

Benzocyclopropenyl Anion: A Stable 8π -Electron Species

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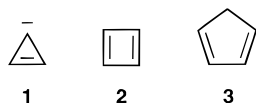
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The conjugate base of benzocyclopropene has been generated in the gas phase. Its reactivity and thermodynamic stability were explored. The measured acidity is $\Delta F_{\text{acid}}^{\circ}(\text{benzocyclopropene}) = 386 \pm 3$ kcal/mol, and the electron affinity of benzocyclopropenyl radical is $0.51 \text{ eV} < \text{EA} < 1.11 \text{ eV}$. *Ab initio* calculations satisfactorily reproduce the experimental results and provide additional insights. Benzocyclopropene is found to be 34.5 kcal/mol more acidic than the allylic position of cyclopropene and only 4 ± 3 kcal/mol less acidic than toluene. These findings are explained in terms of the structure and electronic properties of benzocyclopropenyl anion.

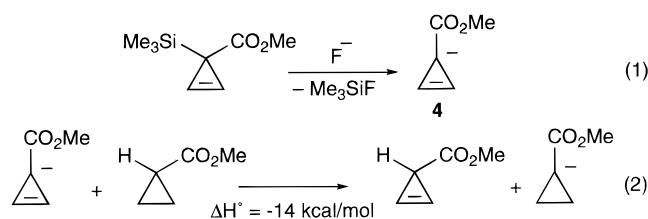
Introduction

The simplest Hückel $4n$ π -electron systems are cyclopropenyl anion (**1**), cyclobutadiene (**2**), and cyclopentadienyl cation (**3**). Each of these species, and their derivatives, has been the subject matter of extensive investigations.^{1–3} These compounds have proven to be difficult to synthesize and, in general, are highly reactive. Nevertheless, **2** and **3** have been characterized spectroscopically,^{4,5} and a stable host–guest complex (hemicarceplex) of **2** has been prepared.⁶ Quantitative measures of their stability based upon experimental data, however, are lacking.⁷

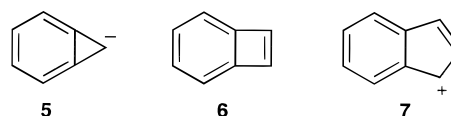


3-Carbomethoxycyclopropenyl anion (**4**) was recently formed in the gas phase via the fluoride-induced desily-

lation of 3-(trimethylsilyl)-3-carbomethoxycyclopropene (i.e., the DePuy reaction, eq 1).⁸ By measuring the proton affinity of **4** and its saturated analog, it was found that the former ion is destabilized relative to the latter one by 14 kcal/mol (eq 2). This result is consistent with the notion that cyclopropenyl anion is destabilized by cyclic conjugation (i.e., it is antiaromatic).^{1,9}



Benzoannulated derivatives of **1–3** (**5–7**) also have been studied.^{10–12} Compounds **6** and **7**, like their parents,



are extremely reactive and appear to be quite unstable. Benzocyclopropenyl anion (**5**), on the other hand, is readily generated and surprisingly stable. For example,

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[Ⓢ] Abstract published in *Advance ACS Abstracts*, October 1, 1997.

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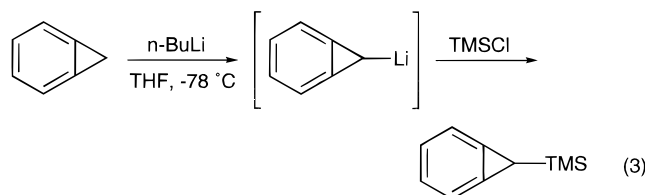
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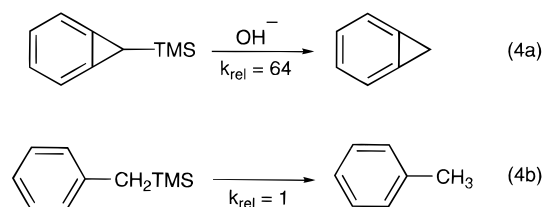
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benzocyclopropene can be deprotonated easily with *n*-butyllithium, and the resulting anion can be trapped by chlorotrimethylsilane (eq 3).^{10c,13} Moreover, Eaborn et al.



have shown that 7-(trimethylsilyl)benzocyclopropene undergoes base-induced cleavage 64 times faster than benzyltrimethylsilane (eq 4). This suggests that benzocyclopropene is more acidic than toluene; a pK_a of 36, compared to toluene's pK_a of 41, was proposed.¹³ This represents a remarkable stabilization of **5** relative to **1** (25 pK_a units).¹⁴



In order to gain additional insight into the stability of the benzocyclopropenyl anion, we have measured the intrinsic acidity of its conjugate acid in the absence of complicating solvation, aggregation, and counterion effects (i.e., in the gas phase). *Ab initio* molecular orbital calculations at a correlated level (MP2) also were carried out in order to elucidate the key factors influencing the stability of **5**.

Experimental Section

Benzocyclopropene (**5H**) and 7-deuteriobenzocyclopropene (**5D**) were prepared as previously described in the literature.^{15,16} They are vile smelling compounds and should be handled accordingly.

All of the reported gas phase experiments were carried out with our variable temperature flowing afterglow (FA) device, except for one acidity measurement which was done with a Finnigan dual-cell Fourier transform mass spectrometer (FTMS) due to pyrimidine's lack of volatility and sluggish reactivity. Since the former apparatus has been described previously,¹⁷ and the latter technique is well-established in the literature,¹⁸ only a brief description of the FA experiments will be given.

Hydroxide, amide, and the atomic oxygen ion (O^-) were generated by electron ionization of a nitrous oxide/methane mixture (~1:2), ammonia, and nitrous oxide, respectively.

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Table 1. MP2/6-31+G(d) Structures for Benzocyclopropene (5H), Benzocyclopropenyl Anion (5), and the Inversion Transition State (5pl)^a

Bond or Angle	5H	5	5pl
C1-C7	1.507 (1.498)	1.467	1.417
C1-C6	1.354 (1.334)	1.390	1.418
C1-C2	1.385 (1.363)	1.379	1.375
C2-C3	1.411 (1.387)	1.446	1.465
C3-C4	1.410 (1.390)	1.389	1.379
C2-H	1.088	1.092	1.090
C3-H	1.089	1.093	1.093
C7-H	1.091	1.098	1.081
C1-C7-C6	53.4 (52.8)	56.5	60.1
C1-C6-C5	124.5 (124.5)	123.5	123.7
C1-C2-C3	113.0 (113.2)	114.5	114.0
H-C7-H	123.1		
H-C2-C1	125.3 (125)	124.7	124.9
H-C3-C2	119.2 (117)	119.2	118.8
α		50.6	

^a All distances are in angstroms and angles in degrees. X-ray crystal data are given in parentheses and are taken from ref 35.

These ions were entrained in a rapidly moving stream of helium and were allowed to undergo thousands upon thousands of collisions ($\sim 10^4$) before being reacted with selected neutral reagents. Sequential reactions were carried out by adding appropriate compounds at a variety of different locations along the flow tube. The ionic products passed through a narrow orifice (0.5 mm) into a quadrupole or triple quadrupole mass filter and were detected using standard pulse counting techniques.

Ab initio calculations were carried out using GAMESS,¹⁹ Gaussian 92,²⁰ and Gaussian 94²¹ on UNIX-based workstations or Cray computers at the Minnesota Supercomputer Institute and the University Computational Center in Zagreb. Geometries were fully optimized within a given point group at the HF/6-31+G(d) and MP2(fc)/6-31+G(d) levels (Table 1).²² This basis set is flexible enough to give a good accounting of the subtle changes in molecular structure induced by fusion of a small strained ring, but since dynamic correlation is important to adequately describe many carbanions, only the MP2 geom-

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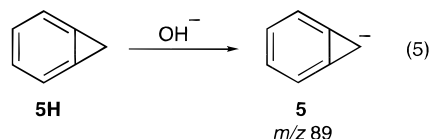
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(23) The Hartree-Fock data are available in the Supporting Information.

eries will be discussed.²³ Vibrational analyses at the HF and MP2 level were performed to verify the nature of all of the stationary points and to obtain thermochemical data (zero-point energies and temperature corrections). In discussing the computed geometries use is made of simple qualitative bond indices such as hybridization²⁴ and Coulson's π -bond orders of the mobile π -electrons.²⁵ For this purpose, s characters were calculated at the correlated level via natural bond orbital (NBO) analysis.²⁶ Second-order Møller–Plesset wave functions also were used for Bader's topological analysis of the electron density distributions.²⁷ In addition, atomic charges, π -electron densities and π -bond orders for the MP2(fc)/6-31+G(d) optimized structures were derived by symmetric Löwdin orthogonalization.²⁸

Results and Discussion

Experiments. Benzocyclopropene (**5H**) reacts with hydroxide in the gas phase to afford an $M - 1$ ion (m/z 89) which we assign as the benzocyclopropenyl anion (**5**, eq 5).²⁹ This conclusion is based upon the following facts: (1) the $M - 1$ ion undergoes 1 hydrogen/deuterium exchange upon reaction with deuterium oxide; (2) 7-deuteriobenzocyclopropene (**5D**) reacts with hydroxide to give both $M - H$ (m/z 90) and $M - D$ (m/z 89) ions;³⁰ (3) the deuterium label in the m/z 90 ion can be washed out by reacting it with H_2O (i.e., 1 H/D exchange occurs). These observations clearly indicate that **5H** is deprotonated at C7 and are in accord with the formation of **5**. The measured acidity of benzocyclopropene (*vide infra*) also agrees well with the computed value for the 7-position but not the 2- or 3- (aromatic) sites.



The deprotonation energy for benzocyclopropene (ΔH_{acid}°) was measured by the bracketing technique. In this approach, a variety of bases of different strength were found to deprotonate **5H**, including amide, hydroxide, furanide, and fluorophenide. Weaker bases such as 1,3-diazinide (the conjugate base of pyrimidine), methoxide, and ethoxide did not abstract a proton from **5H**. In the opposite direction it was found that benzocyclopropenyl anion (**5**) abstracts a proton or a deuteron from methanol-*O-d* and pyrimidine, but not from fluoroben-

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


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(29) 7-Methylbenzocyclopropenyl anion has been suggested previously as a fragment ion in the collision-induced dissociation spectrum of the parent ion of a benzocyclopentanedione. See: Bowie, J. H.; Blumenthal, T.; Laffer, M. H.; Janposri, S.; Gream, G. E. *Aust. J. Chem.* **1984**, *37*, 1447.

(30) The observed m/z 89:90 ratio was approximately 3:1 and the starting material was 90% d_1 .

Table 2. Summary of the Bracketing Data for the Acidity Measurement of Benzocyclopropene (5H**)**

Reference Acid	ΔH_{acid}° ^a	Proton Transfer ^b	
		forward	reverse
NH ₃	403.6	-	Yes
D ₂ O	392.0	No (1H/D) ^c	Yes
H ₂ O	390.7	No	Yes
	388.2	No	Yes
	387.2	No	Yes
	385.2	Yes	No
CH ₃ OD	383.5 ^d	Yes	No
CH ₃ CH ₂ OH	377.4	-	No

^a All values are in kcal/mol and are taken from ref 31 unless otherwise noted. ^b The forward direction corresponds to the reaction between **5** and a reference acid (HX), while the reverse direction is for **5H** + X⁻. "Yes" indicates that proton transfer is observed and "No" indicates that is not. ^c One deuterium is incorporated into **5** but OD⁻ is not observed. ^d Barlow, S. E.; Dang, T. T.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 6832.

zene, furan or deuterium oxide. These results are summarized in Table 2, and enable us to assign $\Delta H_{acid}^\circ(\mathbf{5H}) = 386 \pm 3$ kcal/mol.³¹

The reactivity of **5** was briefly explored. No reaction is observed with nitrous oxide (eq 6), an adduct is formed with carbon disulfide (eq 7), methanethiolate is produced upon reaction with dimethyl disulfide (eq 8), and a number of poorly characterized species are generated upon addition of neopentyl nitrite (*neo*-PnONO, eq 9). Electron transfer occurs with sulfur dioxide (eq 10) but not with molecular oxygen (eq 11) or carbon disulfide. This indicates that the electron affinity (EA) of benzocyclopropenyl radical (**5R**) is between the values for sulfur dioxide (1.11 eV) and carbon disulfide (0.51 eV) or $0.8 \pm .3$ eV (18 ± 7 kcal/mol).^{31,32}

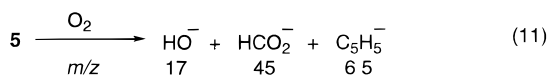
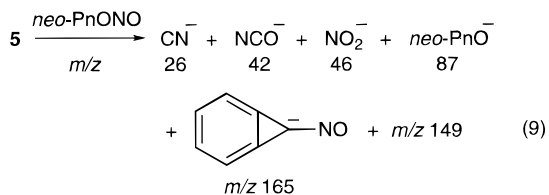
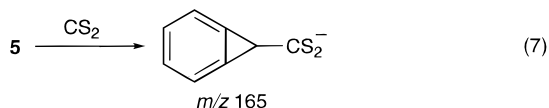
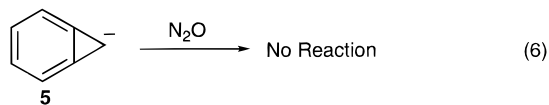
Computations. A. Geometries. Fully optimized MP2(fc)/6-31+G(d) structures for benzocyclopropene (**5H**), benzocyclopropenyl anion (**5**), and the latter's inversion transition state (**5pl**) were computed, and the most important geometrical data are summarized in Table 1.³³ The calculated structure for **5H** is very similar to the previously reported MP2(full)/6-31G(d) geometry³⁴ and

(31) All thermodynamic data, unless otherwise noted, comes from Lias et al. (Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement 1) or the slightly updated form available on a personal computer, NIST Negative Ion Energetics Database (Version 3.00, 1993); NIST Standard Reference Database 19B.

(32) In comparison, the electron affinity of benzyl radical is 0.91 ± 0.004 eV (21.0 ± 0.1 kcal/mol). See: Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(33) For early theoretical work on benzocyclopropenyl anion, see: (a) Eaborn, C.; Stamper, J. G. *J. Organomet. Chem.* **1980**, *192*, 155. (b) Halton, B.; Halton, M. P. *Tetrahedron* **1973**, *29*, 1717.

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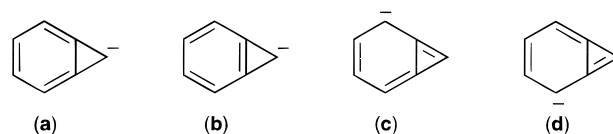
is in reasonable agreement with the experimental X-ray data,³⁵ although the C–C bonds are systematically too long by approximately 0.004 and 0.02 Å, respectively. Apparently, the diffuse sp functions, which are needed to adequately describe the geometry of anions, lead to a slightly poorer structure in this instance. In any case, the aromatic ring exhibits Mills–Nixon (MN)³⁶ type bond fixation, which leads to differences in the bond distances. The distortion of the aromatic ring can be conveniently described by the bond localization index³⁷

$$L(d_{CC}) = \sum_n |d_{CC}^{(n)} - \bar{d}_{CC}| \quad (12)$$

where \bar{d}_{CC} is the average bond length and $d_{CC}^{(n)}$ refers to the n th bond of the benzene moiety. Values for this parameter of zero and 0.36 are obtained for the perfectly symmetric D_{6h} benzene structure and a completely localized cyclohexatriene model system, respectively.³⁸ The calculated $L(d_{CC})$ value of 0.11 for **5H** reflects moderate bond localization and a small accompanying aromatic defect.

Deprotonation of benzocyclopropene leads to benzocyclopropenyl anion and some significant geometry changes in both rings. The cyclopropenyl part of the molecule shows diminished bond length alternation as compared to that in the neutral molecule; the differences in the C1–C7 and C1–C6 distances are 0.077 and 0.153 Å in **5** and **5H**, respectively. This is a consequence of the lengthening of the annelated bond (C1–C6) and shortening of the bonds emanating from the anionic center (C1–C7 and C6–C7) in **5**. It is interesting to note in this connection that deprotonation of cyclopropene causes elongation of

both the single and double bonds.³⁹ As for the benzene moiety in **5**, it exhibits a stronger bond alternation pattern than that in **5H**, as indicated by the increased $L(d_{CC}) = 0.17$ value. The most significant changes relative to the neutral molecule occur at the annelated bond and the C2–C3/C4–C5 bonds. In the anion they are stretched by 0.036 and 0.035 Å, respectively, whereas the C1–C2/C5–C6 and C3–C4 distances are diminished by 0.006 and 0.021 Å, respectively. A plausible explanation for these changes in **5** at the π -electron level is the avoidance of the unfavorable antiaromatic 4π -electron interaction within the small ring and a concomitant perturbation of the aromatic fragment. Consequently, π -electron density will be shifted to some extent from the annelated to the ortho (C1–C2 and C5–C6) bonds producing fixation as described above. The resulting structure is a compromise balancing the aromatic interaction in the six-membered ring against the antiaromatic interaction in the three-membered ring. This conjecture is supported in qualitative terms by the resonance structures below:



The structural distortion represented by Kekulé (Loschmidt)⁴⁰ resonance structure **a** is preferred over its counterpart **b**, since it diminishes the antiaromatic interaction within the three-membered ring. The other relevant resonance structures (**c** and **d**) contribute to the π -electron density drift from the annelated to the ortho bonds and place π -density at C2 and C5. These intuitive results are supported quantitatively by the Löwdin π -bond orders (Table 3). They are 0.48 and 0.72 for the annelated and the ortho bonds in **5**, respectively, as compared to 0.63 and 0.66 in the neutral molecule. Likewise, the π -density at C2 and C5 is 1.3 electrons (e^-) as compared to the anionic center (C7), which possesses 1.5 e^- . Apparently, the lone pair is delocalized significantly into the benzene fragment by the bonding pattern which minimizes antiaromaticity. This is the dominating electronic structural motif. It is worth adding that NBO analysis²⁶ indicates there is little s character in the annelated bond as a consequence of the dramatic rehybridization at the ring junction; in **5H** this σ -bond is made up of two overlapping sp^3 hybrids (25.3% s character), which is highly unusual for three-coordinate carbon, and the s content diminishes further to only 21.6% in **5** (Table 3).

Additional insight into the intrinsic properties of chemical bonds can be obtained from a topological analysis of the electron density distributions (Table 3).^{27a} For instance, it has been shown that weaker bonds in structurally related molecules have less negative $\nabla^2\rho_c$ values while stronger bonds have more negative Laplacian's (i.e., activated bonds have less electron density between the bonding nuclei whereas stronger ones have

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(36) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.

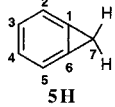
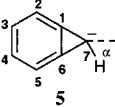
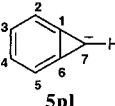
(37) Maksic, Z. B.; Kovacek, D.; Eckert-Maksic, M.; Boeckmann, M.; Klessinger, M. *J. Phys. Chem.* **1995**, *99*, 6410.

(38) Kovacek, D.; Maksic, Z. B.; Novak, I. *J. Phys. Chem.* **1997**, *101*, 1147.

(39) The fully optimized MP2(fc)/6-31+G(d) C_{2v} and C_s structures for cyclopropene (**1H**) and cyclopropenyl anion (**1**) have C–C and C=C bond distances of 1.511 Å (**1H**), 1.563 Å (**1**), 1.305 Å (**1H**), and 1.315 Å (**1**), respectively.

(40) (a) Noe, C. R.; Bader, A. *Chem. Br.* **1993**, *29*, 126. (b) Bader, A. *Proc. R. Inst. Gr. Br.* **1992**, *64*, 197. (c) *The Kekule riddle, a challenge to chemists and psychologists*; Wotiz, J., Ed.; Cache River: Vienna, IL, 1992. (d) Kekule, F. A. *Bull. Soc. Chim. Fr.* **1865**, *3*, 98. (e) Kekule, F. A. *Ann.* **1866**, *137*, 129. (f) Kekule, F. A. *Ber.* **1869**, *2*, 362.

Table 3. Natural Bond Orbital Hybridizations, Bader's Topological Parameters (ρ_c , $\nabla^2\rho_c$, and ϵ), and Löwdin's π -Bond Orders, Atomic Charges, and π -Densities for **5H, **5**, and **5pl****

Cmpd	Bond	NBO s-character	Bader's topological parameters			Löwdin population analysis			
			ρ_c	$\nabla^2\rho_c$	ϵ	π -b.o.	atom	charge	π -density
	C1-C7	30.6-20.4	0.228	-0.328	0.608	0.17	C1	-0.13	1.04
	C1-C6	25.3-25.3	0.334	-0.884	0.042	0.63	C2	-0.19	1.08
	C1-C2	43.9-32.9	0.302	-0.791	0.180	0.66	C3	-0.23	1.08
	C2-C3	35.1-34.9	0.301	-0.795	0.217	0.64	C7	-0.28	1.31
	C3-C4	35.2-35.2	0.301	-0.793	0.211	0.67	C7-H	0.22	
	C7-H	29.4	0.273	-0.959	0.014				
	C1-C7	33.9-22.3	0.241	-0.358	0.386	0.32	C1	-0.10	0.91
	C1-C6	21.6-21.6	0.308	-0.731	0.121	0.48	C2	-0.37	1.30
	C1-C2	44.3-34.4	0.304	-0.778	0.229	0.72	C3	-0.29	1.15
	C2-C3	34.8-34.5	0.280	-0.699	0.195	0.46	C7	-0.50	1.54
	C3-C4	36.5-36.5	0.310	-0.820	0.296	0.79	C7-H	0.20	
	C7-H	25.8	0.258	-0.830	0.045				
	C1-C7	34.7-29.7	0.264	-0.432	0.177	0.41	C1	-0.03	0.80
	C1-C6	19.5-19.5	0.293	-0.629	0.190	0.38	C2	-0.45	1.33
	C1-C2	45.6-34.1	0.304	-0.784	0.292	0.66	C3	-0.29	1.06
	C2-C3	34.4-34.0	0.270	-0.655	0.179	0.33	C7	-0.49	1.43
	C3-C4	37.1-37.1	0.315	-0.838	0.333	0.78	C7-H	0.27	
	C7-H	40.4	0.264	-0.907	0.065				

more).⁴¹ Upon deprotonation of benzocyclopropene there is a substantial increase in $\nabla^2\rho_c$ at the fused bond (-0.884 vs -0.731), and thus it is weakened. This also is reflected in the change in the electron density (ρ_c), but to a smaller extent. In contrast, the ellipticity (ϵ , a measure of the anisotropy of the charge distribution)^{27a,42} of this bond increases upon going from **5H** to **5**. This might appear contradictory since the ellipticity of a π -bond is greater than that for a σ -bond. As previously noted, however, the C1-C6 bond in **5H** has a very low ellipticity because of its diffuse electron density distribution (in the vicinity of the bond critical point) in the plane of the ring and perpendicular to this plane; the former is a consequence of bent bonding, which introduces π character into the molecular plane, while the latter arises due to π -bonding. Upon deprotonation there is a weakening of the π -bond, because of the shift in π -electron density into the neighboring benzene bonds, and this leads to an increase in the ellipticity of the fused bond since the bent bonding is relatively unaffected. In the anion there also is a slightly greater density at the three-membered ring critical point (0.214 vs 0.205), which is indicative of a more pronounced surface delocalization.⁴² In contrast, deprotonation of cyclopropene leads to decreases in the ellipticity (0.21 vs 0.12) and the ring critical point (0.211 vs 0.190), and little change in $\nabla^2\rho_c$ (-0.872 vs -0.860) or ρ_c (0.342 vs 0.337).

Another striking feature of the geometry of **5** is its nonplanarity. The hydrogen at the anionic center is tilted 50.6° out of the ring plane, which is 19.6° less than that in cyclopropenyl anion (at the MP2/6-31+G(d) level). The smaller pyramidalization angle in benzocyclopropenyl anion is a result of the greater delocalization in this species. A planar C_{2v} transition structure (**5pl**) was located for the inversion of **5** at the Hartree-Fock and MP3 levels using the 6-31+G(d) basis set. Second-order Møller-Plesset perturbation theory appears to mischaracterize the nature of this stationary point but not the structural features, in accord with previous results on **1**.⁴³ In particular, the MP2/6-31+G(d) energy minimum

is a second-order saddle point with two imaginary frequencies (756i and 208i), but the geometry is very similar to that of the MP3/6-31+G(d) structure. The bonds emanating from the anionic center (C1-C7 and C6-C7) in **5pl** are 0.05 Å shorter than those in **5**, and the fused bond (C1-C6) is 0.028 Å longer at the MP2 level. These changes, and those for all of the other carbon-carbon bonds, are analogous to the ones that take place upon deprotonation of **5H**, only they are more extreme. Similar results have been noted in going from the C_s cyclopropenyl anion to the C_2 pseudorotation transition structure, but the fused ring in **5pl** prevents the C1-C6 bond from elongating to the same extent (1.698 vs 1.418 Å). As a result, the C-C bonds making up the three-membered ring in **5pl** become essentially equal (1.417 and 1.418 Å). More importantly, there is increased π -bond order alternation within the aromatic ring and the localization index $L(d_{CC})$ becomes larger (0.22) because of the increased overlap of the lone pair with the π -orbital manifold of the aromatic sextet. This is reflected further by a destabilization of **5pl**'s HOMO (i.e., the HOMO energies of **5** and **5pl** are -0.37 and -0.12 eV, respectively). It follows as a corollary that a strong antiaromatic interaction amplifies Mills-Nixon type bond fixation as previously discussed.^{44,45}

B. Energetics. Deprotonation of benzocyclopropene can take place, in principle, at one of three different sites (C2, C3, and C7).^{46,47} The acidity at each position was calculated at the MP2/6-31+G(d) level using HF/6-31+G(d) and MP2/6-31+G(d) optimized structures and

(43) The pseudorotation transition structure for converting cyclopropenyl anion from one C_s structure to another has C_2 symmetry at the HF and MCSCF levels of theory. The MP2/6-31+G(d) structure is a minimum on the potential energy surface, which becomes a transition structure when a larger basis set (6-311+G(2df,2pd)) is used or there is a further accounting of electron correlation (i.e., MP3/6-31+G(d)). Merrill, G. N.; Kass, S. R., submitted for publication.

(44) (a) Mohler, D. L.; Vollhardt, K. P. C.; Wolff, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 563. (b) Eckert-Maksic, M.; Maksic, Z. B.; Hodosek, M.; Poljanec, K. *Int. J. Quantum. Chem.* **1992**, *42*, 869. (c) Faust, R.; Glendening, E. D.; Streitwieser, A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 8263.

(45) For an alternative approach toward bond localization in aromatic compounds, see: (a) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2907. (b) Frank, N. L.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2102. (c) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583.

(46) 2,3-Didehydrobenzyl anion (**8**) also was explored. This anion is surprisingly stable ($E(\mathbf{8}-5) = -1.93$ kcal/mol at the MP2/6-31+G(d)), but as it was not formed upon deprotonation of benzocyclopropene, it will not be discussed further at this time.

(47) The C2 anion derived from 7,7-difluorobenzocyclopropene has been reported. See: Neidlein, R.; Constantinescu, T.; Kohl, M. *Phosphorus, Sulfur, Silicon* **1991**, *59*, 165.

(41) (a) Alcami, M.; Mo, O.; Yanez, M.; Abboud, J. L. M.; Elguero, J. *Chem. Phys. Lett.* **1990**, *172*, 471. (b) Alcami, M.; Mo, O.; Yanez, M.; Abboud, J. L. M. *J. Phys. Org. Chem.* **1990**, *4*, 177. (c) Abboud, J. L. M.; Canada, T.; Homan, H.; Notario, R.; Cativiela, C.; Diaz de Villegas, M. D.; Bordeje, M. C.; Mo, O.; Yanez, M. *J. Am. Chem. Soc.* **1992**, *114*, 4728.

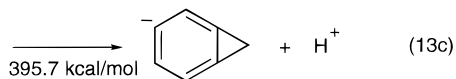
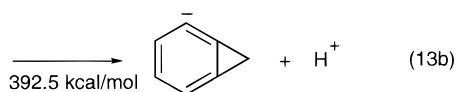
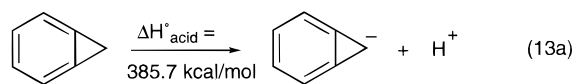
(42) (a) Kraka, E.; Cremer, D. In *Theoretical Models of Chemical Bonding*; Maksic, Z. B., Ed.; Springer Verlag: Berlin-Heidelberg, 1990; Part 2, p 453. (b) Kraka, E.; Cremer, D. In *Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988; pp 65-138.

Table 4. Calculated Electronic Energies, Zero-Point Energies, and Acidities for Benzocyclopropene (5H), Toluene, Benzene, and Cyclopropene (1H)

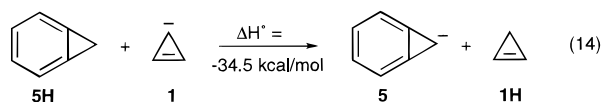
compd	energy ^a		$\Delta H_{\text{acid}}^{\circ}$		energy ^c		$\Delta F_{\text{acid}}^{\circ}$		
	MP2	ZPE ^b	0 K	298 K	MP2	ZPE ^b	0 K	298 K	expt
5H	-269.366 80 (-269.257 98)	0.102 59			-269.368 64 (-269.260 94)	0.10115			
7-anion (5)	-268.737 70 (-268.644 58)	0.086 64	384.8	386.4	-268.740 32 (-268.648 66)	0.084 65	383.9	385.7	386 ± 3
2-anion	-268.729 44 (-268.635 12)	0.088 09	390.8	392.3	-268.731 54 (-268.637 81)	0.087 25	391.1	392.5	
3-anion	-268.723 97 (-268.629 76)	0.087 95	394.2	395.7	-268.726 59 (-268.632 68)	0.087 40	394.3	395.7	
5(pl)	-268.727 27	0.085 28			-268.729 92	0.081 92			
C ₆ H ₅ CH ₃	-270.642 71 (-270.510 97)	0.124 89	383.2	384.7	-270.644 17 (-270.513 55)	0.123 22	382.8	384.3	382.3 ± 0.3 ^d
C ₆ H ₅ CH ₂ ⁻	-270.016 70 (-269.900 25)	0.109 54			-270.018 74 (-269.903 51)	0.107 77			
C ₆ H ₆	-231.470 69 (-231.366 98)	0.098 26	396.3	397.8	-231.472 03 (-231.370 25)	0.095 70	396.8	398.2	401.7 ± 0.5 ^e
C ₆ H ₅ ⁻	-230.824 85 (-230.735 34)	0.083 83			-230.825 93 (-230.738 00)	0.081 88			
1H	-116.210 48 (-116.151 13)	0.05506	418.5	420.1	-116.211 87 (-116.152 72)	0.054 75	418.4	420.1	
1	-115.527 75 (-115.483 97)	0.039 20			-115.529 27 (-115.485 54)	0.038 97			
1pl-s	-115.468 42	0.036 00			-115.469 79	0.035 38			
1pl-l	-115.477 09	0.036 91			-115.479 51	0.036 85			

^a MP2/6-31+G(d)//HF/6-31+G(d) energies and HF vibrational frequencies. Parenthetical values have been corrected to 298 K and include an *RT* work term. ^b HF and MP2 ZPEs are scaled by 0.9135 and 0.9646, respectively. For temperature corrections (0 → 298 K), vibrational frequencies were scaled by 0.8929 (HF) and 0.9427 (MP2). See: Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345. ^c MP2/6-31+G(d) structures, energies, and vibrational frequencies. ^d Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B. *J. Am. Chem. Soc.*, submitted for publication. ^e Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590.

vibrational frequencies (Table 4, eq 13). The former



calculations are computationally less demanding and this simpler model previously has been shown to give good results for hydrocarbons.⁴⁸ In accord with experiment, both approaches indicate that the acidity order is C7 ≫ C2 > C3,⁴⁹ that the most acidic site is C7, and that only this position can be deprotonated by hydroxide (PA(OH⁻) = 390.7 kcal/mol)³¹ in an exothermic reaction. The absolute values at 0 and 298 K for **5H** and three reference compounds (toluene, benzene, and cyclopropene (**1H**)) are given in Table 4. Again, there is very good agreement with experiment; the largest error is 3.5 kcal/mol and the mean deviation is less than 2 kcal/mol at the MP2/6-31+G(d)//MP2/6-31+G(d) level. From these data it is apparent that benzocyclopropene is 34.5 kcal/mol more acidic than cyclopropene (eq 14).



(48) (a) Saunders, W. H., Jr. *J. Phys. Org. Chem.* **1994**, *7*, 268. (b) For alternative theoretical models, see: Maksic, Z. B.; Kovacek, D.; Eckert-Maksic, M.; Zrinski, I. *J. Org. Chem.* **1996**, *61*, 6717.

In order to account for the large acidity difference between **1H** and **5H**, one might consider the hybridization of the carbon atom at the deprotonation site. Quantitative relationships between the acidity and *s* character of a carbon–hydrogen bond or the ¹³C C–H heteronuclear coupling constant (*J*_{13C–H}) are well-known both in solution and the gas phase.⁵⁰ The hybridization of the methylene C–H bonds in **1H** and **5H** are essentially the same (29.4 vs 30.0% *s* character, respectively, via NBO analysis and 33.4 vs 34.0% *s* character from *J*_{13C–H}),^{51,52} so similar acidities would be expected; using the previously reported correlation, $\Delta H_{\text{acid}}^{\circ} = -0.296 J_{13\text{C-H}} + 455.3$,^{50a} values of 406 and 405 kcal/mol are obtained for **1H** and **5H**, respectively. Topological quantities such as $\rho_{\text{c}}(\text{C-H})$ and $\nabla^2 \rho_{\text{c}}(\text{C-H})$ also have been shown to correlate with hydrocarbon acidities, but they fail to account for the difference between cyclopropene and benzocyclopropene too.⁵³ None of this is surprising since both approaches (hybridization and topological parameters of C–H bonds) are local in nature. They are applicable only for the formation of localized carbanions and cannot account for nonlocal effects (e.g., delocalization). It is the increased delocalization in **5** resulting

(49) The largest difference between the two models at 298 K is 0.7 kcal/mol, and the average discrepancy between the six acidities is 0.3 kcal/mol.

(50) (a) Kass S. R.; Chou P. K. *J. Am. Chem. Soc.* **1988**, *110*, 7899. (b) Maksic, Z. B.; Eckert-Maksic, M. *Tetrahedron* **1969**, 5113. (c) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965.

(51) The hybridization was derived using the following relationship: $0.2 J_{13\text{C-H}} = \% \text{ s character}$. For details, see: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987 and references cited therein.

(52) The ¹³C C–H coupling constants for **1H** and **5H** are 167 and 170 Hz, respectively. See: Morris, D. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley: New York, 1987; p 133.

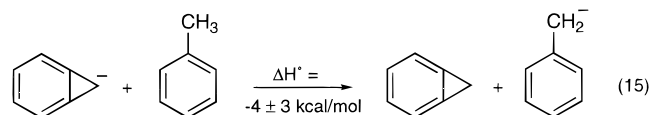
(53) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1990**, *112*, 6514.



Figure 1. Two different MP2/6-31+G(d) optimized structures for cyclopropenyl anion with C_{2v} symmetry.

from the fusion of the aromatic ring, however, which is primarily responsible for the large acidity difference between **1H** and **5H**. This is reflected in the relative inversion barriers of benzocyclopropenyl anion and cyclopropenyl anion. The former value, which is given by the energy difference between **5** and **5pl**, is 4.8 kcal/mol at the MP2/6-31+G(d) level.⁵⁴ The latter barrier, which is given by the energy difference between the C_s and C_{2v} forms of cyclopropenyl anion, is 35.1 kcal/mol, and the difference (30.3 kcal/mol) is almost the same as $\Delta H_{\text{acid}}^{\circ}(\mathbf{1H}-\mathbf{5H})$. It is worth adding that there are two C_{2v} structures for **1**, one has two long paraffinic bonds and a short olefinic bond (**1pl-s**) while the other has two short paraffinic bonds and a long (formerly) olefinic bond (**1pl-l**, Figure 1).⁵⁵ The latter species is 5.2 kcal/mol more stable than the former one, but the fused aromatic ring in **5** makes a short, short, long bond arrangement (i.e., **1pl-l**) energetically inaccessible. Therefore, **1pl-s** was used for the energetic comparison.

In the gas phase, benzocyclopropene is slightly less acidic than toluene (eq 15). The experimental difference



is only 4 ± 3 kcal/mol, which is in good accord with the computed value of 1.4 kcal/mol. Thus, there is a reversal in the relative acidities upon going from the liquid phase to the gas phase.⁵⁶ Presumably, this is due to the diminished importance of delocalization in solution because of solvation and the greater influence exerted by hybridization (i.e., the carbon atom at the acidic site in **5H** is more electronegative and has more s character than in toluene,⁵⁷ whereas delocalization favors benzyl anion over benzocyclopropenyl anion). In a similar vein, propyne is deprotonated exclusively at the acetylenic carbon in the liquid phase but a roughly 1:1 mixture of acetylenic

(54) This quantity has been zero-point energy corrected.

(55) A vibrational analysis indicates that **1pl-l** has two imaginary frequencies (1254i and 1025i cm^{-1}) while **1pl-s** has three (1459i, 961i, and 471i cm^{-1}).

(56) One should keep in mind that we are comparing a kinetic acidity (solution, ref 13) vs a thermodynamic one (gas phase) and the former result might change under equilibrium conditions.

(57) NBO analysis of the C_s MP2(fc)/6-31+G(d) optimized structure for toluene reveals that the methyl C-H bonds have 23.9% and 24.1% s character.

and propargylic (allenic) anions are obtained upon reaction with hydroxide in the gas phase.⁵⁸ The similarity in the acidities of **5H** and toluene is in keeping with simple Hückel theory, although this model predicts that benzocyclopropenyl anion is more stable than benzyl anion by 0.11β . On the other hand, the calculated localization index $L(d_{CC})$ for benzyl anion is less than that for **5** (i.e., $L(d_{CC}) = 0.12$ and 0.17 , respectively). Consequently, the aromatic defect in benzyl anion is smaller, which favors this ion and is consistent with the conclusions reached above.

Conclusions

This paper provides the first experimental measurement of the gas phase acidity of a strained benzoannelated cycloalkene. The resulting value ($\Delta H_{\text{acid}}^{\circ}(\mathbf{5H}) = 386 \pm 3$ kcal/mol) indicates that benzocyclopropene is significantly more acidic than the allylic position of cyclopropene and only 4 ± 3 kcal/mol less acidic than toluene. This experimental finding is satisfactorily reproduced by *ab initio* calculations carried out at the MP2(fc)/6-31+G(d)/HF/6-31+G(d) and MP2(fc)/6-31+G(d) levels of theory. The origin of the increased acidity of benzocyclopropene is discussed and identified. It is a consequence of the increased stability of benzocyclopropenyl anion. This latter finding is rationalized by an interplay of two factors: (a) the propensity of the aromatic ring to alleviate an unfavorable 4π -electron interaction within the three-membered ring and (b) pyramidalization of the anionic center, which minimizes interaction between the lone pair and the aromatic sextet.

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Supporting Information Available: Calculated structures (*xyz* coordinates) and energies for all of the computed species in this work (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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