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# The Electron as a Protecting Group. 3. Generation of Acenaphthyne Radical Anion and the Determination of the Heat of Formation of a Strained Cycloalkyne

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**Abstract:** Acenaphthyne dicarboxylate (**12**) was transferred into the gas phase from solution via electrospray ionization and subsequently was sequentially fragmented in a Fourier transform mass spectrometer to afford acenaphthyne radical anion (**9**). Structural confirmation of **9** was achieved by converting it to acenaphthenone enolate (**13**) and demonstrating that this species is identical to the ion produced upon deprotonation of acenaphthenone (**5**). The reactivity of **9** was explored, and since an electron can serve as a protecting group, we were able to measure the heat of hydrogenation (98 ± 4 kcal mol$^{-1}$) and the heat of formation (160 ± 4 kcal mol$^{-1}$) of acenaphthyne (**1**) via the application of a thermodynamic cycle. Its strain energy (68 kcal mol$^{-1}$) and acenaphthylene's (**10H**) first and second C−H bond dissociation energies (117 ± 4 and 84 ± 2 kcal mol$^{-1}$) also were obtained. Ab initio and density functional theory calculations were carried out on the species of interest to explore their geometries and energetics. Our results were interpreted in comparison to cyclopentyne, and its predicted heat of formation (98 kcal mol$^{-1}$) and strain energy (59 kcal mol$^{-1}$) are reported.

## Introduction

Cycloalkynes have been studied over the years in an attempt to understand molecular strain and its ramifications. The synthetic challenges, enhanced reactivity, distorted geometries, and unique properties of this class of compounds have been the subject of several reviews.[1−3] Cyclooctyne can be isolated[4] whereas the seven-, six-, and five-membered-ring analogues only have been observed in low-temperature matrixes or their existence as transient intermediates has been substantiated by trapping and isotopic labeling studies.[5−12] Despite extensive efforts, cyclobutyne or a derivative of it remains elusive,[13,14] and singlet cyclopropyne is predicted not to be a minimum on the potential energy surface.[15,16]

Acenaphthyne (**1**) is one of a few cyclopentyne derivatives that have been generated. Other examples include norbornyne,[17,18] norbornenyne,[19] benzocyclopentyne,[20] and 2,2,5,5-tetramethyl-1-thiacyclopentyne.[21] Approximately a century after the existence of **1** was postulated based on the recovery of trimer **2**,[22,23] Chapman and co-workers succeeded in obtaining the first spectroscopic data (UV and IR) of **1**.[24] It was generated in an argon matrix at 15 K upon irradiation of bis(diazo) ketone **3** and subsequent loss of carbon monoxide from **4** (eq 1). The cyclopentyne moiety of **1** was found to react with water to give acenaphthenone (**5**) plus a hydrated dimer and with oxygen to afford acenaphthoquinone (**6**, eq 2). Decacyclene (**2**) was recovered when the matrix was allowed to warm to room temperature. The formation of **2** has served as indirect evidence for the generation of acenaphthyne in other work. Specifically, **2** has been observed upon thermolysis of bis(tosylhydrazone) salt **7**, reaction of dibromosulfone **8** with base, and deoxygenation of **6** with titanium(0) or phosphorus pentasulfide (Figure 1).[25−27] The last approach has received recent attention as **2**

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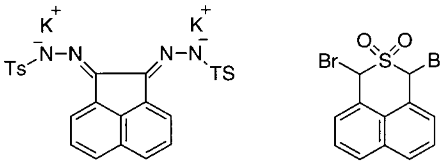
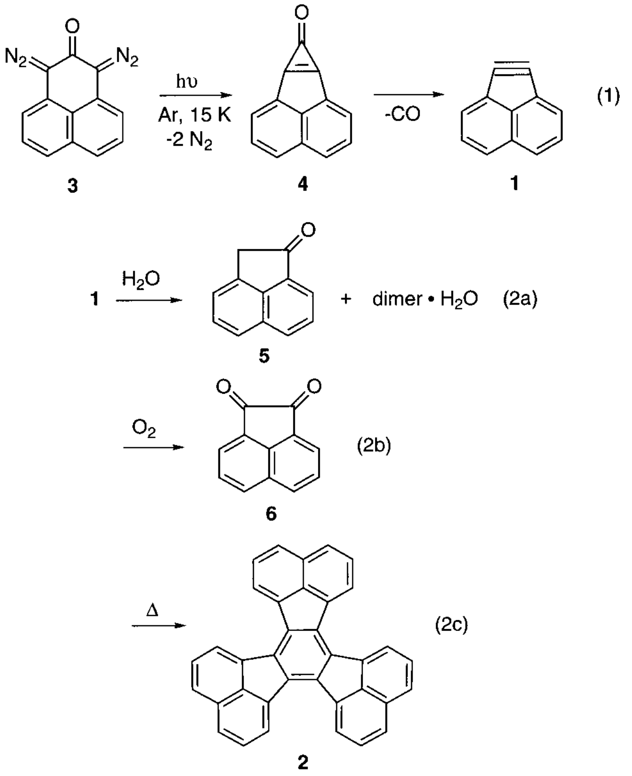


**7** **8**

**Figure 1.** Additional precursors of **2** in which **1** is a proposed intermediate.

has been shown to be a precursor for the synthesis of buckminsterfullerene fragments.[28] At present, successful trapping of **1** with a diene has not been reported.[26,29]



Several probes have been used to assess the strain energy in cycloalkynes: heats of hydrogenation, competitive reactivity studies, correlation of $^{13}$C NMR chemical shifts, frequencies of the carbon–carbon triple bond stretch in IR spectroscopy, and energies of the lowest unoccupied molecular orbitals (LUMO).[2] We were interested in measuring the heat of formation and thus the heat of hydrogenation of acenaphthyne. Previous work with **1** indicates that it would be difficult, if not impossible, to obtain these data by conventional approaches. Therefore, we proposed to use the electron as a protecting group and generate acenaphthyne radical anion (**9**) in a Fourier transform mass spectrometer.[30–32] Measurement of the proton affinity and electron binding energy of this ion provide a means via a thermodynamic cycle to afford the desired thermochemical data for **1**. In the course of this work, we also explored the thermochemistry of acenaphthylene (**10H**) which is an abundant species in combustion processes as well as a known soil contaminant.[33–35] High-level ab initio and density functional theory calculations have been carried out to explore the geometries and energetics of the species studied. Our results are interpreted in comparison to cyclopentyne.

## Experimental Section

1,2-Acenaphthylene dicarboxylic acid (**11**) was prepared in three steps from acenaphthene according to literature procedures.[36,37] All reagents were used as received except for chlorotrimethylsilane which was distilled from quinoline. The acenaphthene impurity (20%) present in commercial acenaphthylene was carried along the synthetic sequence and ultimately separated from the trimethylsilyl derivative **15**. NMR spectra were collected on a Varian VXR-300 spectrometer and are reported in ppm ($\delta$). Infrared data were recorded on a Perkin-Elmer 1600 Series FTIR and the output is given in wavenumbers (cm$^{-1}$). High-resolution mass spectra were obtained on a Finnigan 2001 FTMS or MAT 95.

**Acenaphthenone (5).** Acenaphthenol (0.19 g, 1 mmol) was dissolved in warm ether, the mixture was cooled to 0 °C, and 1.2 mL of an acidic dichromate solution was added. The oxidizing solution was prepared by dissolving 1.0 g of sodium dichromate in 4 mL of water and 0.8 mL of sulfuric acid. After being stirred for ~15 min, the reaction mixture was extracted twice with ether. The combined organic layer was washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated by rotary evaporation. The resulting ketone was purified by column chromatography using 0–10% ethyl acetate in hexanes as the eluting solvent to give 0.12 g (71%) of a white solid product, mp = 119.5–120.5 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.09 (d, $J$ = 8.1 Hz, 1H), 7.96 (dd, $J$ = 6.9 and 0.9 Hz, 1H), 7.82 (d, $J$ = 8.4 Hz, 1H), 7.72 (dd, $J$ = 8.1 and 6.9 Hz, 1H), 7.60 (dd, $J$ = 8.4 and 6.9 Hz, 1H), 7.47 (dd, $J$ = 6.9 and 0.9 Hz, 1H), 3.83 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 203.0, 143.0, 135.0, 134.7, 131.5, 131.0, 128.4, 128.0, 124.0, 121.5, 121.1, 42.0; IR (KBr) 1715, 1651, 1539, 1494, 1362, 1261, 1000, 823, 775 cm$^{-1}$; HRMS-EI $(M)^{+\bullet}$ calcd for $C_{12}H_8O$ 168.0575, obsd 168.0580.

***trans*-1,2-Dibromoacenaphthene.** Acenaphthylene (1.5 g, 9.8 mmol) was dissolved in THF (40 mL) and the mixture cooled to −78 °C. A solution of pyridinium tribromide (3.1 g, 11 mmol) in 15 mL of THF was then added dropwise, and the mixture was allowed to slowly warm to room-temperature overnight. The crude product was diluted with hexanes (~20 mL) and washed with aqueous sodium hydrosulfite (2×), water, and saturated NaCl. The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporation to afford 2.9 g (93%) of a light brown solid sufficiently clean to be carried on. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.84 (d, $J$ = 3 Hz, 2H), 7.82 (d, $J$ = 3 Hz, 2H), 7.62 (t, $J$ = 3 Hz, 2H), 6.05 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 140.5, 134.9, 131.0, 128.9, 126.0, 122.7, 55.0; HRMS-EI $(M)^{+\bullet}$ calcd for $C_{12}H_8Br_2$ 309.8993, obsd 309.8993.

**1-Bromoacenaphthylene.** A mixture of *trans*-1,2-dibromoacenaphthene (0.5 g, 1.6 mmol), diazobicyclo[5.4.0]undec-7-ene (DBU) (0.3 g, 1.9 mmol), and 35 mL of DMF was heated at 85 °C for 3 h. The reaction was allowed to cool and then poured into ice water. The product was extracted (2×) with a mixture of ether and hexanes. The combined

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(30) Anions often are easier to generate and less prone to rearrangements and fragmentations than their neutral counterparts. They also can be used to probe neutral molecules. Consequently, the electron can be viewed as a protecting group. While we are not aware of this terminology being used before, the concept of using anions to probe neutral molecules is not new and many examples can be found in the literature. For instance, see refs 31 and 32 (parts 1 and 2 of this series), and references therein.

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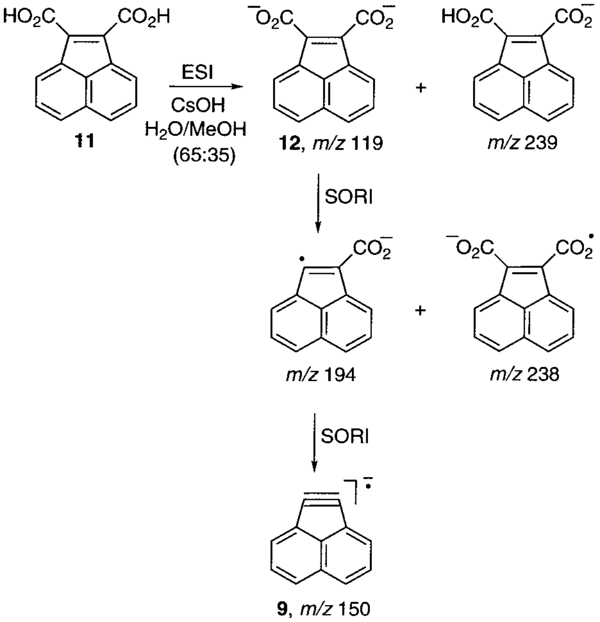
organic layer was washed with water, 1 M HCl, water, saturated $NaHCO_3$, and saturated NaCl, and then dried over $MgSO_4$ and concentrated by rotary evaporation. The crude product was purified by flash chromatography with hexanes as the eluting solvent to afford 0.31 g (81%) of a yellow oil. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.87 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.70 (d, $J = 6.6$ Hz, 1H), 7.62 (d, $J = 6.9$ Hz, 1H), 7.61 (dd, $J = 8.1$ and 6.9 Hz, 1H), 7.51 (dd, $J = 8.1$ and 6.6 Hz, 1H), 7.16 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 138.3, 138.0, 129.0, 128.6, 128.0, 127.7, 127.1, 123.7, 123.5, 122.3, 120.8, 119.2; IR (neat) 3039, 1427, 1262, 1029, 832, 765, 727 cm$^{-1}$; HRMS-CI (4% ammonia in methane mixture) $(M + H)^+$ calcd for $C_{12}H_8Br$ 230.9809, obsd 230.9802.

**1-Trimethylsilylacenaphthylene (15).** 1-Bromoacenaphthylene (0.59 g, 2.6 mmol) was dissolved in 60 mL of anhydrous THF and cooled to $-78$ °C. *n*-Butyllithium (2.5 M in hexanes, 1.1 mL) was added and the mixture was stirred for 1 h. Chlorotrimethylsilane (0.9 g, 8 mmol) was then added and the reaction was allowed to slowly warm to room-temperature overnight. The crude product was diluted with hexanes and washed with 1 M HCl and water. The organic material was dried over $MgSO_4$ and concentrated by rotary evaporation. Purification by column chromatography with hexanes afforded 0.49 g (85%) of the desired silane as a yellow oil. For the gas-phase experiments, the compound was further purified by medium-pressure liquid chromatography again using hexanes as the eluent. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J = 8.1$ Hz, 2H), 7.74 (d, $J = 6.9$ Hz, 1H), 7.66 (d, $J = 6.6$ Hz, 1H), 7.55 (dd, $J = 8.1$ and 6.9 Hz, 1H), 7.53 (dd, $J = 8.1$ and 6.6 Hz, 1H), 7.25 (s, 1H), 0.39 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 143.4, 143.2, 140.5, 137.9, 130.4, 128.5, 127.83, 127.77, 127.3, 126.9, 124.8, 123.6, $-0.15$; IR (neat) 3037, 2954, 1482, 1427, 1249, 1150, 931, 838, 770, 755 cm$^{-1}$; HRMS-EI $(M)^{+\bullet}$ calcd for $C_{15}H_{16}Si$ 224.1021, obsd 224.1042.

**Gas-Phase Experiments.** All work was carried out in a dual cell Finnigan Model 2001 Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet and interfaced with a custom-built Analytica electrospray ionization (ESI) source. Acenaphthylene dicarboxylate was sprayed (3 $\mu$L/min) into the gas phase from a 750 $\mu$M solution of the diacid in methanol$-$water (35:65 v/v) which contained 2 equiv of cesium hydroxide (pH 8$-$9). Ions were accumulated for 0.5 s in the hexapole of the ESI source and then allowed to travel to the FTMS cell during a 45 $\mu$s period (time-of-flight). The following typical settings for the ESI source were found to give optimal signal of acenaphthylene dicarboxylate: cylinder (needle housing) 2.6 kV, end plate 3.6 kV, capillary 6.0 kV (front) and $-36$ V (back), skimmer cone $-11$ V, acceleration lenses 319 V, deceleration lenses 19.0 V, and high voltage element in acceleration/deceleration lens stack 1.35 kV. Fluoride ion was prepared by electron ionization of carbon tetrafluoride at 6 eV and used to generate **10** and **13** upon reaction with 1-trimethylsilylacenaphthylene and acenaphthenone, respectively. In general, ions of interest were isolated by ejecting unwanted species with a SWIFT waveform[38] or a chirp broad band excitation[39] for low masses and were vibrationally cooled with pulses of argon ($10^{-5}$ Torr). Neutral reagents were introduced via slow leak or pulsed valves, and all reactions were monitored as a function of time.

**Computations.** All calculations were performed with Gaussian98[40] installed on IBM and SGI workstations. Geometries were optimized by using the B3LYP functional and the 6-31+G(d) basis set,[41] and the nature of stationary points was investigated by a full vibrational analysis. Zero-point-energy corrections were made in all cases, and for computing acidities the energies were adjusted to 298 K. The structures of acenaphthyne (**1**) and cyclopentyne (**16**) and their alkene analogues (**10H** and **17**) were also investigated at the CAS(4,4)/cc-pVDZ and CAS(2,2)/cc-pVDZ levels of theory, respectively, and the energies were corrected with zero-point energies from BPW91/cc-pVDZ optimized geometries.[42,43] For these calculations, the active space was comprised of the C1$-$C2 $\pi$ bonding and antibonding orbitals. Dynamic electron correlation was accounted for by carrying out CASPT2 calculations on the CAS structures.[44]

**Scheme 1.** Synthesis of Acenaphthyne Radical Anion (**9**)



## Results and Discussion

We have generated the radical anion of acenaphthyne (**9**) in a Fourier transform mass spectrometer (FTMS) and explored its reactivity and thermochemistry to gain insight into the corresponding neutral cyclopentyne (i.e., **1**). A methodology recently developed in our laboratory was used to prepare **9** (Scheme 1).[31] Specifically, dicarboxylate **12** (*m*/*z* 119) was sprayed from a basic solution of diacid **11** into our FTMS where it was isolated and then fragmented by sustained off-resonance irradiation (SORI).[45] This technique involves kinetically exciting an ion by applying energy to its cyclotron frequency off-resonance in the presence of an inert collision gas. In this case, application of 1.3 eV (lab) of energy for 30 ms concurrent with a pulse of argon ($\sim 10^{-5}$ Torr) led to the loss of carbon dioxide and an electron (*m*/*z* 194). Further excitation (1.1 eV (lab) for 10 ms) afforded the desired ion **9** (*m*/*z* 150, Scheme 1, and Figure 2). On-resonance irradiation of **12** gives **9** directly, but the efficiency of this process is considerably lower than that of the stepwise route. In addition to the loss of an electron and carbon dioxide, electron detachment of dicarboxylate dianion **12** without fragmentation to yield the corresponding radical anion at *m*/*z* 238 is a minor dissociation pathway.

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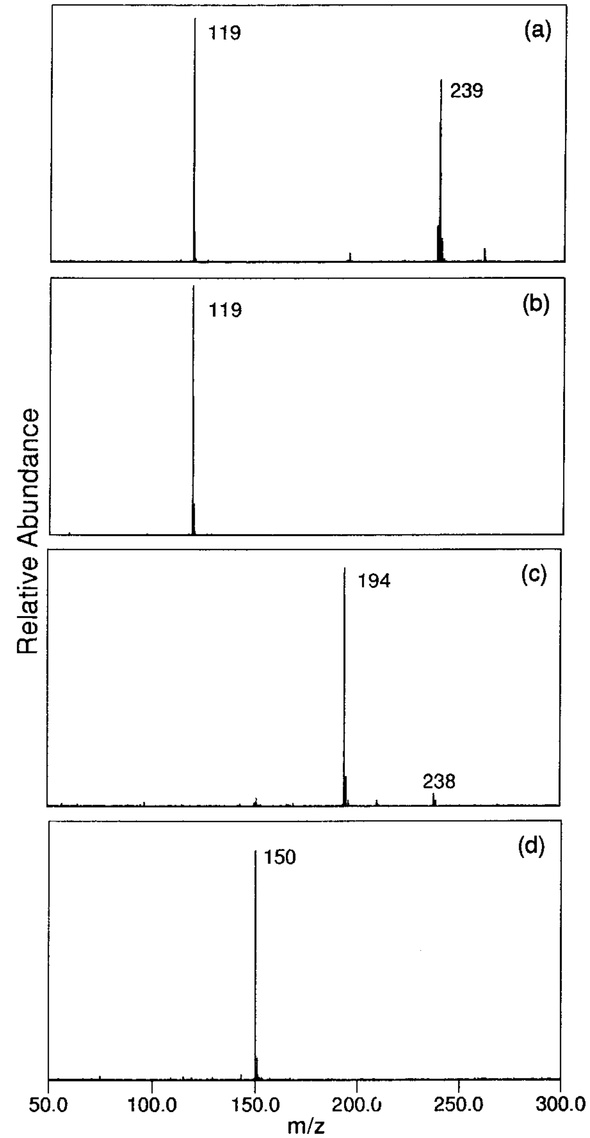


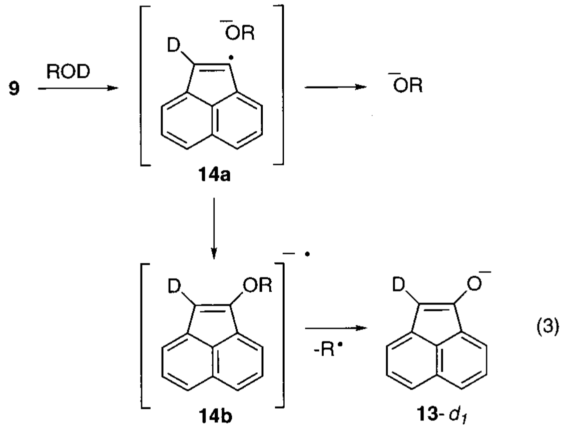
**Figure 2.** (a) Spectrum obtained upon electrospray ionization of the dicesium salt of 1,2-acenaphthylene dicarboxylic acid. Dicarboxylate **11** is at *m*/*z* 119 and the protonated dianion is at *m*/*z* 239. (b) Isolation of **11**. (c) Spectrum obtained upon SORI of **11**, *m*/*z* 238 and 194 correspond to loss of an electron, and carbon dioxide and an electron, respectively. (d) SORI dissociation of *m*/*z* 194 and isolation of acenaphthyne radical anion (**9**, *m*/*z* 150).

**Table 1.** Summary of Deuteron Transfer and Hydrogen−Deuterium Exchange Results for Enolate **13** Generated upon Reaction of **9** with *tert*-Butyl Alcohol (Derivative) and by Deprotonation of **5** (Authentic)

| | | derivative | | authentic | |
|---|---|---|---|---|---|
| acid | $\Delta H°_{acid}$[a] | $D^+$ transfer | H/D exchange[b] | $D^+$ transfer | H/D exchange |
| $CF_3CH_2OD$ | 361.8 ± 2.5 | no | no | no | no |
| $(CH_3)_3CSD$ | 352.5 ± 2.2 | no | no | no | no |
| $C_6H_5OD$ | 349.2 ± 2.1 | slow | yes, 1 | slow | yes, 1 |
| $CD_3CO_2D$ | 348.6 ± 2.9 | yes | no | yes | no |

[a] Acidities are for the protio reagents and are in kcal $mol^{-1}$. They are taken from ref 51. [b] For these experiments, **13**-$d_1$ was prepared and reacted with the protio reference acid. This was done because the experiment was carried out in one cell; *tert*-butyl alcohol-OD was pulsed at pressures of $1 \times 10^{-6}$ Torr and the reference acid was present at $4 \times 10^{-8}$ Torr.

To verify the structure of acenaphthyne radical anion (**9**), it was derivatized to acenaphthenone enolate (**13**) and compared with an authentic sample. Ion **9** was found to readily afford **13** upon reaction with alcohols (eq 3); this reactivity is analogous to the conversion of neutral acenaphthyne to acenaphthenone upon reaction with water. A plausible mechanism for this transformation is initial proton (or deuteron if ROD is employed) transfer to afford intermediate **14a** which may dissociate to give $RO^-$ or combine to lead to adduct **14b**. Subsequent fragmentation of $R^•$ yields acenaphthenone enolate (**13**).[46] The reactivity of **13** formed in this way was found to be identical with that observed for the ion generated upon deprotonation of acenaphthenone with fluoride ion. In both cases the enolate undergoes one hydrogen−deuterium exchange with phenol-OD as well as a small amount of deuteron transfer (Table 1). The latter reaction channel is observed with acetic acid-$d_4$, but not with compounds whose $\Delta H°_{acid}$ is larger than 350 kcal $mol^{-1}$, which leads to a bracketed acidity of 349 ± 2 kcal $mol^{-1}$ for acenaphthenone. Enolate **13** is rather robust and does not react with dimethyl disulfide or neopentyl nitrite in the manner characteristic of more basic enolates that possess an α hydrogen.[47,48] Moreover, fragments of **13** are not observed under CID or SORI conditions, and large energies (>25 eV (lab)) are required to produce ion signal loss.[49]



(3)

R = $C_2H_5$, $(CH_3)_2CH$, $(CH_3)_3C$, $FCH_2CH_2$, $CF_3CH_2$

With confirmation of its structure, we began to explore the thermochemistry of acenaphthyne radical anion. The proton affinity of **9** or, equivalently, $\Delta H°_{acid}$ of its conjugate acid (**10r**), was measured by the bracketing method. This involves reacting **9** with a series of reference acids and monitoring the occurrence or nonoccurrence of proton transfer (Table 2). Acenaphthyne radical anion was found to deprotonate ethanol and stronger acids which allows us to assign $\Delta H°_{acid}$(**10r**) = 379 ± 2 kcal $mol^{-1}$.[50,51] This result can be compared with a 298 K computed value of 376.4 kcal $mol^{-1}$ at the B3LYP/6-31+G(d) level. In accord with its proton affinity, **9** is able to undergo up to four hydrogen−deuterium exchanges at less acidic sites with deuterium oxide.[52] It is also worth noting that **9** reacts with methanol-OD primarily by a reaction channel that produces

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(46) For a related mechanistic discussion addressing the reactivity of *o*-benzyne radical anion with alcohols, see: Guo, Y.; Grabowski, J. J. *J. Am. Chem. Soc.* **1991**, *113*, 5923−5931.

(47) King, G. K.; Maricq, M. M.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 7133−7140.

(48) Grabowski, J. J.; Zhang, L. *J. Am. Chem. Soc.* **1989**, *111*, 1193−1203.

(49) This behavior contrasts with 1- and 2-naphthoxide which (1) do not undergo H/D exchange, (2) are less basic (PA = 344 ± 2 kcal $mol^{-1}$), and (3) give fragment ions upon collision-induced dissociation. See ref 31 for additional details.

**Table 2.** Results for the Proton Affinity Bracketing of **9**

| acid | $\Delta H^\circ_{acid}$ (kcal mol$^{-1}$)[a] | proton transfer |
|---|---|---|
| $ND_3$ | 403.6 ± 0.8 | no |
| $D_2O$ | 392.9 ± 0.1 | no[b] |
| $C_6H_5F$ | 387.2 ± 2.5 | no |
| $CH_3OD$ | 383.5 ± 0.7 | no[c] |
| $CH_3CH_2CH_2C{\equiv}CH$ | 379.8 ± 2.5 | no |
| $CH_3CH_2OD$ | 378.3 ± 1.0 | yes |
| $(CH_3)_2CHOH$ | 375.9 ± 1.2 | yes |
| $(CH_3)_3COH$ | 374.6 ± 2.1 | yes |
| $CD_3CN$ | 372.9 ± 2.1 | yes[d] |
| $FCH_2CH_2OH$ | 371.2 ± 2.9 | yes[e] |
| $C_6H_5C{\equiv}CH$ | 370.7 ± 2.3 | yes |
| $CF_3CH_2OH$ | 361.8 ± 2.5 | yes |

[a] Values taken from ref 51. [b] Four hydrogen−deuterium exchanges are observed. [c] Reaction leads to loss of the ion signal, see text. [d] Cyanide ion is the major product (ratio 2:1). [e] Ions at *m*/*z* 39 and 83 which are assigned as $HF{\cdot}F^-$ and $HF{\cdot}FCH_2CH_2O^-$ clusters also are observed and both make up 7% of the relative product distribution.

**Table 3.** Product Distributions in the Reaction of **9** with Alcohols at a Pressure of 3 × $10^{-8}$ Torr[a]

| alcohol (ROH) | % proton transfer | % enolate **13** formation | BDE (RH), kcal mol$^{-1}$ |
|---|---|---|---|
| $C_2H_5OH$ | 37 | 63 | 101.1 ± 0.4 |
| $(CH_3)_2CHOH$ | 22 | 78 | 97.8 ± 0.5 |
| $(CH_3)_3COH$ | 8 | 92 | 96.6 ± 0.3 |
| $FCH_2CH_2OH$ | 20 | 80 | |
| $CF_3CH_2OH$ | 76 | 24 | 106.7 ± 1.1 |

[a] Bond energies are taken from ref 55.

virtually no ionic (detectable) products; a small trace of enolate **13** is observed. Based on similar reactivity studies with benzyne and benzocyclobutadiene radical anions, the former pathway is assumed to be net abstraction of a molecule of hydrogen from methanol to afford acenaphthylene (**10H**), formaldehyde, and an electron.[32,46] Strained cycloalkynes also dehydrogenate alcohols in the condensed phase.[53,54] As mentioned earlier, **9** reacts with the other reference alcohols to give enolate **13** (eq 3). The product distributions were found to correlate empirically with the corresponding R−H bond dissociation energies (BDEs, Table 3). For example, enolate formation accounts for 92% of the products with *tert*-butyl alcohol (BDE($(CH_3)_3C{-}H$) = 96.6 ± 0.3 kcal mol$^{-1}$) whereas with 2,2,2-trifluoroethanol this value is only 24% (BDE($CF_3CH_2O{-}H$) = 106.7 ± 1.1 kcal mol$^{-1}$).[55]

**Table 4.** Results for the Electron Affinity Bracketing of **1**

| compd | EA (eV)[a] | electron transfer |
|---|---|---|
| carbon disulfide | 0.51 ± 0.10 | no |
| perfluoropyridine | 0.68 ± 0.11 | no |
| *o*-trifluoromethylbenzonitrile | 0.70 ± 0.10 | no |
| *p,p′*-difluorobenzophenone | 0.78 ± 0.05 | no |
| perfluorotoluene | 0.86 ± 0.11 | yes |
| perfluorobenzonitrile | 1.08 ± 0.11 | yes |

[a] Values taken from ref 51.

The electron binding energy of **9**, or equivalently, the electron affinity (EA) of **1**, was determined by the bracketing method as well. Acenaphthyne radical anion was found to undergo electron transfer with perfluorotoluene and perfluorobenzonitrile, but not with other compounds whose radical anions have smaller electron binding energies (Table 4). These results lead to a value of 0.82 ± 0.07 eV (18.9 ± 1.6 kcal mol$^{-1}$) for the EA of **1**.[56] Although the B3LYP hybrid functional generally reproduces experimental electron affinities,[57] it does a poor job (44.4 kcal mol$^{-1}$) in this instance. Given that the substrate is a ground-state singlet with considerable biradical character, this failing is not surprising because the Hartree−Fock part of the B3LYP hybrid functional is a single determinant method that is inadequate in this case. Similar errors are observed with *o*-benzyne, EA = 13.0 ± 0.2 (expt) and 20.5 kcal mol$^{-1}$ (B3LYP/6-31+G(d)), and related molecules.[58,59] One approach to avoid this difficulty that has been successfully employed in some cases is to compute the energy difference between the radical anion and its corresponding neutral in its triplet electronic state and then subtract the singlet−triplet (S−T) gap obtained by some other means (i.e., experiment or a different level of theory).[31,60] Application of this approach to acenaphthyne gives mixed results. In particular, using a B3LYP/aug-cc-pVDZ value of 58.7 kcal mol$^{-1}$ for the energy difference between **9** and $^3$**1**[61] and the experimentally determined S−T gap for *o*-benzyne (37.5 ± 0.3 kcal mol$^{-1}$)[59] as an estimate for the value of **1**, gives an EA of 21.2 kcal mol$^{-1}$ for **1** in good accord with experiment. If, on the other hand, one uses computed BPW91/cc-pVDZ or CASPT2(4,4)/cc-pVDZ//CAS(4,4)/cc-pVDZ singlet−triplet gaps (13.9 and 22.1 kcal mol$^{-1}$, respectively) and corrects (adds) for the previously reported errors for *o*-benzyne (6.3 and 7.1 kcal mol$^{-1}$, respectively),[62,63] one obtains electron affinities of 38.5 and 29.5 kcal mol$^{-1}$ which are in poor agreement with experiment. These results suggest that S−T gaps obtained at the BPW91/cc-pVDZ and CASPT2/cc-pVDZ (with small active spaces) levels may not be generally reliable despite previous successes.[64−68]

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(50) Isomerization of **9** to an *o*-aryne radical anion can be ruled out on the basis of our chemical derivatization experiment. In addition, (1) *o*-aryne radical anions derived from naphthalene do not undergo H/D exchange with $D_2O$, more acidic reagents are needed. (2) *o*-Aryne radical anions derived from naphthalene react differently with a wide variety of reagents (e.g., ROH, $SO_2$, $CS_2$, MeSSMe, etc.). See ref 31 for further details. (3) The computed PA of 371.3 kcal mol$^{-1}$ for 6,7-dehydroacenaphthylene (using the numbering scheme in Table 5) is 5.1 kcal mol$^{-1}$ smaller than that for **9** and is in poor agreement with experiment.

(51) All acidities, unless otherwise noted, come from the following: Bartmess, J. E. In *Secondary NIST Chemistry WebBook*; NIST Standard Reference Database Number 69, Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg MD 20899 (http://webbook.nist.gov).

(52) Following the numbering scheme in Table 5 and defining the radical site to be C1, the acidity at C6 in **10r** is computed to be 382.9 kcal mol$^{-1}$ (B3LYP/6-31+G(d)). This indicates that isomerization of **9** to a 1,*n* radical anion is endothermic. H/D exchange can take place, nevertheless, because $D_2O$ is capable of exchanging less acidic sites in a molecule. For example, see: Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 4256−4258.

(53) Krebs, A.; Colberg, H. *Chem. Ber.* **1980**, *113*, 2007−2014.

(54) Spang, W.; Hanack, M. *Chem. Ber.* **1980**, *113*, 2025−2027.

(55) Second electronic edition: Lide, D. L. In *CRC Handbook of Chemistry and Physics*, 80th ed.; CRC Press: Boca Raton, FL, 1999. See: http://www.knovel.com/knovel/Databook/default.htm?WCI=BrowseBook&WCE=34&WCU=1.

(56) The reaction between **9** and perfluorotoluene is fast (≥∼5 × $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) indicating that electron transfer is exothermic. The electron affinities and their uncertainties were assigned by using the following relationships: $\bar{y} = (y_1 + y_2)/2$ and $\Delta y = [\{(y_1 - y_2)/2\}^2 + (\{(\Delta y_1^2 + \Delta y_2^2)^{1/2}\}/2)^2]^{1/2}$ where, for example, $y_1 \pm \Delta y_1 = 0.86 \pm 0.11$ eV and $y_2 \pm \Delta y_2 = 0.78 \pm 0.05$ eV.

(57) Merrill, G. N.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 12322−12337.

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

(59) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 5279−5290.

(60) This approach for computing electron affinities was suggested to us by Prof. W. T. Borden.

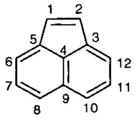
(61) B3LYP/6-31+G(d) zero-point energies were used and the same energy difference is obtained by using a larger triple-ζ basis set (i.e., B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVDZ).

(62) The latter error was obtained at the CASPT2(8,8)/cc-pVDZ//CAS-(8,8)/cc-pVDZ level, see ref 63.

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

(64) Cramer, C. J.; Squires, R. R. *J. Phys. Chem. A* **1997**, *101*, 9191−9194.

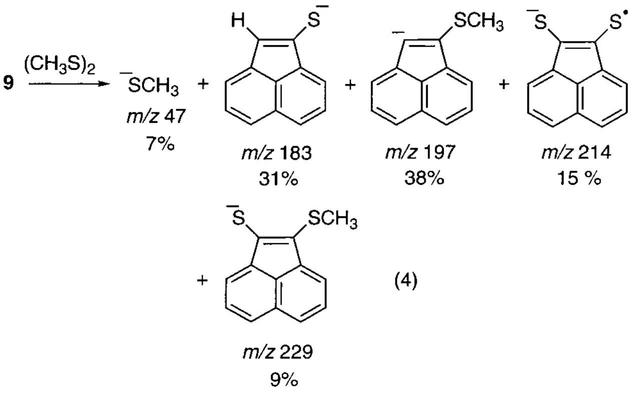
**Table 5.** Calculated Acidities at 298 K for the Various Positions in Acenaphthylene at the B3LYP/6-31+G(d) Level of Theory



**10H**

| position | $\Delta H^\circ_{acid}$(kcal mol$^{-1}$) |
|---|---|
| **1** | 390.4 |
| **6** | 388.0 |
| **7** | 392.0 |
| **8** | 388.8 |

The reactivity of **9** was briefly explored. Analogous to the chemistry observed with alcohols, **9** undergoes proton transfer and $S^{\bullet-}$ abstraction with 2-propanethiol to afford the corresponding thioenolate at *m*/*z* 183. Upon reaction with sulfur dioxide the ion signal for **9** is quenched and only a small amount of atomic sulfur radical anion is detected. Presumably, acenaphthoquinone (**6**) which arises from abstraction of two oxygen atoms from $SO_2$ is the neutral product. Signal loss also is observed with carbonyl sulfide and carbon disulfide, two commonly used probe reagents. Products arising from the reaction of **9** with dimethyl disulfide and neopentyl nitrite were found to be plentiful and illustrate **9**'s radical behavior. The assigned structures of the products in the former reaction and their relative amounts after a 4 s reaction period are given in eq 4; the dominant ions correspond to net addition of $SCH_3$ (*m*/*z* 197, 38%) and SH (*m*/*z* 183, 31%). With neopentyl nitrite, abstraction of NO is observed along with other products.



(4)

**Table 6.** Results for the Proton Affinity Bracketing of **10**

| acid | $\Delta H^\circ_{acid}$ (kcal mol$^{-1}$)[a] | proton transfer | H/D exchange |
|---|---|---|---|
| $ND_3$ | 403.6 ± 0.8[b] | no | 3 |
| $(CH_3)_2ND$ | 396.5 ± 0.7[b] | no | 3 |
| $D_2O$ | 392.9 ± 0.1 | slow[c] | 7 |
| $H_2O$ | 390.7 ± 0.1 | slow[d] | |
| $C_6H_5F$ | 387.2 ± 2.5 | yes | |
| $CH_3OD$ | 383.5 ± 0.7 | yes | no |

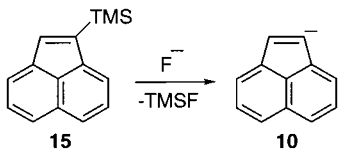
[a] Acidities are taken from ref 51. [b] Values for the protio reagents are given. [c] After a 4 s reaction period with $D_2O$ ($8 \times 10^{-8}$ Torr), $OD^-$ (16%), H/D exchange (73%), and an adduct (11%) are observed. [d] After a 8 s reaction period with $H_2O$ ($4 \times 10^{-8}$ Torr), $OH^-$ (13%), the starting (or an isomerized) ion (76%), and an adduct (11%) are observed.

**Table 7.** Results for the Electron Affinity Bracketing of **10r**

| compd | EA (eV)[a] | electron transfer |
|---|---|---|
| sulfur dioxide | 1.11 ± 0.01 | no |
| perfluoronitrobenzene | 1.45 ± 0.11 | no |
| perfluorobenzophenone | 1.52 ± 0.11 | no |
| tetramethyl-*p*-benzoquinone | 1.62 ± 0.06 | no |
| 2,5-dimethyl-*p*-benzoquinone | 1.76 ± 0.06 | yes |
| 2-methyl-*p*-benzoquinone | 1.85 ± 0.09 | yes |

[a] Values from ref 51.

To measure the heat of hydrogenation of acenaphthyne, we needed the C1−H bond energy of acenaphthylene (**10H**). This was obtained by carrying out measurements on acenaphthyl anion **10**. Since the computed acidities for the various positions in **10H** (Table 5) are similar and suggest that a mixture of ions would be generated upon deprotonation, we prepared the desired ion at C1 by fluoride-induced desilylation of 1-trimethylsilylacenaphthylene (**15**, eq 5).



(5)

The necessary thermochemistry for **10** was obtained by the bracketing method. The proton affinity of **10** was assigned to be 392 ± 3 kcal mol$^{-1}$ based on the following observations (Table 6). The ion deprotonates fluorobenzene and methanol-OD as well as deuterium oxide and water to a small extent. While an acid-catalyzed isomerization of the 1-anion to the 6 position (Table 5) may be taking place, the observation of three hydrogen−deuterium exchanges with dimethylamine-$d_1$ indicates that these two positions must be very similar (0−2 kcal mol$^{-1}$) in acidity. As is often the case, deuterium oxide exchanges several different sites and all seven hydrogens can be replaced with deuteriums. The electron binding energy of **10** was determined to be 1.69 ± 0.08 eV (39 ± 2 kcal mol$^{-1}$) based on observed electron transfer with 2,5-dimethyl-*p*-benzoquinone and 2-methyl-*p*-benzoquinone and the absence of this reaction channel with tetramethyl-*p*-benzoquinone (Table 7).[56] This result is in good accord with the predicted B3LYP/6-31+G(d) value of 1.65 eV.

Acenaphthyl anion **10** was also allowed to react with probe reagents and its reactivity was found to be similar to that of other aryl ions. It readily abstracts an oxygen atom from sulfur dioxide and does the same with nitrous oxide, but less efficiently. Sulfur atom transfer is observed upon reaction with carbonyl sulfide and carbon disulfide as well as adduct formation. These processes are competitive with the former reagent (∼1:1) while atom abstraction is favored in the latter instance (∼28:1). Upon reaction with carbon dioxide, **10** forms an adduct, and with dimethyl disulfide, $CH_3S^-$ and $CH_3SCH_2S^-$ are observed in a 13:1 ratio.

The proton affinity and the electron binding energy of **9** can be combined with the analogous thermochemical quantities for **10** along with the known ionization potential of hydrogen atom and the bond dissociation energy of molecular hydrogen to

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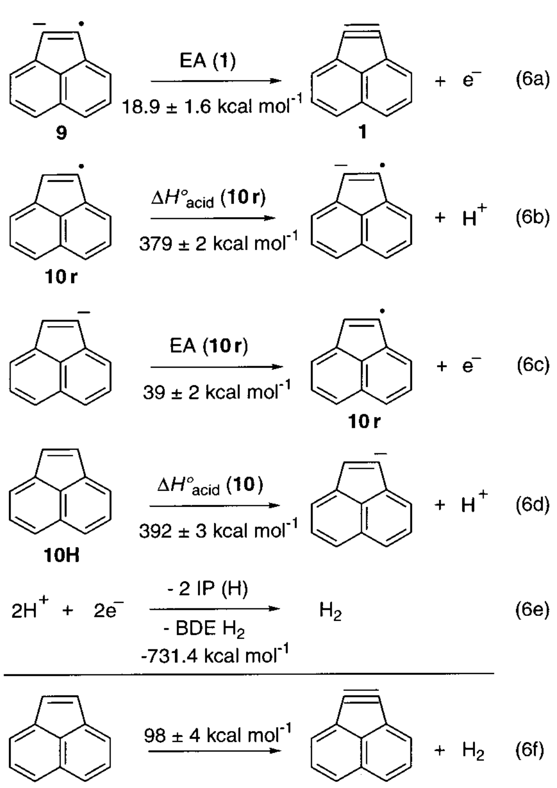
(65) Cramer, C. J.; Nash, J. J.; Squires, R. R. *Chem. Phys. Lett.* **1997**, *277*, 311−320.

(66) Worthington, S. E.; Cramer, C. J. *J. Phys. Org. Chem.* **1997**, *10*, 755−767.

(67) Cramer, C. J.; Debbert, S. *Chem. Phys. Lett.* **1998**, *287*, 320−326.

(68) We explored the basis set dependence of the computed S−T gap for cyclopentyne and found that upon going from cc-pVDZ to cc-pVTZ (via single-point calculations) that the BPW91 and CASPT2(4,4) energies increase by 2.9 and 3.7 kcal mol$^{-1}$, respectively. Changes of this magnitude would be insufficient to bring the computed EA into accord with experiment, but in conjunction with a larger active space (e.g. 14,14), the latter method might be satisfactory.

afford the heat of hydrogenation of **1** (98 ± 4 kcal mol$^{-1}$, eq 6). This result is in good agreement with the 0 K value (101.8 kcal mol$^{-1}$) obtained from the CASPT2/cc-pVDZ//CAS/cc-pVDZ energies for **1** and **10H** and the exact energy for $H_2$ including the zero-point energy (−1.164019 hartrees).[69,70] Given that the heat of formation of **10H** (62.1 ± 1.1 kcal mol$^{-1}$) has been determined by combustion calorimetry,[71] we can derive $\Delta H°_f(\mathbf{1}) = 160 \pm 4$ kcal mol$^{-1}$. The first and second C−H bond energies of **10H** (117 ± 4 and 84 ± 2 kcal mol$^{-1}$, respectively) also were obtained by using the data in eq 6. These quantities indicate that the second $\pi$ bond in acenaphthyne is weak (33 ± 4 kcal mol$^{-1}$) in comparison to that in acetylene (76 kcal mol$^{-1}$)[72] but similar to that for *o*-benzyne (36 ± 3 kcal mol$^{-1}$)[73] even though the heat of hydrogenation for **1** is 11 ± 5 kcal mol$^{-1}$ larger than that for *o*-benzyne.[74]

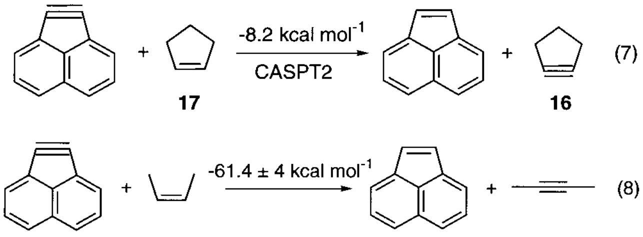


Calculations (CASPT2(4,4)/cc-pVDZ//CAS(4,4)//cc-pVDZ) were used to compare **1** with cyclopentyne (**16**). Equation 7 indicates that the triple bond is favored in the latter compound by 8.2 kcal mol$^{-1}$.[75] The energetics of this equation also can be used to estimate the $\Delta H°_f$ of **16** (98 kcal mol$^{-1}$) by using the known heats of formation of the other molecules (Table 8). While several factors contribute to the heat of reaction 7, the differences in strain energy (SE) undoubtedly play a major role. This quantity was estimated for **1** (69 kcal mol$^{-1}$) by the use of strain-free (Benson's) group equivalents.[76−78] A similar value (68 kcal mol$^{-1}$) is obtained by using an approach employed by Johnson and Daoust for other cycloalkynes.[79] Specifically, the strain energy of **1** is taken to be the heat of reaction 8 plus the SE of **10H** (6.1 kcal mol$^{-1}$, Table 8). We have also derived the strain energy of cyclopentyne (59 kcal mol$^{-1}$) based on the SE of **1** (68 kcal mol$^{-1}$) and the heat of reaction 7.[80] The latter quantity was adjusted to −8.7 kcal mol$^{-1}$ to account for the difference in the strain energies of **17** and **10H**. In contrast, Johnson and Daoust computed a strain energy for cyclopentyne of 74 kcal mol$^{-1}$ by carrying out an analogous comparison to that in eq 8 using MP4(SDTQ)/6-31G(d)//MP2/6-31G(d) energies; apparently this estimate is too high as a consequence of using a single determinant wave function and deficiencies in the basis set.[81]

**Table 8.** Experimental Heats of Formation ($\Delta H°_f$) and Computed Strain Energies (SE)

| compd | $\Delta H°_f$[a] | SE[b] |
|---|---|---|
| cyclopentane | −18.3 ± 0.2 | 6.7 |
| **17** | 8.1 ± 0.3 | 5.6 |
| **16** | 98[c] | 59[c] |
| acenaphthene | 37.3 ± 0.7 | 5.3 |
| **10H** | 62.1 ± 1.1 | 6.1 |
| **1** | 160 ± 4[d] | 68[e] |
| *cis*-2-butene | −1.70 ± 0.2 | |
| 2-butyne | 34.82 ± 0.3 | |

[a] All values are in kcal mol$^{-1}$ and come from ref 71 unless otherwise noted. [b] Computed by using Benson's group equivalents. See refs 76 and 77. [c] Derived from eq 7, see text. [d] Value comes from this work. [e] Obtained using eq 8. Application of Benson's strain-free equivalents gives a value of 69 kcal mol$^{-1}$. See text for additional details.



The strain energy in acenaphthyne arises from its rigid geometry which is unable to accommodate a triple bond. In **1**, the C1−C2−C3 bond angle (α) is 111.5° (CAS(4,4)/cc-pVDZ) which is 68.5° smaller than the optimum value for an alkyne (Table 9). Shortening of the C1−C2 bond (1.269 Å) in **1** is accompanied by a decrease in the C2−C3−C4 bond angle ($\beta$, 102.8° in **1** versus 105.8° in **10H**). This contributes to the strain energy as well since it is a further deviation from the typical value of 120° for an sp$^2$-hybridized center. Lengthening of the C3−C4 and C4−C5 bonds (0.015 Å) in **1** relative to **10H** also is disfavored because it disrupts the delocalization (aromaticity) in the naphthalene fragment. In contrast, cyclopentyne is

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(69) Herzberg, G.; Howe, L. L. *Can. J. Phys.* **1959**, *37*, 636−659.

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

(71) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. In *Thermochemical Data of Organic Compounds*; Chapman and Hall: New York, 1986.

(72) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750−6755.

(73) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 11865−11871.

(74) Recent calculations by Cramer and Thompson indicate that the $\pi$ bond strength and heat of hydrogenation of 1,2-didehydroindene are essentially the same (±1 kcal mol$^{-1}$) as for *o*-benzyne. These results in combination with ours indicate that cyclopentyne and 1,2-didehydroindene have essentially the same heats of hydrogenation. Cramer, C. J.; Thompson, J. To be submitted for publication.

(75) B3LYP/6-31+G(d) predicts a value of −8.5 kcal mol$^{-1}$ for eq 7. Apparently, the errors associated with computing strained cycloalkynes at this level of theory cancel in this isodesmic equation.

(76) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419−2438.

(77) Benson, S. W. In *Thermochemical Kinetic*s, 2nd ed.; John Wiley and Sons: New York, 1976.

(78) A value of 24.6 kcal mol$^{-1}$ was used for the $C_t$-$(C_B)$ carbon. See ref 76.

(79) Johnson, R. P.; Daoust, K. J. *J. Am. Chem. Soc.* **1995**, *117*, 362−367.

(80) If one uses $\Delta H_f°(\mathbf{16}) = 98$ kcal mol$^{-1}$ and Benson's group equivalents (ref 76) then a SE of 58 kcal mol$^{-1}$ is obtained for cyclopentyne.

(81) It is interesting to note that B3LYP/6-31+G(d) poorly predicts the energy of eq 7 (−80.0 kcal mol$^{-1}$), and in the analogous comparison with cyclopentyne gives virtually the same result ($\Delta H°_{rxn} = -71.5$ vs −68.1 kcal mol$^{-1}$) as reported by Johnson and Daoust in ref 79.

**Table 9.** Computed Geometries for Acenaphthylene (**10H**) and Cyclopentene (**17**) at the CAS(2,2)/cc-pVDZ Level of Theory and Acenaphthyne (**1**) and Cyclopentyne (**16**) at the CAS(4,4)/PVDZ Level[a]

| parameter | **10H** $C_{2v}$[b] | **1** $C_{2v}$ | **17** $C_s$ | **18** $C_s$ |
|---|---|---|---|---|
| C1−C2 | 1.362 (1.366) [1.395] | 1.269 (1.243) | 1.342 (1.338) | 1.253 (1.228) |
| C2−C3 | 1.486 (1.474) [1.466] | 1.485 (1.474) | 1.513 (1.514) | 1.510 (1.511) |
| C3−C4 | 1.412 (1.418) [1.441] | 1.427 (1.441) | 1.543 (1.554) | 1.569 (1.590) |
| C5−C6 | 1.362 (1.383) [1.382] | 1.357 (1.375) | | |
| C6−C7 | 1.429 (1.427) [1.425] | 1.431 (1.430) | | |
| C7−C8 | 1.368 (1.387) [1.383] | 1.367 (1.386) | | |
| C8−C9 | 1.426 (1.428) [1.434] | 1.428 (1.430) | | |
| C4−C9 | 1.382 (1.398) [1.386] | 1.380 (1.395) | | |
| C1−C2−C3 ($\alpha$) | 108.9 (109.0) [108.8] | 111.5 (112.6) | 111.6 (112.0) | 114.7 (115.8) |
| C2−C3−C4 ($\beta$) | 105.8 (105.9) [106.9] | 102.8 (102.0) | 102.9 (103.0) | 99.6 (98.7) |
| C3−C4−C5 ($\gamma$) | 110.6 (110.2) [108.6] | 111.4 (110.0) | 105.5 (105.5) | 106.6 (106.3) |

[a] Bond lengths and angles are in angstroms and degrees, respectively. Numbering schemes follow that shown in Table 5. Parenthetical numbers were obtained at the B3LYP/6-31+G(d) level. [b] The numbers in brackets correspond to electron diffraction data from: Wood, R. A.; Welberry, R.; Rae, A. D. *J. Chem. Soc., Perkin Trans*. 2 **1985**, 451−456.

somewhat more flexible and is able to undergo slightly larger structural distortions upon introduction of a second $\pi$ bond (i.e., the C3−C4 bond lengthens by an additional 0.011 Å, $\alpha$ increases, and $\beta$ decreases by an additional 0.3−0.5° relative to the corresponding alkenes). These differences in conjunction with hyperconjugative interactions between the in-plane low-lying $\pi^*$ orbital of the C1−C2 triple bond and the C3−H and C3−C4 $\sigma$ bonds presumably accounts for the greater stability of cyclopentyne (and 1,2-dehydroindene)[74] relative to acenaphthyne.[82]

## Conclusion

Acenaphthyne radical anion (**9**) was generated in a FTMS by dissociation of dicarboxylate dianion **12**. We have provided structural evidence for **9** by converting it to acenaphthenone enolate and comparing the reactivity of this ion with an authentic sample. The heat of hydrogenation (98 ± 4 kcal mol$^{-1}$) and formation (160 ± 4 kcal mol$^{-1}$) of acenaphthyne (**1**) were determined by the application of a thermodynamic cycle. Acenaphthyne is estimated to have a strain energy of 68 kcal mol$^{-1}$ and is computed (CASPT2(4,4)/cc-pVDZ//CAS(4,4)/cc-pVDZ) to be destabilized relative to cyclopentyne by 9 kcal mol$^{-1}$. We have also briefly explored the reactivity of acenaphthyne radical anion with probe reagents and found it to exhibit both anion and radical behavior.

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**Supporting Information Available:** Computed structures and energies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[82] We wish to thank one of the referees for suggesting hyperconjugation as an explanation to account for the difference in energy between **1** and **16**.