J. Am. Chem. Soc. **1996,** *118,* 11865−11871

o-, *m*-, and *p*-Benzyne Negative Ions in the Gas Phase: Synthesis, Authentication, and Thermochemistry

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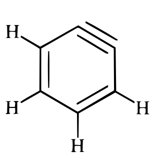
Received February 29, 1996[⊗]

Abstract: The isomeric *m*- and *p*-benzyne anions have been generated in the gas phase in a flowing afterglow-triple quadrupole instrument from the reactions of molecular fluorine (F_2) with *m*- and *p*-(trimethylsilyl)phenyl anions. The mechanism of the F_2 reaction involves electron transfer from the (trimethylsilyl)phenyl anion to F_2, followed by nucleophilic attack on the resulting (trimethylsilyl)phenyl radical by the nascent F^- formed within the intermediate ion/molecule complex. The structures of *o*-, *m*-, and *p*-benzyne anion are unambiguously identified by a classical derivatization scheme wherein the ions are first converted to the corresponding *o*-, *m*-, and *p*-nitrobenzoates by stepwise addition of CO_2 and NO_2. These derivatives are then identified by forming proton-bound dimers of each ion with CHF_2CO_2H, and comparing the $O_2NC_6H_4CO_2^-/CHF_2CO_2^-$ yield ratios obtained by collision-induced dissociation (CID) with those obtained from analogous experiments with the authentic nitrobenzoate ions. Estimates of the electron affinities of *m*- and *p*-benzyne have been determined by the kinetic method. Adducts of SO_2 with phenide ion and each of the isomeric benzyne anions are formed that produce measurable yields of $SO_2^{\bullet-}$ and the corresponding $C_6H_n^-$ ion upon CID. A calibration relation is derived between the CID yield ratios obtained for the $C_6H_5SO_2^-$ and o-$C_6H_4SO_2^{\bullet-}$ adducts and the known electron affinities of phenyl radical (25.3 ± 0.1 kcal/mol) and *o*-benzyne (12.9 ± 0.2 kcal/mol). The measured CID ratios for the *m*- and *p*-benzyne SO_2 adducts are then combined with this relation to obtain EA(*m*-benzyne) = 19.5 ± 0.3 kcal/mol and EA(*p*-benzyne) = 28.8 ± 0.5 kcal/mol. These data are used to derive the following gas-phase acidities for the different ring positions of phenyl radical and the corresponding C−H bond strengths for the phenide ion ($\Delta H_{\mathrm{acid}}(C_6H_5)$, $DH_{298}[C_6H_4^- -H]$, kcal/mol): *ortho* 378.2 ± 3.1, 93.7 ± 3.1; *meta* 386.9 ± 3.1, 102.4 ± 3.1; *para* 393.5 ± 2.9, 109.0 ± 2.9.

A detailed picture of the physical properties, chemical reactivity, and electronic structures of the isomeric dehydrobenzenes (*o*-, *m*-, and *p*-benzyne, **1**−**3**) is emerging from more than half a century of experimental and theoretical investigation.[1]



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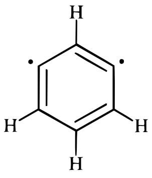

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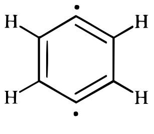

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Traditional interests in the benzynes as reactive organic intermediates have been augmented by the recent discovery that *p*-benzyne derivatives formed by Bergman cyclization reactions[2] are involved in the DNA-cleaving activity of calicheamicin and related antitumor antibiotics,[3] and by the many new synthetic applications of *o*-benzynes and other dehydroaromatic reagents in organic and organometallic chemistry.[4] Because of the well-defined geometric relationships between the radical sites in the isomeric benzynes, these molecules have also served as instructive paradigms in computational studies of biradicals.[5] Recent advances in electronic structure theory and high-performance computers have enabled rigorous theoretical treatments of the benzynes using multireference and multiconfigurational wave functions constructed from large-scale basis sets.[6] As a result, credible *ab initio* predictions of the structures, relative and absolute stabilities, and spectroscopic properties of the benzynes are now available.

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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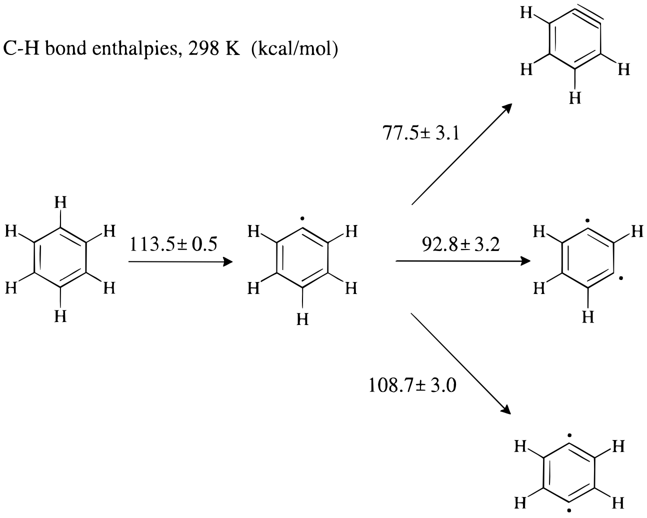
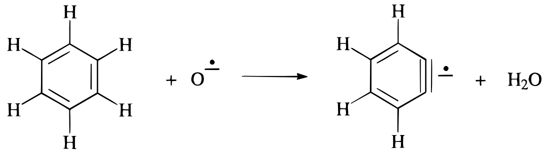
S0002-7863(96)00663-4 CCC: $12.00

Scheme 1

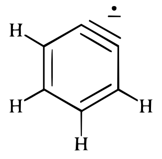


We have been investigating the gas-phase thermochemical properties of the benzynes[7] and other biradicals[8] using the flowing afterglow-triple quadrupole technique. These studies provide a fascinating view of the sequential C−H bond energies of benzene (Scheme 1). The C−H bond strengths derived for the *ortho*-, *meta*-, and *para*-positions of phenyl radical are lower than that of benzene[9] by *ca.* 36, 21, and 5 kcal/mol, respectively. Chen and co-workers have proposed a simple valence bond promotion energy model for understanding these bond strength reductions which equates them, to a first approximation, with the triplet excitation energies of the corresponding benzyne singlet ground states (ΔE_{ST}).[10] For *o*-benzyne, the singlet−triplet splitting is accurately known to be 37.7 ± 0.7 kcal/mol[11]—in good agreement with the *ortho* C−H bond energy reduction noted above. The singlet−triplet splittings in *m*- and *p*-benzyne have not been determined experimentally. However, *ab initio* molecular orbital calculations using MCSCF and CISD procedures with medium-sized basis sets give ΔE_{ST} values of 17−18 kcal/mol for the *meta* isomer and 2−3 kcal/mol for *p*-benzyne,[6f,g] in reasonable accord with the measured reductions in the *meta* and *para* C−H bond strengths in phenyl radical.

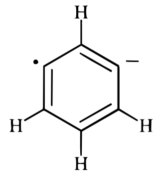
Experimental measurements of the singlet−triplet splittings in *m*- and *p*-benzyne are obviously desirable, not only for calibrating the theoretical estimates noted above and for further testing the promotion energy model, but also because these particular data are essential for further understanding through-bond and through-space coupling,[5a,12] and electron repulsion and exchange effects[13] in (σ,σ) aromatic biradicals—an important class of "chemically-accessible" biradicals that have attracted considerable attention recently.[14] One of the best experimental methods for determining accurate singlet−triplet splittings in biradicals, carbenes, and other open-shell organic species is negative ion photoelectron spectroscopy (NIPES).[15] In this experiment, an intense beam of mass-selected and structurally-defined negative ions is crossed with a fixed-frequency laser, and the energy spectrum of the resulting photoelectrons is recorded. From the differences in energy between selected features in the photoelectron spectrum, electronic state splittings in the neutral product can be assigned, often with uncertainties less than ±0.01 eV. In fact, this experimental method was used to determine ΔE_{ST} for *o*-benzyne.[11] These particular measurements were made possible by the ready availability of *o*-benzyne anion (**1a**) from the well-known gas-phase ion/molecule reaction between atomic oxygen ion and benzene (eq 1).[16,17] Deuterium labeling studies indicate that the reaction with benzene proceeds almost entirely by 1,2-abstraction of $H_2^{\bullet+}$ yielding mainly the *ortho* radical anion isomer.[16] Although 1,3-, 1,4-, and higher-order $H_2^{\bullet+}$ abstractions by $O^{\bullet-}$ from certain unsaturated hydrocarbons and arenes are known,[18−20] only the *o*-aryne anion isomers are produced in significant yields with benzene, naphthalene, and other simple unsubstituted aromatic compounds.[21] Therefore, the $O^{\bullet-}$ reaction is not applicable to the synthesis of *m*-benzyne anion (**2a**) and *p*-benzyne anion (**3a**).

 (1)

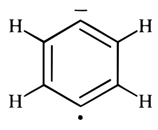
1a



1a



2a



3a

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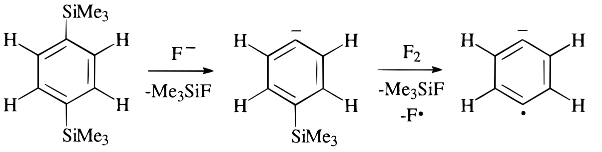
We sought a new method for synthesizing *m*- and *p*-benzyne anions and other biradical negative ions in a regiospecific manner with absolute ion yields that were suitable for NIPES measurements (10−100 pA). The broad applicability of the fluoride-induced desilylation procedures developed by DePuy and co-workers for regiospecific formation of gas-phase carbanions[22] inspired us to examine the possibilities for "double-desilylation" of bis(trimethylsilyl)benzenes, wherein the two trimethylsilyl groups would determine the positions of the charged and odd-spin sites in the radical anion products. Using this strategy, we recently developed a stepwise synthetic procedure for generating gas-phase benzyne anions by first forming a (trimethylsilyl)phenyl anion from the corresponding bis(trimethylsilyl)benzene using the DePuy procedure, and then allowing this ion to react with *molecular fluorine*, F_2, in order to effect the displacement of the remaining trimethylsilyl group (e.g., eq 2). A preliminary account of this new method of radical anion formation has been published,[23] along with a brief description of its applications in the synthesis of *m*- and *p*-benzyne anions and the trimethylenemethane anion, $C(CH_2)_3^{\bullet-}$.



(2)

3a

In this paper we present the details of the benzyne anion syntheses and a discussion of the mechanism, along with a description of an experimental procedure for unambiguously distinguishing and authenticating the structures of the three benzyne anion isomers, **1a**−**3a**. The electron affinities of *m*- and *p*-benzyne have been determined by a tandem mass spectrometric procedure, and the results are used to derive gas-phase acidities for the different ring positions of phenyl radical and the corresponding C−H bond strengths for the phenide ion.

Experimental Section

All of the gas-phase experiments described in this paper were carried out at room temperature in a flowing afterglow-triple quadrupole instrument described elsewhere.[24] For the present studies, helium buffer gas was maintained in the 1 m × 7.3 cm flow reactor at a total pressure of 0.4 Torr, with a flow rate of 200 STP cm^3/s and bulk flow velocity of 9700 cm/s. The primary reactant ions F^- and OH^- were produced by electron ionization (EI) of NF_3 and a N_2O/CH_4 mixture, respectively, in the upstream end of the flow tube. These ions are transported down the tube by the flowing helium, where they are allowed to react with gaseous neutral reagents introduced through leak valves. Reaction of F^- with *m*- and *p*-bis(trimethylsilyl)benzene produces the corresponding *m*- and *p*-(trimethylsilyl)phenyl anions. These ions can also be formed by EI of the bis(trimethylsilyl)benzenes. The ions in the flow tube are thermalized to ambient temperature by *ca.* 10^5 collisions with the helium buffer gas. The negative ions in the flowing plasma are extracted from the flow tube through an orifice, and then focused into an EXTREL triple quadrupole analyzer for either single-stage or tandem mass spectrometric analysis. Collision-induced dissociation (CID) experiments were carried out in the rf-only, gas-tight second quadrupole (Q2) with argon target. The product ions and undissociated parent ion are extracted from Q2 with an electrostatic lens into the third quadrupole, where they are mass analyzed and then detected with an electron multiplier.

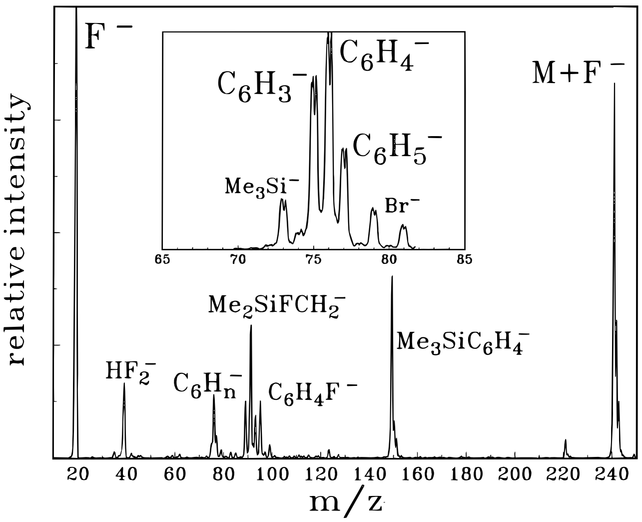


Figure 1. Mass spectrum of ionic products formed in the flowing afterglow apparatus when 5% F_2 in helium is allowed to react with the mixture of negative ions produced by fluoride-induced desilylation of *m*-bis(trimethylsilyl)benzene; P_{total} = 0.4 Torr, T = 298 K.

Materials. The bis(trimethylsilyl)benzenes were prepared by refluxing *m*- and *p*-dibromobenzene in tetrahydrofuran in the presence of magnesium and chlorotrimethylsilane and were purified according to standard procedures. All other reagents were obtained from commercial sources and were used as supplied. Gas purities were as follows: He (99.995%), F_2 (5% in He), NF_3 (98%), NO_2 (99.5%), CO_2 (99.5%), and SO_2 (99.98%).

Results and Discussion

Ion Synthesis. Fluoride-induced desilylation of *m*- and *p*-bis(trimethylsilyl)benzene produces the corresponding *m*- and *p*-(trimethylsilyl)phenyl anions (*m/z* 149), along with variable amounts of the F^- adducts (*m/z* 241) and $Me_2Si(F)CH_2^-$ (*m/z* 91). The (trimethylsilyl)phenyl anions can also be formed by EI of the neutral precursors added near the electron emission source. Reaction of these ions with F_2, added downstream in the flow tube as a 5% mixture in helium, yields intense negative ion signals with *m/z* 76 corresponding to $C_6H_4^{\bullet-}$. An illustrative mass spectrum of the ion mixture obtained with *m*-bis(trimethylsilyl)benzene is presented in Figure 1. Other carbanions formed as primary and/or secondary products include $C_6H_3^-$ (*m/z* 75), $C_6H_5^-$ (*m/z* 77), and $C_6H_4F^-$ (*m/z* 95). Fluoride ion (*m/z* 19), fluorine molecular anion ($F_2^{\bullet-}$, *m/z* 38), bifluoride ion (HF_2^-, *m/z* 39) and other negative ion clusters derived from the HF impurity in the F_2 mixture are also evident in the mass spectrum. The observed $C_6H_4^{\bullet-}$ ions are assigned the *m*- and *p*-benzyne radical anion structures (**2a** and **3a**, respectively) based on their synthetic origins and the results of the derivatization experiments described in the next section.

Our view of the mechanism of benzyne anion formation is illustrated for the *para* isomer in Scheme 2. Electron transfer from the (trimethylsilyl)phenyl anion to F_2 readily occurs within the initial ion/molecule collision complex since the electron affinity of F_2 is 3.01 ± 0.07 eV,[25] while the electron binding energy of the carbanion is only about 1 eV.[26] The resulting (trimethylsilyl)phenyl radical then undergoes a second desilyl-

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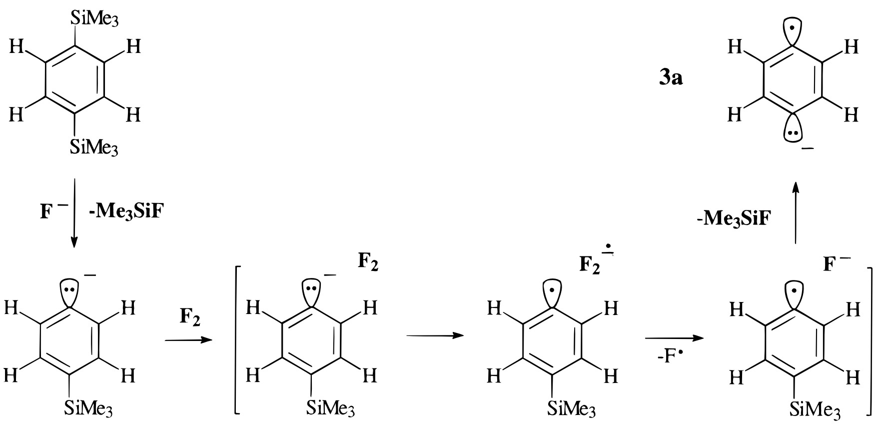
Scheme 2



ation within the complex, with either the $F_2^{\bullet-}$ ion or F^- (formed by dissociation of $F_2^{\bullet-}$) serving as the nucleophile. Note that the exothermicity of the initial electron transfer (*ca*. 46 kcal/mol) is well in excess of the $F_2^{\bullet-}$ bond energy, $D_0 = 27.9 \pm 1.6$ kcal/mol,[25] so loss of a fluorine atom following electron transfer is thermodynamically feasible.

The carbanion byproducts indicated in Figure 1 reveal additional features of the F_2 reaction. The unsubstituted phenyl anion, $C_6H_5^-$, appears to be formed as a significant *primary* product in the reactions of both *m*- and *p*-(trimethylsilyl)phenyl anion. In fact, the corresponding even-electron "$[M - H]^-$" ions have been observed along with the "$[M - 2H]^{\bullet-}$" radical anions in all of the F_2-initiated double-desilylations examined to date. However, control experiments with HF (0.5% in helium) show that the phenyl anion is not derived from reaction of the (trimethylsilyl)phenyl anions with F_2, but rather it is formed by reaction of the (trimethysilyl)phenyl anions with the unavoidable HF impurity that is present in the F_2/helium mixture (eq 3). This HF-impurity reaction also probably accounts for the $[M - H]^-$ ions observed in all the other F_2-initiated double-desilylation experiments.

$$\mathrm{Me_3SiC_6H_4^-} + \mathrm{HF} \rightarrow \mathrm{Me_3SiF} + \mathrm{C_6H_5^-} \qquad (3)$$

The $C_6H_3^-$ ions are also produced by both bis(trimethylsilyl)-benzene precursors, and they appear to be formed as both primary and secondary reaction products. That is, while the $(C_6H_3^-)/(C_6H_4^{\bullet-})$ ion signal ratio increases with increasing F_2 flow rate, it is significant even at low concentrations of added F_2. The structures of these ions and mechanisms of their formation are presently under further investigation.[27] The preliminary results indicate that they are isomeric tris-dehydrobenzene anions, presumably formed by dissociative electron transfer from the benzyne anion to F_2 within the ion/molecule collision complex, followed by proton abstraction from the neutral benzyne by the nascent F^-. The origins of the fluorophenyl anion, $C_6H_4F^-$, are unclear. It may arise from direct nucleophilic attack on F_2 by the (trimethylsilyl)phenyl anion followed by desilylation within the resulting F^-/(trimethylsilyl)fluorobenzene complex, or by coupling between the nascent benzyne anion and the fluorine atom byproduct within the decomposing product complex.

Structure Verification. Like most carbanions, ions **1a**,[17] **2a**, and **3a** react with CO_2 under flowing afterglow conditions by nucleophilic addition; in this case forming *o*-, *m*-, and *p*-dehydrobenzoate anions (eq 4).

$$\mathrm{C_6H_4^{\bullet-}}\ (\mathbf{1a},\ \mathbf{2a},\ \text{or}\ \mathbf{3a}) + \mathrm{CO_2} \rightarrow [\mathrm{C_6H_4CO_2}]^{\bullet-} \qquad (4)$$

A few gas-phase ion/molecule reactions of the *o*-dehydrobenzoate ion have been reported by Guo and Grabowski;[17] the thermochemical properties and reactivity of the *m*- and *p*-dehydrobenzoates are currently under investigation in our laboratory.[28] The most significant finding for the present study is that whereas the benzyne anions **1a**−**3a** each react with NO_2 exclusively by electron transfer, the carboxylated forms of these ions give abundant adducts with NO_2 (Scheme 3). This reaction sequence provides the key to the identification and authentication of the benzyne radical anions. The ions produced by sequential addition of CO_2 and NO_2 to **1a**, **2a**, and **3a** are presumably the isomeric *o*-, *m*-, and *p*-nitrobenzoate ions **1b**, **2b**, and **3b**, respectively. The structures of **1b**, **2b**, and **3b** can be verified by comparing their relative basicities to those of authentic nitrobenzoate ions prepared from the corresponding nitrobenzoic acids. This strategy for identifying the structures of the isomeric benzyne anions by determining the acid−base properties of their nitrobenzoate derivatives is analogous to the classical qualitative organic analysis procedures developed nearly a century ago for identifying substituted aromatic compounds.[29]

The relative basicities of the nitrobenzoate derivatives were characterized by the kinetic method,[30] wherein hydrogen-bonded cluster ions ("proton-bound dimers") are formed with a suitable reference carboxylic acid, and the ratios of carboxylate ions produced by CID of each of the cluster ions are measured (eq 5).

$$\underset{\mathbf{1b},\ \mathbf{2b},\ \text{or}\ \mathbf{3b}}{\mathrm{ArCO_2^-}} + \mathrm{RCO_2H} \rightarrow [\mathrm{ArCO_2^-\cdots H^+\cdots {}^-O_2CR}] \xrightarrow{\text{CID}} \mathrm{ArCO_2^-} + \mathrm{RCO_2^-} \qquad (5)$$

Comparison of the measured CID ratios with those determined for proton-bound dimers made from the authentic nitrobenzoates can equate the structures of the derivatives, and thereby confirm the structures of the isomeric benzyne anions. Survey experiments established difluoroacetic acid, CHF_2CO_2H, as a suitable reference acid since it has a gas-phase acidity ($\Delta H_{acid} = 331.0$ kcal/mol)[31] that is similar to that of the isomeric nitrobenzoic acids ($\Delta H_{acid} = 331.8$, 331.6, 328.9 kcal/mol for the *ortho*-, *meta*-, and *para*-isomers, respectively).[32] Formation, carboxyl-

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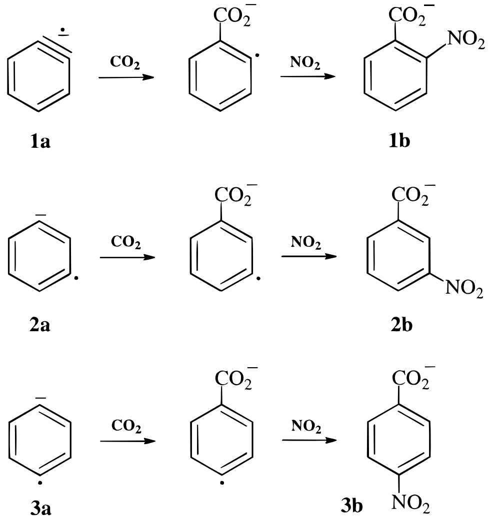
Scheme 3



ation, and nitration of each benzyne anion in the upstream portions of the flow tube followed by addition of CHF_2CO_2H through a downstream inlet produces the proton-bound dimer ions, $[ArCO_2^{-}\cdots H^{+}\cdots {}^{-}O_2CCHF_2]$, where $ArCO_2^-$ is **1b**, **2b**, or **3b**. The CID spectra for these ions are shown in the left half of Figure 2. The major CID products produced with a collision energy of 20 eV (lab) are $CHF_2CO_2^-$, *m/z* 95, and $ArCO_2^-$, *m/z* 166. A minor fragment ion obtained from the **1b** cluster is the corresponding nitrophenyl anion ($C_6H_4NO_2^-$, *m/z* 122), which results from decarboxylation of the nitrobenzoate ion. Some unidentified minor fragments are also present in the CID spectrum obtained for the **2b** cluster; these are marked with an asterisk in Figure 2. These fragments are attributed to dissociation of an impurity ion (or ions) with the same mass as the proton-bound dimer (*m/z* 262). However, control experiments (shutting the flow of *m*-bis(trimethylsilyl)benzene to the flow tube) show that these impurities do not produce fragment ions with *m/z* 95 or 166, so they do not affect the CID yield ratio measurements. The CID yield ratios, $r = I(ArCO_2^-)/I(CHF_2CO_2^-)$, determined for the cluster ions derived from **1b**, **2b**, and **3b** are $r = 0.62$, 1.25, and 2.83, respectively.

The reference proton-bound dimer ions were generated simply by fluoride-induced desilylation of the trimethylsilyl esters of *o*-, *m*-, and *p*-nitrobenzoic acid in the upstream portion of the flow tube,[33] followed by addition of CHF_2CO_2H through a downstream inlet. The CID spectra recorded for these cluster ions are shown in the right half of Figure 2. The excellent correspondence between the spectra obtained for the derivatives and the authentic ions is immediately evident. The CID yield ratios obtained from CID of the proton-bound dimers made from authentic nitrobenzoate ions are $r = 0.63$, 1.24, and 2.85 for *o*-, *m*-, and *p*-nitrobenzoate ions, respectively. These results unambiguously identify **1b**, **2b**, and **3b** as the *o*-, *m*-, and *p*-nitrobenzoate ions which, in turn, requires that the precursor ions **1a**, **2a**, and **3a** possess dehydrocarbon atoms in *ortho, meta,* and *para* relationships, respectively.

Thermochemistry. Having established the structures of the isomeric benzyne anions, we next turned to a determination of their thermochemical properties. We have found that the reactions of **1a**−**3a** with SO_2 provide a convenient method for estimating the electron affinities of the benzynes. Guo and Grabowski[17] report that **1a** reacts with SO_2 at the collision rate mainly by electron transfer (>96%). This is consistent with the fact that the electron affinity of SO_2 ($EA(SO_2) = 1.107 \pm 0.008$ eV)[34] is significantly greater than that of *o*-benzyne ($EA(o\text{-}C_6H_4) = 0.56$ eV).[11] In contrast, SO_2 reacts with **3a** mainly by addition, and only a small amount (*ca.* 5%) of $SO_2^{\bullet-}$ is formed (eq 6).

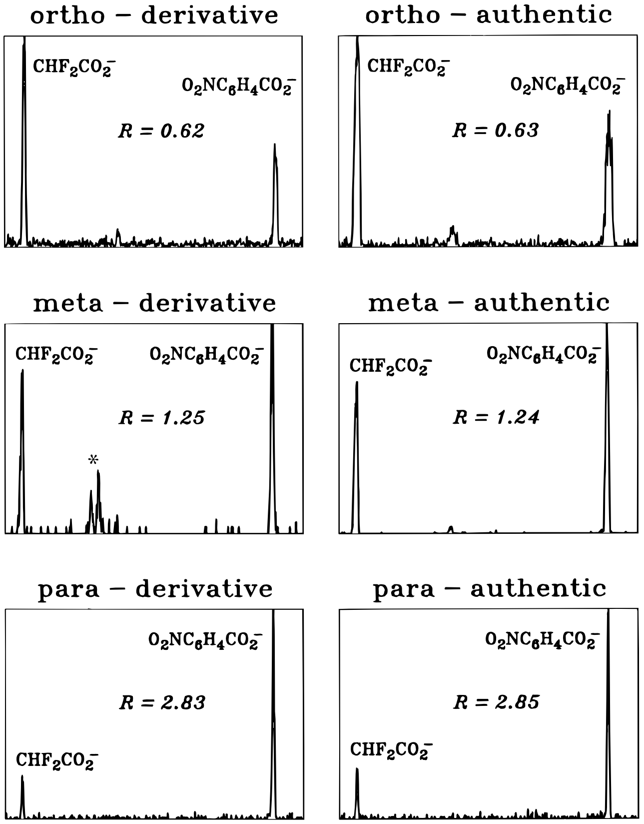

ortho – derivative
ortho – authentic
meta – derivative
meta – authentic
para – derivative
para – authentic

Figure 2. Collision-induced dissociation spectra for proton-bound cluster ions produced from difluoroacetic acid and isomeric nitrobenzoate ions, $[O_2NC_6H_4CO_2^{-}\cdots H^{+}\cdots {}^{-}O_2CCHF_2]$. In the series of CID spectra on the left, the nitrobenzoate ions were formed by derivatization of the corresponding benzyne anion by reaction with CO_2 followed by NO_2. In the series of spectra on the right the nitrobenzoate ions were produced by fluoride-induced desilylation of the trimethylsilyl esters of authentic *o*-, *m*-, and *p*-nitrobenzoic acids. The minor fragments that are visible in the *m*-benzyne anion derivative spectrum (marked with an asterisk) arise from an isobaric impurity which does not produce any CID product ions with the same mass as either $CHF_2CO_2^-$ or $O_2NC_6H_4CO_2^-$. See text for discussion.

$$\begin{array}{llllll} & & & \%\,\mathbf{1a} & \%\,\mathbf{2a} & \%\,\mathbf{3a} \\ C_6H_4^{\bullet-} + SO_2 & \rightarrow & [C_6H_4SO_2]^{\bullet-} & 4 & 40 & 95 \\ & \rightarrow & SO_2^{\bullet-} & 96 & 60 & 5 \end{array} \qquad (6)$$

Phenide ion ($EA(C_6H_5) = 1.097$ eV)[26] reacts with SO_2 in a similar fashion, giving 97% addition and 3% electron transfer. Ion **2a** exhibits intermediate behavior, producing $SO_2^{\bullet-}$ and $C_6H_4SO_2^{\bullet-}$ in roughly equal amounts. The differing amounts of electron transfer observed in the reactions of SO_2 with the benzyne ions and phenide ion are probably a reflection of their relative electron binding energies. Thus, the results suggest that *o*-benzyne has the lowest EA of the three isomers and the EA of *m*-benzyne is slightly higher, while the EA of *p*-benzyne is higher still and comparable to that of phenyl radical.

In order to investigate this further, we examined the CID behavior of the SO_2 adducts produced by these reactions. For

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(32) ΔH_{acid}(benzoic acid) = 340.2 ± 2.2 kcal/mol: Caldwell, G.; Renneboog, R.; Kebarle, P. *Can. J. Chem.* **1989**, *67*, 611. Substituted benzoic acids are anchored to benzoic acid in: McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 2222.

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these experiments, the SO_2 adducts could be made directly, as in eq 6. However, for **1a** and **2a** the yields are low because of competing electron transfer. Improved yields could be achieved by making use of a novel "electrophile switching" reaction first demonstrated by Guo and Grabowski for the *o*-benzyne anion (eq 7).[17] Carboxylation of the benzyne anions produces the

$$\underset{\mathbf{1a},\ \mathbf{2a},\ \text{or}\ \mathbf{3a}}{C_6H_4^{\bullet-}} \xrightarrow{CO_2} [C_6H_4CO_2]^{\bullet-} \xrightarrow[-CO_2]{+SO_2} [C_6H_4SO_2]^{\bullet-} \tag{7}$$

dehydrobenzoates (eq 4), each of which reacts with SO_2 to give the corresponding dehydrosulfinate anion, $C_6H_4SO_2^{\bullet-}$, as the major product (along with a small amount of an SO_2 cluster). Collision-induced dissociation of the SO_2 adducts derived from **1a**, **2a**, and **3a** (argon target; 20 eV (lab) collision energy) produces $C_6H_4^{\bullet-}$ (*m/z* 76) and $SO_2^{\bullet-}$ (*m/z* 64) as the only ionic products, but with markedly different yield ratios for the three isomers. The yield ratios, $r = I(m/z\ 76)/I(m/z\ 64)$, obtained from replicate measurements with the SO_2 adducts of **1a**, **2a**, and **3a** are 0.032 ± 0.003, 0.408 ± 0.027, and 14.8 ± 1.7, respectively. An analogous CID experiment performed with the SO_2 adduct of phenide ion, $C_6H_5SO_2^-$, produces $C_6H_5^-$ and $SO_2^{\bullet-}$ as the only ionic products with a measured yield ratio, $I(m/z\ 77)/I(m/z\ 64)$, of 3.74 ± 0.39.

Quantitative estimates of the electron affinities of *m*- and *p*-benzyne can be derived from these data using the analytical procedures developed by Cooks and co-workers for evaluating relative proton,[35] ion,[36] and electron[37,38] affinities from the competitive cleavages of activated molecular cluster ions, i.e., the kinetic method.[30] An often-stated prerequisite for success in applying the kinetic method is that the two ions or neutral species competing for the nominal binding element of the cluster (a proton, ion, or electron) should be "structurally similar" so that the yields of the competing dissociations are determined by energetic rather than dynamical factors.[30] This criterion is certainly not met in the present systems, where a (presumably) covalently-bonded molecular anion dissociates to two negative ion fragments with very different structures and electron binding sites. Indeed, the fact that the SO_2 adduct derived from phenide ion, $C_6H_5SO_2^-$, yields more $C_6H_5^-$ than $SO_2^{\bullet-}$, despite the slightly greater electron binding energy of the latter, indicates that the dynamics are playing an important role in these dissociations. Nevertheless, these factors should remain constant for the series of $C_6H_nSO_2^-$ ($n = 4, 5$) ions, so the relative fragmentation yields should properly reflect the thermochemistry. From the known electron affinities for *o*-benzyne and phenyl radical (Table 1), and the measured CID yield ratios noted above for *o*-$C_6H_4SO_2^{\bullet-}$ and $C_6H_5SO_2^-$, the calibration relation shown in eq 8 is obtained. The electron affinities of

$$\mathrm{EA} = (21.8 \pm 0.2\ \text{kcal/mol}) + (2.60 \pm 0.09\ \text{kcal/mol}) \ln r \tag{8}$$

m- and *p*-benzyne calculated with this equation from measured CID yield ratios for the corresponding SO_2 adducts are 19.5 ± 0.3 and 28.8 ± 0.5 kcal/mol, respectively, where the assigned uncertainties reflect the random errors in the experiment and are calculated in a manner described previously.[39] Thus, the quantitative trend in the electron affinities of *o*-, *m*-, and *p*-benzyne obtained from these measurements is consistent with the qualitative ordering predicted from the reactivity of **1a**, **2a**, and **3a** with SO_2. Preliminary results from negative ion photoelectron measurements with **3a** are in excellent agreement with the electron affinity for *p*-benzyne estimated in this study.[40]

Table 1. Supplemental and Derived Thermochemical Data

compd	$\Delta H^\circ_{f,298}$(g), kcal/mol	ref
o-benzyne (**1**)	106.6 ± 3.0	*a*
m-benzyne (**2**)	121.9 ± 3.1	*a*
p-benzyne (**3**)	137.8 ± 2.9	*a*
o-benzyne anion (**1a**)	93.7 ± 3.1	this work
m-benzyne anion (**2a**)	102.4 ± 3.1	this work
p-benzyne anion (**3a**)	109.0 ± 2.9	this work
C_6H_6	19.7 ± 0.3	*b*
C_6H_5	81.2 ± 0.6	*c*
$C_6H_5^-$	55.7 ± 0.6	*c*
H	52.1	*d*
H^+	365.7	*e*
	ΔH_{acid}, kcal/mol	ref
C_6H_6	401.7 ± 0.5	*c*
C_6H_5, *ortho* CH	378.2 ± 3.1	this work
	379 ± 5	*f*
C_6H_5, *meta* CH	386.9 ± 3.1	this work
C_6H_5, *para* CH	393.5 ± 2.9	this work
	EA, kcal/mol	ref
o-benzyne (**1**)	12.9 ± 0.2	*g*
m-benzyne (**2**)	19.5 ± 0.3	this work
p-benzyne (**3**)	28.8 ± 0.5	this work
phenyl, C_6H_5	25.3 ± 0.1	*h*
benzyl, $C_6H_5CH_2$	21.0 ± 0.1	*i*
SO_2	25.5 ± 0.2	*j*
	DH_{298}, kcal/mol	ref
$C_6H_5{-}H$	113.5 ± 0.5	*c*
C_6H_5, *ortho* CH	77.5 ± 3.1	*a*
C_6H_5, *meta* CH	92.8 ± 3.2	*a*
C_6H_5, *para* CH	108.7 ± 3.0	*a*
$C_6H_5^-$, *ortho* CH	90.1 ± 3.1	this work
$C_6H_5^-$, *meta* CH	98.8 ± 3.1	this work
$C_6H_5^-$, *para* CH	105.4 ± 2.9	this work

[a] Reference 7. [b] Pedley, J. B.; Rylance, C. *Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex, 1977. [c] Reference 9. [d] Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1 (JANAF Tables). [e] Reference 31. [f] Reference 17. [g] Reference 11. [h] Reference 26. [i] Davico, G.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B. *Int. J. Mass Spectrom. Ion Processes*. In press. [j] Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574.

The electron affinities of the benzynes can be combined with other data in order to derive additional thermochemical properties. These are listed in Table 1, with assigned uncertainties computed from the root-square sum of the component uncertainty intervals. The absolute heats of formation of the benzyne anions are derived by subtracting the measured electron affinities from the 298 K heats of formation for the corresponding neutral benzyne[7] (the small temperature correction is ignored). These data reveal a compression in the relative stabilities of the benzyne anions compared to the neutral biradicals, which is due to the opposing trends in the electron affinities and absolute energies of the three isomers. The anion heats of formation can be used in conjunction with the appropriate thermochemical cycle to compute the gas-phase acidities for the three different ring positions of phenyl radical (eq 9) and the C−H bond

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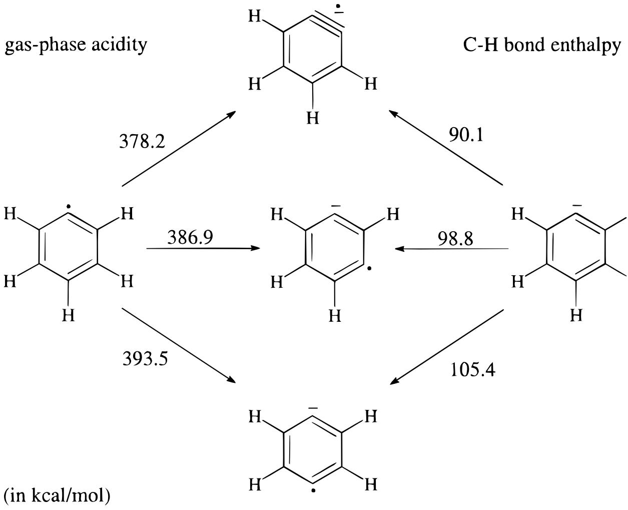
(39) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 11890.

(40) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. Work in progress.

Scheme 4



strengths at the different ring positions of phenide ion (eq 10). Phenyl radical is determined to be more acidic than benzene

$$\Delta H_{\mathrm{acid}}(\mathrm{C_6H_5}) = \Delta H_{\mathrm{f}}\,(\mathbf{1a},\ \mathbf{2a},\ \text{or}\ \mathbf{3a}) + \Delta H_{\mathrm{f}}(\mathrm{H^+}) - \Delta H_{\mathrm{f}}(\mathrm{C_6H_5}) \quad (9)$$

$$\mathrm{DH}[\mathrm{C_6H_4}^{-}{-}\mathrm{H}] = \Delta H_{\mathrm{f}}\,(\mathbf{1a},\ \mathbf{2a},\ \text{or}\ \mathbf{3a}) + \Delta H_{\mathrm{f}}(\mathrm{H}) - \Delta H_{\mathrm{f}}(\mathrm{C_6H_5}^{-}) \quad (10)$$

($\Delta H_{\mathrm{acid}} = 401.7 \pm 0.5$ kcal/mol)[9] in the *ortho*-, *meta*-, and *para*-positions by 23.5, 14.8, and 8.2 kcal/mol, respectively. It follows that the *o*-, *m*-, and *p*-CH bonds in phenide ion are weaker than that in benzene ($\mathrm{DH_{298}[C_6H_5{-}H]} = 113.5 \pm 0.5$ kcal/mol)[9] by these same amounts (Scheme 4). The large difference for the *para* C−H bonds is especially striking; it arises from the additive effects of the greater electron affinity and smaller hydrogen atom affinity of *p*-benzyne compared to phenyl radical.

Summary

In this work we have presented a detailed description of the gas-phase synthesis, authentication, and thermodynamic properties of the isomeric *o*-, *m*-, and *p*-benzyne negative ions. The *m*- and *p*-benzyne anion isomers are produced in high yields by gas-phase reactions between molecular fluorine and the corresponding *m*- and *p*-(trimethylsilyl)phenyl anions. A mechanism for these reactions is proposed involving oxidation of the trimethylsilyl-substituted phenyl anion by F_2, followed by nucleophilic displacement of the silyl group in the resulting ion−radical complex by either $F_2^{\bullet-}$ or F^-. The structures of all three benzyne anions are unambiguously determined by a classical derivatization approach wherein they are first converted to the corresponding nitrobenzoate ions by sequential reactions with CO_2 and NO_2. These derivatives are then identified by quantitatively comparing their basicities to authentic nitrobenzoate ions using the kinetic method. The electron affinities of *m*- and *p*-benzyne are estimated to be 19.5 ± 0.3 and 28.8 ± 0.5 kcal/mol, respectively, from the relative yields of the $C_6H_4^{\bullet-}$ and $SO_2^{\bullet-}$ fragments produced by CID of the corresponding $C_6H_4SO_2^{\bullet-}$ derivatives. The EA of *p*-benzyne is found to be slightly greater than that of phenyl radical ($\mathrm{EA(C_6H_5)} = 25.3 \pm 0.1$ kcal/mol), suggesting some degree of odd-spin and charge delocalization in the *p*-benzyne negative ion. The EA of *m*-benzyne is roughly halfway between that of the *ortho* ($\mathrm{EA}(o\text{-}\mathrm{C_6H_4}) = 12.9 \pm 0.2$ kcal/mol) and *para* isomers. The synthetic procedures, structural analysis protocols, and the EA estimation method described in this paper should be generally applicable to other dehydroaromatic negative ions, such as the naphthyne anions and heteroaryne anions. Experiments of this kind are currently in progress.

The isomeric benzyne anions belong to the family of distonic radical anions derived by ionization of a biradical. Radical ions of this type may possess multiple low-lying electronic states and, for this reason, may exhibit unusual structural features and chemical reactivity. In the following paper[41] we present a general theoretical description of distonic negative ions derived from biradicals, along with a discussion of the problem of artifactual symmetry-breaking in calculations on these species. An account is given of an extensive series of *ab initio* molecular orbital and density functional theory calculations of the structures, electronic state orderings and thermodynamic properties of the isomeric benzyne anions.

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

JA960663+

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