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Review Commentary

Reactive intermediates via Fourier transform mass spectrometry[†]

Steven R. Kass* **and Katherine M. Broadus**

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431, USA

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ABSTRACT: A new method for the selective preparation of radical anions in the gas phase is described. Dicarboxylate anions are generated in a Fourier transform mass spectrometer via electrospray ionization, and both carboxylates and an electron are removed to afford odd-electron anions via sequential fragmentations. Energetic measurements on these species enable the heats of formation of neutral compounds to be determined. The heats of hydrogenation of benzocyclobutadiene and acenaphthyne are used to illustrate this methodology and the antiaromaticity and/or strain energy of these molecules are discussed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: reactive intermediates; Fourier transform mass spectrometry; energetics; dianions; electrospray ionization; antiaromaticity; benzocyclobutadiene; acenaphthyne

INTRODUCTION

Most chemical transformations proceed via the formation and subsequent decay of intermediate compounds. These transient species often have short lifetimes and are hard to study, but they provide the key to understanding and ultimately controlling chemical reactions. Not surprisingly, then, reactive intermediates have been the subject of countless investigations and have supplied the impetus for numerous instrumental and methodological developments. They also have provided a stringent testing ground for semiempirical, *ab initio* and density functional theory calculations.

To characterize and understand fully reactive molecules such as carbenium ions, radicals or carbanions, it is necessary to know something about their structures, spectroscopic properties, reactivities and energetics. Gas-phase ion chemistry is particularly well suited for obtaining thermochemical information, not only for positively and negatively charged species, but also for neutral compounds.[1] For example, by measuring the gas-phase acidity ($\Delta H^\circ_{\text{acid}}$) of R—H and the electron affinity (*EA*) of $R^\cdot$, and combining these data with the ionization potential (*IP*) of $H^\cdot$ in a thermodynamic cycle, the corresponding R—H bond dissociation energy (BDE) can be derived:

$$\mathrm{RH} \longrightarrow \mathrm{R}^- + \mathrm{H}^+ \qquad \Delta H^\circ = \Delta H^\circ_{\text{acid}}(\mathrm{R{-}H}) \tag{1}$$

$$\mathrm{R}^- \longrightarrow \mathrm{R}^\cdot + \mathrm{e}^- \qquad \Delta H^\circ = EA(\mathrm{R}^\cdot) \tag{2}$$

$$\mathrm{H}^+ + \mathrm{e}^- \longrightarrow \mathrm{H}^\cdot \qquad \Delta H^\circ = -IP(\mathrm{H}^\cdot) \tag{3}$$

$$\mathrm{RH} \longrightarrow \mathrm{R}^\cdot + \mathrm{H}^\cdot \qquad \Delta H^\circ = BDE(\mathrm{R{-}H}) \tag{4}$$

where

$$BDE(\mathrm{R{-}H}) = \Delta H^\circ_{\text{acid}}(\mathrm{R{-}H}) + EA(\mathrm{R}^\cdot) - IP(\mathrm{H}^\cdot) + [\text{thermal correction}] \tag{5}$$

The term for the temperature correction corresponds to the integrated heat capacities according to the equation

$$[\text{thermal correction}] = \int_0^{298} \mathrm{d}T[C_\mathrm{p}(\mathrm{R}^\cdot) - C_\mathrm{p}(\mathrm{R}^-) + C_\mathrm{p}(\mathrm{H}^\cdot) - C_\mathrm{p}(\mathrm{H}^+)] \tag{6}$$

and arises since the *EA* and *IP* are 0 K measurements whereas $\Delta H^\circ_{\text{acid}}$ usually is reported at 298 K.[2] Since this adjustment is invariably less than 0.3 kcal mol^{-1} (1 kcal = 4.184 kJ) and typically amounts to around 0.05 kcal mol^{-1}, it is routinely omitted in the application of Eqn. (5). The resulting bond dissociation energies and radical heats of formation are in excellent accord with

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*Correspondence to: S. R. Kass, Department of Chemistry, University of Minnesota, 207 Pleasant St. S.E., Minneapolis, Minnesota 55455-0431, USA.
E-mail: kass@chem.umn.edu

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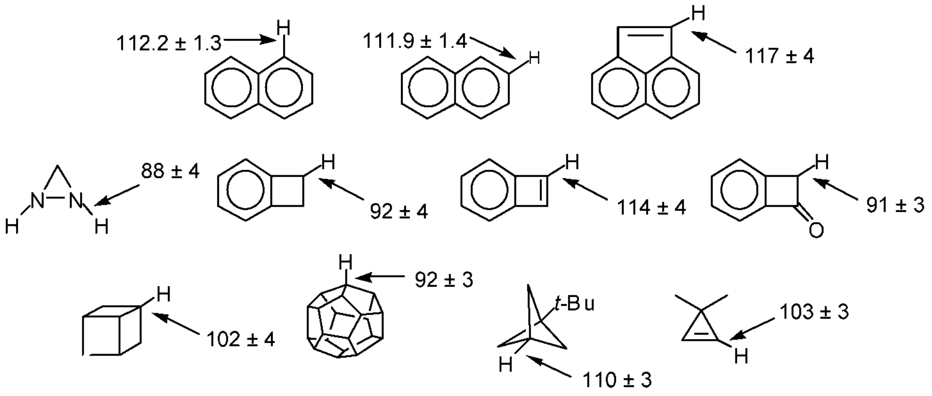


Figure 1. Measured C—H or N—H bond dissociation energies via anion chemistry and the application of Eqn. (5)

those determined by other methods such as radical kinetics and photoionization mass spectrometry.[2]

Carbanions most commonly are generated by one of three processes: (1) deprotonation, (2) decarboxylation of a carboxylate anion by collision-induced dissociation (CID)[3] or (3) fluoride-induced desilylation of a substituted trialkylsilane, a transformation which has come to be known as the DePuy reaction.[4,5] Subsequent measurements on these anions have resulted in a wealth of energetic data on radicals via Eqn. (5) including a variety of bond dissociation energies that we determined over the past few years (Fig. 1)[1,6–14] (R. E. McCarthy, M. R. Ahmad, S. R. Kass, M. Pollack, R. Gunion and W. C. Lineberger, unpublished data) Radicals, however, are not the only reactive intermediates of interest to chemists. Carbenes, biradicals, transient alkenes and alkynes and many other compounds also are of importance, but much less is known about them because there are far fewer general methods for obtaining their heats of formation. Gas-phase negative ion chemistry is also applicable in this case, particularly, since the requisite radical anions (Fig. 2) commonly are stable to unimolecular rearrangements and fragmentations, and are formed in the absence of neutral molecules with which to undergo bimolecular reactions.[15–20] This contrasts with the behavior of the corresponding neutral species and has led us to suggest that *the electron can be thought of as a useful protecting group*.[7,21,22] A major obstacle to this approach has been the formation of the desired radical anions because few suitable methods have been described.

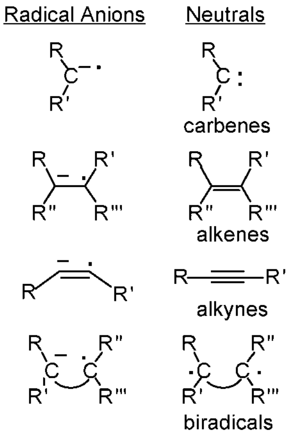
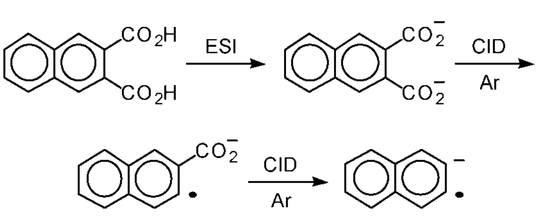
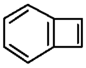


Figure 2. Requisite anions for obtaining energetic information on carbenes, alkenes, alkynes and biradicals



Scheme 1. Synthesis of 2,3-dehydronaphthalene radical anion from 2,3-naphthalenedicarboxylic acid

Recently, we reported that negative ion electrospray ionization (ESI) in conjunction with CID can be used to violate the ‘even-electron rule’ and regioselectively afford odd-electron species.[7,21,22] For example, ESI of 2,3-naphthalenedicarboxylic acid gives the dicarboxylate anion, which loses a molecule of carbon dioxide *and* an electron upon CID to yield useful signals of the corresponding distonic ion (Scheme 1). Subsequent fragmentation of this species leads to the loss of a second molecule of carbon dioxide and the formation of the radical anion of 2,3-dehydronaphthalene; this species can also be formed in one step from the dicarboxylate anion but the efficiency of this route is not as good as the two-step protocol. In this paper, we describe how this methodology can be used to determine the energetics of two fleetingly stable species: benzocyclobutadiene (**1**) and acenaphthyne (**2**).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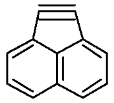
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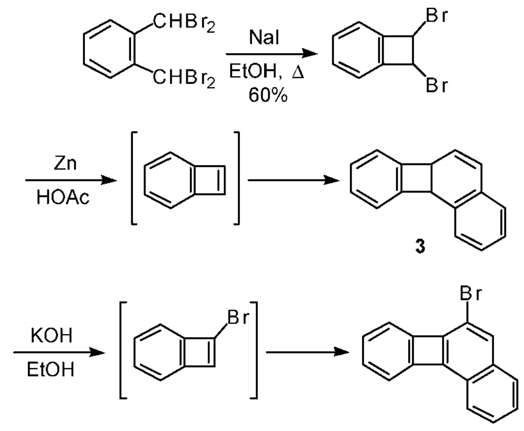
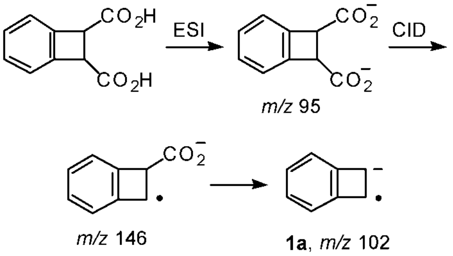
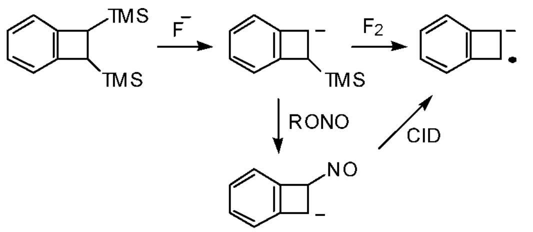


Scheme 2. Preparation of the first benzocyclobutene derivative and attempts to convert it into benzocyclobutadiene or 1-bromobenzocyclobutadiene



Scheme 3. Benzocyclobutadiene radical anion synthesis from 1,2-benzocyclobutenedicarboxylic acid



Scheme 4. Benzocyclobutadiene radical anion syntheses from 1,2-bis(trimethylsilyl)benzocyclobutene

RESULTS AND DISCUSSION

Benzocyclobutadiene

Nearly a century ago, Finkelstein, under the direction of Thiele at the University of Strasbourg, synthesized the first benzocyclobutene derivative and attempted unsuccessfully to isolate benzocyclobutadiene (Scheme 2).[23,24] The preparation and identification of the former compound was a significant achievement, especially since it was commonly assumed at the time that such a strained species was incapable of existence. Curiously, this work was withheld from publication and only was serendipitously rediscovered and supplemented by Cava ~50 years later after reading the title of Finkelstein's doctoral dissertation in Thiele's obituary in the *Berichte*.[23,25,26] Whatever the reason for this hiatus, Cava and Napier established the existence of benzocyclobutadiene by trapping experiments and the recovery of its angular dimer (**3**). Numerous studies have been carried out subsequently on **1**, including its matrix isolation,[27] the recording of its fast-flow ^{1}H NMR spectrum[28] and, most recently, its metal-catalyzed cyclotrimerization.[29]

Benzocyclobutadiene is an 8π electron species and can be viewed as a combination of benzene and cyclobutadiene. This raises the question of which 'nature' wins out in **1**. Does the aromatic or antiaromatic component dominate or do the two elements 'cancel' each other and result in a non-aromatic molecule? Given the reactive nature of benzocyclobutadiene (e.g. it rapidly dimerizes above 75 K),[27] it typically is assumed to be antiaromatic, but this view has been questioned.[28,30] The ^{1}H NMR spectrum of **1** has been interpreted as indicating that it is a non-aromatic molecule (this outlook also has been questioned).[31,32] Likewise, a combination of spin-coupled valence bond theory and complete active space self-consistent field calculations led Gerratt and co-workers to conclude that benzocyclobutadiene is 'unambiguously' non-aromatic.[30] Other computations of the magnetic properties and energetics of **1** indicate that it is antiaromatic.[33,34] To address this issue and demonstrate the utility of the electron as a protecting group, as well as our approach to generating radical anions, we experimentally determined the heat of hydrogenation of benzocyclobutadiene and a variety of additional thermodynamic data.

Electrospray ionization of an aqueous methanol solution of 1,2-benzocyclobutenedicarboxylic acid in our Fourier transform mass spectrometer (FTMS) affords the corresponding dicarboxylate anion (*m/z* 95) as the base peak in the mass spectrum.[22] Off-resonance irradiation of this ion in the presence of argon results in the loss of carbon dioxide and an electron to yield an odd electron species (*m/z* 146, Scheme 3). Subsequent fragmentation induced by collisional activation yields the desired benzocyclobutadiene radical anion (**1a**, *m/z* 102) in good abundance. The target ion (**1a**) also was

Table 1. Bracketing results for the electron affinity (*EA*) of benzocyclobutadiene (**1**)

Reference compound	*EA* (eV)[a]	Electron transfer
SO_2	1.107 ± 0.008	Yes
CS_2	0.51 ± 0.10	Yes
O_2	0.451 ± 0.007	Yes
PhCHO	0.429 ± 0.009	Yes
$PhCOCH_3$	0.334 ± 0.004	Yes
Phenanthrene	0.307 ± 0.012	No
NO	0.026 ± 0.005	No

[a] *EA*s taken from Ref. 1.

Table 2. Bracketing results for the acidity of 1-benzocyclobutenyl radical

Reference acid	$\Delta H°_{acid}$ (kcal mol^{-1})[a]	Proton transfer
CF_3CH_2OH	361.8 ± 2.5	Yes
$(CH_3)_2C=NOH$	366.0 ± 2.2	Yes
$C_6H_5CH_2OH$	370.0 ± 2.1	No
$C_6H_5C{\equiv}CH$	370.7 ± 2.3	No
FCH_2CH_2OH	371.2 ± 2.9	No
CD_3CN	372.9 ± 2.1[b]	No
$(CH_3)_3COD$	374.6 ± 2.1[b]	No
$CH_3CH_2CH_2C{\equiv}CH$	379.8 ± 2.5	No
CH_3OD	383.5 ± 0.7	No

[a] Acidities taken from Ref. 1.

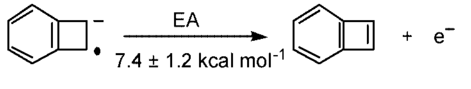
[b] Values for the protio reagent are given.

independently produced from 1,2-bis(trimethylsilyl)benzocyclobutene by two different routes (Scheme 4); the reaction using molecular fluorine is the Squires protocol and represents the only other general method for the selective formation of radical anions.[20,35,36]

The electron binding energy of **1a** or equivalently the electron affinity of **1** was measured by the bracketing technique.[37] In this approach, reference compounds with known electron affinities are allowed to react with **1** as a function of time and the occurrence or non-occurrence of electron transfer is monitored. Since endothermic reactions do not take place in the gas phase (or occur only slowly) and electron transfer typically is a barrierless process, the *EA* can be assigned as the average of the value for the reference compound with the lowest *EA* that undergoes electron transfer and the highest value that does not. In this case, based on the data in Table 1, we assign *EA*(**1**) = 0.32 ± 0.05 eV (the statistical error is 0.01 eV, but 0.05 eV is a more realistic estimate), which is in excellent agreement with the B3LYP/6–31 + G(d) result of 0.36 eV.

The proton affinity of **1a** or equivalently the acidity of 1-benzocyclobutenyl radical also was determined by the bracketing technique. In this case, proton transfer occurs between **1a** and trifluoroethanol and acetone oxime, but not with weaker acids (Table 2). These data enable us to assign $\Delta H°_{acid} = 368 \pm 2$ kcal mol^{-1}, which is in good agreement with the B3LYP/6–31 + G(d) result of 371.8 kcal mol^{-1}.

The acidity of benzocyclobutene and the electron affinity of 1-benzocyclobutenyl radical have been measured by Glasovac *et al.*,[9] and thus the measurements carried out on **1a** enable the heat of hydrogenation to be derived based entirely on experimental data. The resulting value of 49 ± 4 kcal mol^{-1} is in very good accord with computed values of 55 kcal mol^{-1} (B3LYP/6–31+ G(d)) and 52 kcal mol^{-1} (group equivalents based on HF/6–31G* energies),[31] and can be used to derive $\Delta H°_f(\mathbf{1}) = 97 \pm 4$ kcal mol^{-1} given that $\Delta H°_f$(benzocyclobutene) = 47.7 ± 0.2 kcal mol^{-1}, which was determined by bomb calorimetry.[9] The first and second C—H *BDE*s of benzocyclobutene also can be derived (92 ± 4 and 62 ± 2 kcal mol^{-1}, respectively), and their difference gives a π bond energy of only 30 ± 4 kcal mol^{-1} compared with 58 kcal mol^{-1} for cyclobutene.[39,40]



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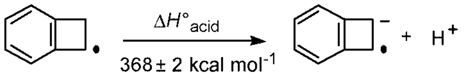

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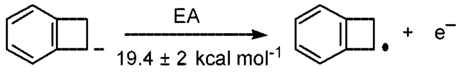

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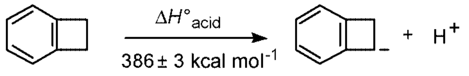

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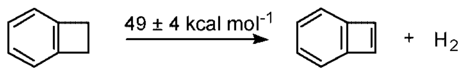
$$2H^+ + 2e^- \xrightarrow[\text{- BDE } H_2]{\text{- 2 IP (H•)}} H_2 \qquad (11)$$

-731.4kcal mol^{-1}



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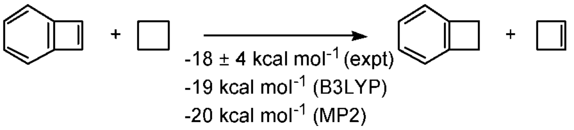
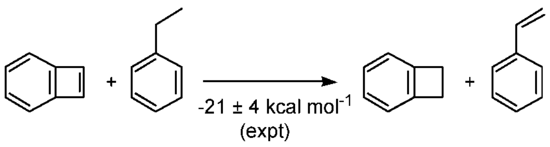
We are now in a position to comment upon the stability of benzocyclobutadiene. If one compares it with its saturated derivative in the following isodesmic reaction:



(13)

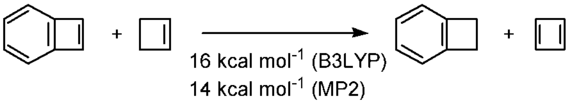
an antiaromatic destabilization energy (*ADE*) of 18 ± 4 kcal mol^{-1} is obtained. If one uses styrene as an acyclic analog an *ADE* of 21 ± 4 kcal mol^{-1} results. Likewise, an *ADE* of 19 kcal mol^{-1}



(14)

is obtained if one uses Benson's group equivalents to derive a strain and antiaromaticity-free energy for benzocyclobutadiene, and use the strain energy of benzocyclobutene (33.2 kcal mol^{-1}) plus the difference in strain between 3,4-dimethylenecyclobutene and cyclobutene (6.8 kcal mol^{-1}) for **1**.[41,42] In all three cases the ADE is around 19 kcal mol^{-1}, and thus based on the energy criterion for aromaticity and antiaromaticity, benzocyclobutadiene clearly is antiaromatic.

Benzocyclobutadiene also can be compared to cyclobutadiene in the following isodesmic reaction:



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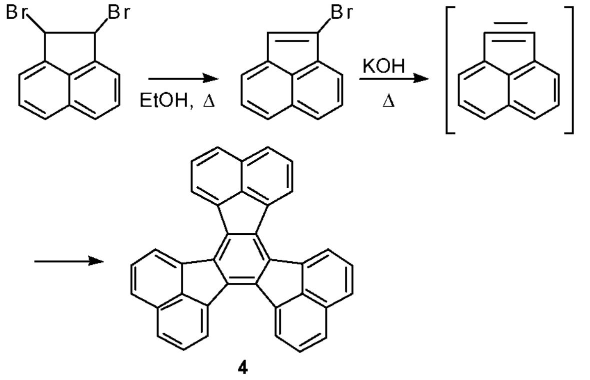
Given that both computational methods [B3LYP/6–31 + G(d) and MP2/6–31 + G(d)] reproduce the reaction energy in Eqn. (13), we expect that this difference should also be reliable. The computed energy in conjunction with our heat of formation for **1** and literature values for cyclobutene and benzocyclobutene enable us to derive a heat of formation for cyclobutadiene of 102 kcal mol^{-1} and an *ADE* of 38 kcal mol^{-1}. The former result is in excellent accord with G2 theory estimates of 101 and 102 kcal mol^{-1} for this quantity,[43,44] but is at the very lower limit of an estimated value of 114 ± 11 kcal mol^{-1} based on a photoacoustic experiment.[45] Consequently, an experimental determination of this number would be desirable.

Acenaphthyne

More than a century ago, Blumenthal[46] and later Dziewonski[47] attempted to prepare acenaphthyne (**2**) and postulated its existence on the basis of recovered trimer.[48,49] Since that time, numerous cycloalkynes have been studied,[48–50] and even a few transient cyclopentyne derivatives have been generated.[51–56] In 1981 Chapman and co-workers succeeded in synthesizing **2** under matrix-isolation conditions and reported its UV and IR spectra.[57] Upon warming the matrix, decacyclene (**4**) was obtained in accord with the earlier work on **2**. More recently, the trimerization of **2** has taken on renewed interest because **4** is a precursor to buckminsterfullerene fragments.[58] It therefore seemed of interest to find out how strained acenaphthyne really is by measuring its heat of formation. Such a determination would be difficult by conventional techniques, if not impossible, so we turned to our radical anion methodology and the use of an electron as a protecting group to obtain the desired energetics. In the process we also measured the vinyl C—H *BDE* of acenaphthylene (**5**), an abundant combustion by-product and known soil contaminant.[59–61]



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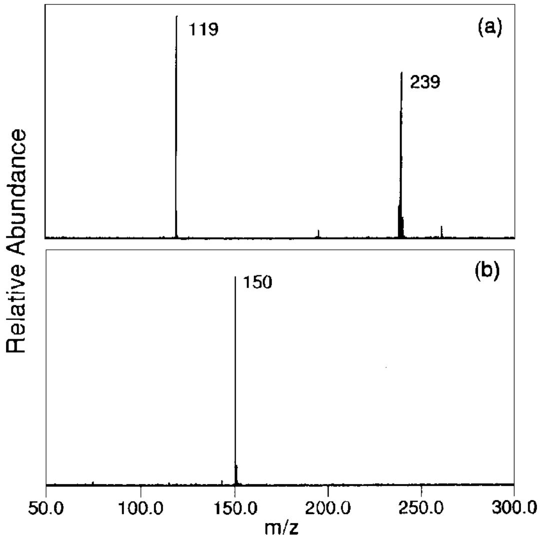
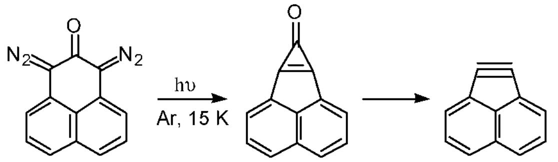


Figure 3. Generation of acenaphthyne radical anion (**2a**). (a) Initial mass spectrum. The ions at *m/z* 239 and 119 are the mono- and dicarboxylate anions of 1,2-acenaphthylenedicarboxylic acid. (b) Isolation of **2a** after sequential fragmentation of the dicarboxylate



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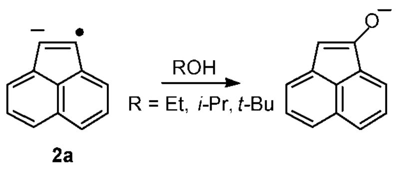
1,2-Acenaphthylenedicarboxylate (*m/z* 119) was sprayed into the gas phase from a slightly basic methanol–water (35:65, v/v) solution of the corresponding dicarboxylic acid.[7] This dianion was sequentially fragmented in an analogous manner to the pathways shown in Schemes 1 and 3 to afford an abundant signal of the desired acenaphthyne radical anion (**2a**, *m/z* 150) as shown in Fig. 3. To verify the structure of **2a** it was converted to acenaphthenone enolate in a process analogous to the conversion of **2** to acenaphthenone, and compared with an independently prepared sample.



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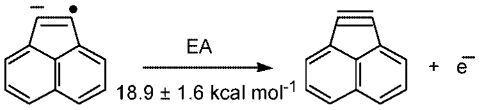
Acenaphthyne radical anion was reacted with a series of standard reference acids (Table 3) to determine the acidity of 1-acenaphthylenyl radical (**5r**). Since **2a** is able to deprotonate ethanol and stronger acids but not 1-pentyne and weaker acids, we assign $\Delta H^\circ_{\mathrm{acid}}(\mathbf{5r}) = 379 \pm 2\,\mathrm{kcal\,mol^{-1}}$. This value is in excellent accord with a computed acidity of $376.4\,\mathrm{kcal\,mol^{-1}}$ at the B3LYP/6–31 + G(d) level. In a similar manner (Table 4), the electron affinity of acenaphthyne was found to be 0.82 ± 0.07 eV. These data along with analogous results for acenaphthylene (**5**) were combined as shown below [along with Eqn. ((11))] to give a heat of hydrogenation for **2** of $98 \pm 4\,\mathrm{kcal\,mol^{-1}}$ and $\Delta H^\circ_f(\mathbf{2}) = 160 \pm 4\,\mathrm{kcal\,mol^{-1}}$.[7]



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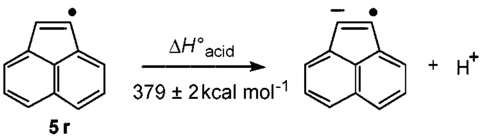

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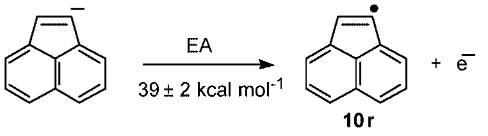

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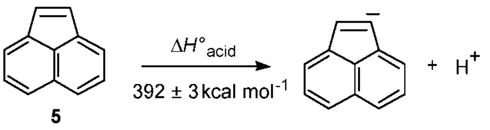

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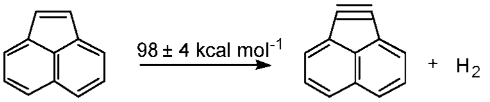


(23)

From these results, the first ($117 \pm 4\,\mathrm{kcal\,mol^{-1}}$) and second ($84 \pm 2\,\mathrm{kcal\,mol^{-1}}$) C—H *BDE*s of **5** can be derived, and the triple bond in **2** is found to be worth $33 \pm 4\,\mathrm{kcal\,mol^{-1}}$. This last quantity is significantly less than that for acetylene ($76\,\mathrm{kcal\,mol^{-1}}$)[62] but is about the same as that for *o*-benzyne ($36 \pm 3\,\mathrm{kcal\,mol^{-1}}$),[20] even though their heats of hydrogenation differ by $11 \pm 5\,\mathrm{kcal\,mol^{-1}}$; **2** has the larger value.

Table 3. Bracketing results for the acidity of 1-acenaphthylenyl radical (**5r**)

Reference acid	$\Delta H^\circ_{\mathrm{acid}}$ ($\mathrm{kcal\,mol^{-1}}$)[a]	Proton transfer
CD_3CN	372.9 ± 2.1[b]	Yes
$(CH_3)_3COH$	374.6 ± 2.1	Yes
$(CH_3)_2CHOH$	375.9 ± 1.2	Yes
CH_3CH_2OD	378.3 ± 1.0[b]	Yes
$CH_3CH_2CH_2C{\equiv}CH$	379.8 ± 2.5	No
CH_3OD	383.5 ± 0.7	No
C_6H_5F	387.2 ± 2.5	No
D_2O	392.9 ± 0.1	No

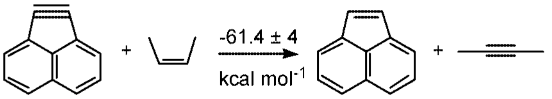
[a] Acidities taken from Ref. 1.

[b] Values for the protio reagent are given.

Table 4. Bracketing results for the electron affinity (*EA*) of acenaphthyne (**2**)

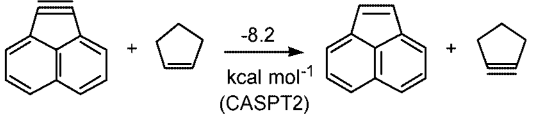
Reference compound	*EA* (eV)[a]	Electron transfer
Perfluorobenzonitrile	1.08 ± 0.11	Yes
Perfluorotoluene	0.86 ± 0.11	Yes
p,p′-Difluorobenzophenone	0.78 ± 0.05	No
o-Trifluoromethylbenzonitrile	0.70 ± 0.10	No
Perfluoropyridine	0.68 ± 0.11	No
Carbon disulfide	0.51 ± 0.10	No

The strain energy of acenaphthyne ($68\,\mathrm{kcal\,mol^{-1}}$) can be evaluated from the following isodesmic reaction if one corrects the reaction energy by adding the *SE* of **5** ($6.1\,\mathrm{kcal\,mol^{-1}}$):



(24)

Alternatively, one can use Benson's strain-free group equivalents[41,63] to derive $SE(\mathbf{2}) = 69\,\mathrm{kcal\,mol^{-1}}$. In contrast, cyclopentyne is predicted to have a strain energy of $59\,\mathrm{kcal\,mol^{-1}}$ after adjusting the computed CASPT2(4,4)/cc-pVDZ//CAS(4,4)/cc-pVDZ energy for Eqn. (25) to $-8.7\,\mathrm{kcal\,mol^{-1}}$



(25)

to account for the difference ($0.5\,\mathrm{kcal\,mol^{-1}}$) in strain between cyclopentene and acenaphthylene. Cyclopentyne thus appears to be less strained than previously suggested.[64] As for the difference in *SE* between acenaphthyne and cyclopentyne, it probably is best accounted for by hyperconjugation between the in-plane low-lying π^* orbital of the triple bond and the allylic C—H and C—C bonds. The somewhat greater flexibility of the latter compound should also be considered.

CONCLUSIONS

Radical anions can be selectively synthesized in the gas phase by a combination of ESI and CID of the resulting dianions. By measuring the proton affinities and electron binding energies of these species and combining these results in an appropriate thermodynamic cycle, the energetics of a wide variety of neutral molecules, including those with short lifetimes, can be determined. The electron can thus be viewed as a powerful protecting group. Applications of this methodology provide the heats of hydrogenation of benzocyclobutadiene (49 ± 4 kcal mol^{-1}) and acenaphthyne (98 ± 4 kcal mol^{-1}), and a variety of additional thermochemical data. Our results clearly indicate that benzocyclobutadiene is antiaromatic ($ADE \approx 19$ kcal mol^{-1}) based upon its energy relative to classical saturated and acyclic models. Acenaphthyne, on the other hand, is a highly strained cycloalkyne ($SE = 68$ kcal mol^{-1}), which is predicted to be 9 kcal mol^{-1} less stable than cyclopentyne. Hyperconjugation into the low-lying π^* orbital is the likely cause of this difference, although the additional flexibility of the latter compound is also a factor.

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