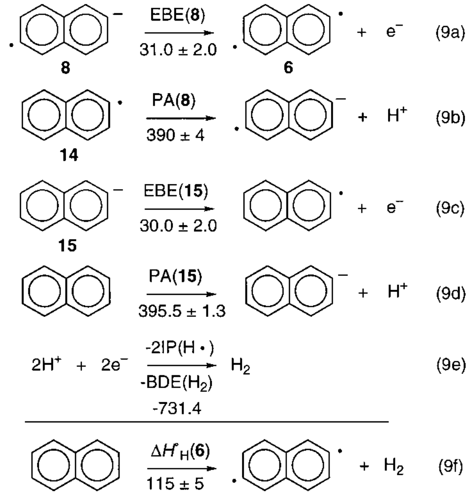
cmpd	$\Delta H^\circ_{f,298\,(g)}$	PA	EBE	BDE
2-naphthyl anion (**15**)	65.9 ± 1.3	395.5 ± 1.3[b]	30.0 ± 2.0[b]	93 ± 3 (C3−H), 106 ± 4 (C6−H)
2,6-dehydronaphthalene radical anion (**8**)	120 ± 5	390 ± 4	31.0 ± 2.0	
2,3-dehydronaphthalene radical anion (**9**)	107 ± 4	377 ± 3	13.8 ± 2.5	
naphthalene	36.05 ± 0.25[c]			111.9 ± 2.4 (C2−H)[b]
2-naphthyl radical (**14**)	95.9 ± 2.4			77 ± 4 (C3−H), 107 ± 4 (C6−H)
2,6-dehydronaphthalene (**6**)	151 ± 5			
2,3-dehydronaphthalene (**7**)	121 ± 5			

[a] All values in kcal/mol. [b] References 55 and 56. [c] Reference 60.

izing it to more stable isomers. We did find, however, that electron transfer occurs upon reaction with pentafluoronitrobenzene (EBE = 1.45 ± 0.11 eV) but not sulfur dioxide (EBE = 1.107 ± 0.008 eV), suggesting an EBE for **8** of 1.28 ± 0.19 or 29 ± 4 kcal/mol. The EBE of **8** also was determined via a kinetic method which previously has been used for 1- and 2-naphthyl anions and *m*- and *p*-benzyne radical anions.[14,55] Results from these experiments, which involve measuring the $SO_2^{\bullet-}$ to **8** ratio upon collision-induced dissociation of the $(\mathbf{8} + SO_2)^{\bullet-}$ adduct ion and comparing it to a calibration line, give a value of 31.0 ± 2.0 kcal/mol.[56]

Electron binding energies of aryl anions such as phenyl and 1- and 2-naphthyl anions are well-reproduced using B3LYP/6-31+G(d) calculations.[55] This method, however, is unsuitable for anions whose corresponding neutral is a ground-state singlet biradical or a singlet species with considerable biradical character as is the case for 2,6- and 2,3-dehydronaphthalene. This failing is a consequence of the fact that a singlet biradical requires at least two configurations to adequately describe its wave function, whereas the Hartree−Fock part of the B3LYP functional is a single-determinant method. This difficulty can be overcome by calculating the energy difference between the anion of interest and its corresponding neutral in the triplet state, as the latter species can be adequately described with a single configuration. The resulting EBE must be corrected for the singlet−triplet (S−T) gap, which can be done using experimental data or some reliable (not B3LYP) computational approach.[57] Application of this procedure in conjunction with the experimental S−T gap for *o*-benzyne (37.5 ± 0.3 kcal/mol) leads to a computed electron binding energy for **3o** of 12.9 kcal/mol, which is in excellent agreement with the measured value of 13.01 ± 0.16 kcal/mol.[18] Likewise, if we use the S−T gap for 2,6-dehydronaphthalene computed by Squires and Cramer at the CASPT2/cc-pVDZ level (1.4 kcal/mol at 0 K),[58] then the calculated B3LYP/6-31+G(d) EBE of **8** is 30.9 kcal/mol, which is within the experimental uncertainty of our measurement.

The thermochemistry of 2,6-dehydronaphthalene radical anion can now be used to derive the heat of formation of 2,6-dehydronaphthalene (Table 1). The electron binding energy (EBE = 31.0 ± 2.0 kcal/mol) and proton affinity (PA = 390 ± 4 kcal/mol) of **8** can be combined with the same quantities that we recently measured for 2-naphthyl anion (EBE = 30.0 ± 2.0 kcal/mol and PA = 395.5 ± 1.3 kcal/mol)[55,56] along with the ionization potential of hydrogen atom (IP = 313.6 kcal/mol) and the bond dissociation energy of molecular hydrogen (BDE = 104.2 kcal/mol) in a thermodynamic cycle to yield a value of 115 ± 5 kcal/mol for the heat of hydrogenation of 2,6-dehydronaphthalene (eq 9). This result is in excellent accord with the predicted B3LYP/6-31+G(d) value of 117.4 kcal/mol[59] and leads to an experimental heat of formation for **6** of 151 ± 5 kcal/mol given the well-known heat of formation of naphthalene (36.05 ± 0.25 kcal/mol).[60] One can use this quantity to derive the C6−H bond dissociation energy for 2-naphthyl radical (BDE2 = 107 ± 5 kcal/mol), which is 5 ± 5 kcal/mol less than the C2−H BDE for naphthalene (BDE1 = 111.9 ± 2.4).[55,56] This small energy difference is in accord with the results for *p*-benzyne (BDE1 − BDE2 = 3.8 ± 2.9 kcal/mol),[18] and the 298 K predicted S−T gap for 2,6-dehydronaphthalene of 1.6 kcal/mol.[58] It also is in keeping with the small through-bond coupling expected in such a system.[58,61]



The absolute heat of formation of 2,6-dehydronaphthalene radical anion and the C6−H homolytic bond energy of 2-naphthyl anion (106 ± 4 kcal/mol, Table 1) also can be readily derived from our data. The latter result indicates that a radical center, a lone pair of electrons, or a carbon−hydrogen bond at C2 has little impact on the C6−H bond strength, a finding that was previously noted in the benzene/*p*-benzyne system.[18]

2,3-Dehydronaphthalene Radical Anion. Generation. Electrospray ionization of the cesium salt of 2,3-naphthalenedicar-

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(54) The H/D exchange results with D_2O indicate that **8** does not directly isomerize to 1,2- or 2,3-dehydronaphthalene radical anion in a single process, at least much of the time, and, therefore, strongly suggests PA(**8**) ≤ 393 kcal/mol. In addition, if the PA was much greater than 393, then one would expect to observe OH^- upon reaction with H_2O. The observation that **8** deprotonates fluorobenzene suggests that PA(**8**) ≥ 387 kcal/mol, and thus we assign the proton affinity a value of 390 kcal/mol. We also adopt a conservative estimate of ±4 kcal/mol for the uncertainty.

(55) Reed, D. R.; Kass, S. R. *J. Mass Spectrom.* **2000**, *35*, 534−539.

(56) The EBE was determined using the calibration line given in ref 55 and the observed $SO_2^{\bullet-}$ to **8** ratio of 11.0 ± 1.0; a value of 31.0 ± 0.5 kcal/mol results. This uncertainty, however, is apt to be too small, so a more conservative estimate of ±2 kcal/mol obtained by averaging the uncertainties from both methods (±4 and ±0.5) and rounding to the nearest whole number was adopted. For consistency sake, the same (larger) error also was used for the electron binding energy of **15**.

(57) This approach for computing EBE was suggested to us by Prof. W. T. Borden.

(58) Squires, R. R.; Cramer, C. J. *J. Phys. Chem.* **1998**, *102*, 9072−9081.

(59) Kolos, W.; Wolniewicz, L. *Phys. Rev. Lett.* **1968**, *20*, 243−244.

(60) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(61) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499−1509.

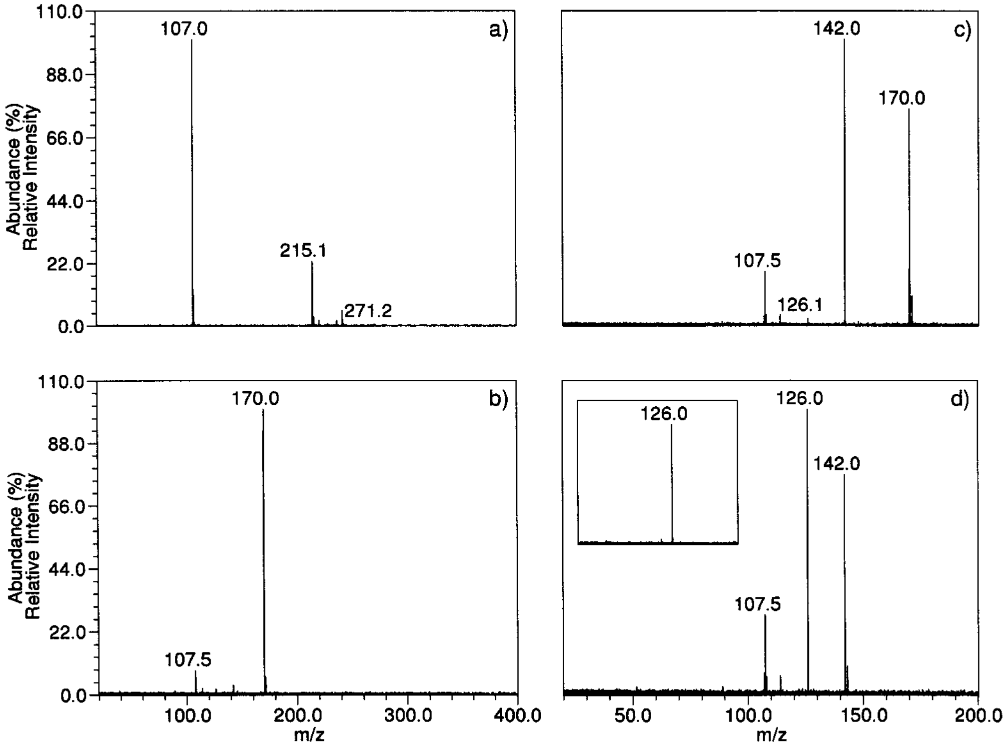
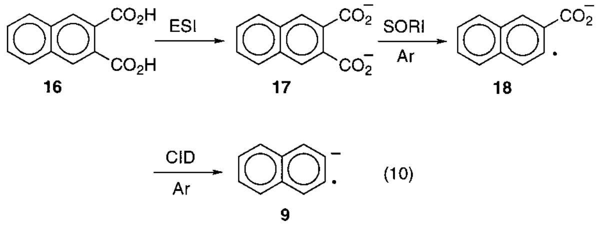


Figure 3. (a) Electrospray ionization mass spectrum of the cesium salt of 2,3-naphthalene dicarboxylic acid (**16**) in a 3:1 water/methanol solution from *m*/*z* 20 to 400 (**17**, *m*/*z* 107; (**16**−H)$^-$, *m*/*z* 215). (b) Mass selection of 2,3-naphthalenedicarboxylate and its sustained off-resonance irradiation with argon plotted from *m*/*z* 20 to 400 (**18**, *m*/*z* 170; **17**-^{13}C, *m*/*z* 107.5). (c) Sustained off-resonance irradiation of **18** with argon shown from *m*/*z* 20 to 200 (**18**−CO, *m*/*z* 142; **9**, *m*/*z* 126). (d) Collision-induced dissociation of **18** with argon plotted from *m*/*z* 20 to 200 (**9**, *m*/*z* 126). Inset (*m*/*z* 20 to 200) corresponds to the isolation of **9**.

boxylic acid (**16**) from a 3:1 (v/v) water/methanol solution affords the dianion **17** as the base peak in the mass spectrum (Figure 3). After isolation of **17**, two molecules of carbon dioxide and an electron can be detached via sequential SORI and CID fragmentations (eq 10). The reactivity of **9** is distinctly



different from **8** but analogous to *o*-benzyne radical anion (**3o**). For example, **9** reacts with sulfur dioxide via electron transfer rather than oxygen atom abstraction and does not undergo sulfur atom transfer with carbon disulfide. It also undergoes rapid signal loss with some alcohols (e.g., MeOD), as does **3o**,[2] and behaves similarly to the M − 2 ion(s) formed by reacting $O^{\bullet-}$ with naphthalene.[62]

Thermochemistry. The proton affinity of **9** was measured by bracketing it with a series of standard reference acids. Deprotonation of *t*-BuOD, CD_3CN, FCH_2CH_2OH, and phenylacetylene (ΔH°_{acid} = 374.6 ± 2.1, 372.9 ± 2.1, 371.2 ± 2.9, and 370.7 ± 2.3 kcal/mol, respectively) was observed but not 1-pentyne (ΔH°_{acid} = 379.8 ± 2.5 kcal/mol), MeOD, and weaker acids. Consequently, we assign PA(**9**) = 377 ± 3 kcal/mol, which is in excellent agreement with the computed B3LYP/6-31+G(d) value of 375.5 kcal/mol. The electron binding energy of **9** also was examined by the bracketing method. Electron transfer takes place with pentafluoropyridine (EBE = 0.68 ± 0.11 eV) and sulfur dioxide, but not weaker reagents such as carbon disulfide and carbonyl sulfide (EBE = 0.51 ± 0.10 and 0.46 ± 0.20 eV, respectively). This enables us to assign EBE (**9**) = 0.60 ± 0.11 eV or 13.8 ± 2.5 kcal/mol, which is within the experimental uncertainty of the computed (as described above) B3LYP/6-31+G(d) value of 15.7 kcal/mol; the S−T gap computed by Squires and Cramer for 2,3-dehydronaphthalene at the CASPT2/cc-pVDZ level (39.6 kcal/mol) was used.[58]

The thermochemistry of 2,3-dehydronaphthalene radical anion can be used to derive the heat of formation of 2,3-dehydronaphthalene. By combining the electron binding energy (EBE = 13.8 ± 2.5 kcal/mol) and proton affinity (PA = 377 ± 3 kcal/mol) of **9** as in eq 9, one obtains a value of 85 ± 5 kcal/mol for the heat of hydrogenation of 2,3-dehydronaphthalene (Table 1). This result is in essentially perfect accord with the predicted B3LYP/6-31+G(d) value of 85.4 kcal/mol and is in good agreement with a BLYP/6-311G(d,p) energy of 84.0 kcal/mol previously reported by Cioslowski et al.[47] This quantity also leads to $\Delta H_f^\circ(\mathbf{7})$ = 121 ± 5 kcal/mol, which is in good accord with a previous estimate of 126 ± 6 kcal/mol by Linnert and Riveros[63] but in poor agreement with an older estimate of 91 kcal/mol based upon ionization potentials and appearance energies.[64−66]

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(62) The product ion, presumably, consists largely of a mixture of 1,2- and 2,3-dehydronaphthalene radical anions. A small amount of (1,*n*) and/or (2,*n*) radical anions also is formed as indicated by a small amount of deuterium incorporation upon reaction with D_2O.

(63) Linnert, H. V.; Riveros, J. M. *Int. J. Mass Spectrom. Ion Processes* **1994**, *140*, 163−176.

(64) Grutzmacher, H. F.; Lohmann, J. *Liebigs Ann. Chem.* **1970**, *733*, 88−100.

(65) Grutzmacher, H. F.; Lehmann, W. R. *Liebigs Ann. Chem.* **1975**, 2023−2032.

(66) In ref 64, ΔH°_f(1,2- − 2,3-dehydronaphthalene) = 26 kcal/mol, which is unreasonably large and is much greater than the computed difference of −2.7 (B3LYP/6-31G(d)) and −2.8 (BLYP/6-311G(d, p) (ref 47).

One can use our experimental heat of formation to derive the C3−H bond dissociation energy for 2-naphthyl radical (BDE2′ = 77 ± 4 kcal/mol), which is 35 ± 5 kcal/mol less than BDE1. This energy difference can be equated to the π bond strength of 2,3-dehydronaphthalene and is the same as in *o*-benzyne (i.e., BDE1 − BDE2 = 36.0 ± 3.1 kcal/mol).[14]

The absolute heat of formation of 2,3-dehydronaphthalene radical anion and the C3−H homolytic bond energy of 2-naphthyl anion (93 ± 3 kcal/mol) also can be derived from our results. In this case, as in the benzene/*o*-benzyne system, the presence of a radical center, a lone-pair of electrons, or a carbon−hydrogen bond at C2 has a large impact on the adjacent C3−H bond strength. Not surprisingly, the BDE for the anion is between that of the radical and the parent hydrocarbon since the two-center three-electron interaction in the radical anion is better than in the 2-naphthyl radical but not as effective as π bond formation (a two-center two-electron interaction) in 2,3-dehydronaphthalene.

Conclusions

A new method for the selective formation of radical anions via the collision-induced dissociation of dianions formed by electrospray ionization mass spectrometry, laser desorption, chemical ionization, or electron ionization has been described. Ion structures were authenticated by reaction studies and/or classical derivatization experiments. Subsequent measurements on 2,3- and 2,6-dehydronaphthalene radical anions provided their proton affinities and electron binding energies, which were combined in thermodynamic cycles to afford the heat of formation of 2,3- and 2,6-dehydronaphthalene. From these data, second bond dissociation energies of naphthalene were derived, and the results were contrasted to the analogous energetic quantities for benzene. Further application of this methodology for obtaining valuable thermodynamic information on transient neutral molecules will be reported.

Acknowledgment. Support from the National Science Foundation and the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, and the Minnesota Supercomputer Institute are gratefully acknowledged.

JA002351J