

Benzocyclobutene: The Impact of Fusing a Strained Ring onto Benzene

Zoran Glasovac and Mirjana Eckert-Maksic*

Ruder Boskovic Institute, P.O. Box 1016, HR-10001 Zagreb, Croatia

Katherine M. Broadus, Michael C. Hare,[†] and Steven R. Kass*

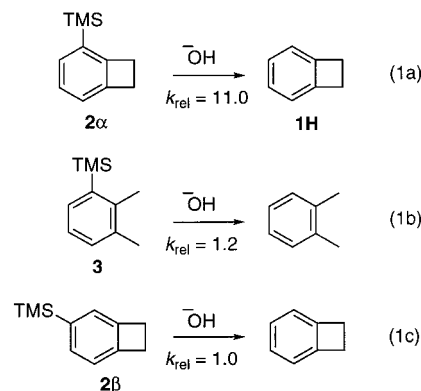
Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received November 29, 1999

The gas-phase acidities of the two aromatic sites in benzocyclobutene were measured in a Fourier transform mass spectrometer using a kinetic technique (i.e., the DePuy method). Fusion of a cyclobutane ring onto benzene is found to have a slight acidifying effect at the α -position (3.2 ± 1.7 kcal mol⁻¹) and little, if any, influence on the β -site (0.8 ± 1.9 kcal mol⁻¹). Energetic data ($\Delta H_{\text{acid}}^{\circ} = 386.2 \pm 3.0$ kcal mol⁻¹, EA = 0.84 ± 0.11 eV, and C–H BDE = 92 ± 4 kcal mol⁻¹) for the benzylic position were obtained via the bracketing technique and application of a thermodynamic cycle. Differences in the reactivities of the three conjugate bases also were explored. Ab initio and density functional theory calculations were carried out to provide geometries, energies, and insights into the carbanions' electronic structures.

Introduction

Fusion of an angularly strained ring(s) to a benzene moiety influences the structure and reactivity of the aromatic fragment to a considerable extent.^{1–3} These effects originate from rehybridization of the carbon junction atoms; the hybrid orbital emanating from the annelated bond toward the α position of the benzene ring (see below) possesses a significant amount of s-character as a result of the increased p-character in the bonds of the strained ring.^{1–5} This hybridization pattern presumably contributes to the enhanced acidity and the accompanying reactivity of benzocyclobutene (**1H**) observed earlier by Eaborn et al.⁴ In particular, the α -trimethylsilyl derivative (**2 α**) was found to undergo base-induced desilylation in dimethyl sulfoxide 8.8 times faster than the acyclic dimethyl substituted reference compound **3**, and 11.0 times more rapidly than the β derivative (**2 β** , eq 1). The latter compound, however, exhibits little, if any, rate acceleration in comparison to 1,2-dimethyl-4-trimethylsilylbenzene ($k_{\text{rel}} = 1.38$ (**2 β**) vs 1.00). In accord with these data, Streitwieser and co-workers determined the α position of **1H** is 7 times more reactive than the β site upon treatment with cesium cyclohexylamide.² More-



over, electrophilic reactions with benzocyclobutene are known to yield β -substituted products almost exclusively.⁵ A recent theoretical analysis revealed this preference arises from two different modes of partial π -electron localization.⁶ The first, which occurs in the ground state, is induced by fusion of a small ring. The second is present in the transition state structure and resembles Wheland's σ -complex. It appears that the competition between these two antagonistic localization patterns is responsible for the enhanced reactivity of the β position with electrophilic reagents.

All of the reported work to date on benzocyclobutene has been carried out in the condensed phase, and consequently, solvation, aggregation, and counterion effects need to be considered. In this gas-phase study, we have examined the intrinsic reactivity and acidity of benzocyclobutene at the α and β positions. In addition, the chemistry of the most stable benzocyclobutenyl anion, **1**, was explored, and the benzylic C–H bond dissociation energy is reported. Ab initio and density functional calculations have been carried out to elucidate the electronic structure of the three isomers and address the key features influencing their stability.

[†] Current address: Department of Chemistry, Ohio University, Athens, OH 45701.

(1) (a) For a recent review see: Maksic, Z. B.; Eckert-Maksic, M.; M \acute{o} , O.; Yañez, M. In *Pauling's Legacy: Modern Modelling of the Chemical Bond*; Maksic, Z. B., Orville-Thomas, W. J., Eds. *Theoretical and Computational Chemistry*; Politzer, P., Maksic, Z. B., Eds.; Elsevier: Amsterdam, 1999; Vol. 3, and references therein. (b) *Carbocyclic Three- and Four-Membered Ring Compounds*; de Meijere, A., Ed.; Thieme: Stuttgart, 1997; Houben-Weyl, Vol. E/17d, and references therein. (c) Muller, P. Chemistry of Cyclopropanes. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 3, pp 37–107.

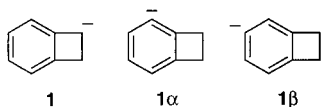
(2) Streitwieser, Jr., A.; Ziegler, G. R.; Mowery, P. C.; Lewis, A.; Lawler, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 1357–1358.

(3) Finnegan, R. A. *J. Org. Chem.* **1965**, *30*, 1333–1335.

(4) (a) Eaborn, C.; Najam, A. A.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2481–2484. (b) Eaborn, C.; Najam, A. A.; Walton, D. R. M. *J. Organomet. Chem.* **1972**, *46*, 255–261.

(5) (a) Taylor, R. *Electrophilic Aromatic Substitution*; John Wiley: Chichester, 1990. (b) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471–487.

(6) Eckert-Maksic, M.; Maksic, Z. B.; Klessinger, M. *Int. J. Quantum Chem.* **1994**, *49*, 383–396.



Experimental Section

All compounds were prepared under an inert atmosphere of dried and deoxygenated nitrogen. Solvents were purified according to literature procedures. Commercially available reagents were used as received. Benzocyclobutene was synthesized by flash vacuum pyrolysis as previously described.⁸ 2-Trimethylsilylbenzocyclobutene⁹ was prepared by a series of reactions¹⁰ that include preparation of a (η^6 -naphthalene)-chromium tricarbonyl complex,¹¹ naphthalene-benzocyclobutene ligand exchange,¹² silylation of the (η^6 -benzocyclobutene)-chromium tricarbonyl complex,⁹ and finally oxidative cleavage.⁹ Treatment of 3-bromobenzocyclobutene¹³ with *n*-butyllithium in diethyl ether at 0 °C with subsequent stirring for 2 h at room temperature followed by quenching with chlorotrimethylsilane (0 °C) afforded 3-trimethylsilylbenzocyclobutene¹⁴ in a 56% yield. 7-Trimethylsilylbenzocyclobutene¹⁵ was prepared from a Grignard reaction with the requisite chloride precursor.¹⁶ All products were further purified by preparative gas chromatography on a 12 ft \times 0.25 in. 10% SE 30 column at 160 °C and analyzed by ¹H and ¹³C NMR spectra recorded on a Varian Gemini 300 spectrometer. The results agree with reported data.^{8,9,15}

The gas-phase experiments were carried out in a dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3.0 T superconducting magnet and controlled by a Sun workstation running the Odyssey Software 4.0 package. The isomeric anions were generated regiospecifically by fluoride-induced desilylation of the appropriate trimethylsilane precursor. Fluoride was prepared by electron ionization at 6 eV of carbon tetrafluoride. Anion **1** also was generated by deprotonation of benzocyclobutene with hydroxide, which was formed upon electron ionization at 3 eV of a 3:1 mixture of nitrous oxide and methane. The benzocyclobutenyl anions were isolated by ejecting undesired ions with a SWIFT waveform,¹⁷ and then transferred to the second cell where they were cooled with an argon pulse (2×10^{-5} Torr). Neutral probe reagents were introduced into the cell through pulsed or slow leak valves, and the product ions were monitored as a function of time.

For the DePuy kinetic acidity measurement, hydroxide was prepared in the manner mentioned above and transferred to the other cell where a static pressure of the silane of interest was present. Argon was pulsed into the cell (ca. 10^{-5} Torr). After a period of 500 ms, all product ions were ejected to eliminate any results arising from nonthermalized hydroxide.

(7) Moore, L.; Lubinski, R.; Baschky, M. C.; Dahlke, G. D.; Hare, M.; Arrowood, T.; Glasovac, Z.; Eckert-Maksic, M.; Kass, S. R. *J. Org. Chem.* **1997**, *62*, 7390–7396.

(8) Schiess, P.; Rutschmann, S.; Toan, V. V. *Tetrahedron Lett.* **1982**, *23*, 3669–3672.

(9) Kündig, E. P.; Perret, C.; Rudolph, B. *Helv. Chim. Acta* **1990**, *73*, 1970–1979.

(10) The procedure described in ref 11 was followed with the exception that the reaction mixture was refluxed in decalin for 18 h. The reaction was carried out in an apparatus similar to that described in Hudecek, M.; Toma, S. *J. Organomet. Chem.* **1990**, *393*, 115–118.

(11) Hudecek, M.; Gajda, V.; Toma, S. *J. Organomet. Chem.* **1991**, *413*, 155–160.

(12) Kündig, E. P.; Perret, C.; Spichiger, S.; Bernardelli, G. *J. Organomet. Chem.* **1985**, *286*, 183–200.

(13) Loyd, J. B. F.; Ongley, P. A. *Tetrahedron* **1965**, *21*, 245–254.

(14) Bassindale, A. R.; Eaborn, C.; Walton, D. R. M. *J. Chem. Soc. B* **1969**, 12–15.

(15) Way, H. G.; Betz, P.; Butenschön, H. *Chem. Ber.* **1991**, *124*, 465–474.

(16) 7-Chlorobenzocyclobutene was prepared by reduction and subsequent chlorination of benzocyclobutenone as described by Azadi-Ardakani, M.; Wallace, T. W. *Tetrahedron* **1988**, *44*, 5939–5952.

(17) (a) Chen, L.; Wang, T. C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1987**, *59*, 449–460. (b) Wang, T. C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1986**, *58*, 2935–2938.

The ratio of product ions ($\text{Me}_3\text{SiO}^-/\text{R}(\text{Me})_2\text{SiO}^-$) was then measured and found to be constant over time (0.75–3 s). Signals were isotopically corrected, and an error analysis that accounted for the quality of the linear correlation and the uncertainties in the calibration data was carried out.¹⁸

Calculations were performed with Gaussian 94¹⁹ or GAMESS-US²⁰ programs implemented on Unix-based workstations and Cray supercomputers at the Minnesota Supercomputer Institute and Linux-based Pentium II PC's at Ruder Boskovic Institute in Zagreb. Geometry optimizations of **1H** and its anions, **1**, **1 α** , and **1 β** , were carried out at the MP2 and B3LYP levels of theory with a 6-31+G(d) basis set.²¹ The diffuse functions are necessary for properly describing the electronic structure of anions and enthalpy changes upon deprotonation.²² The nature of the stationary points were characterized by vibrational frequency calculations, which were also used to obtain zero-point vibrational energies (ZPEs) and temperature corrections (0 to 298 K). To this end, the following scaling factors of 0.9646 and 0.9427 for the MP2 ZPEs and harmonic frequencies, respectively, were employed, and no adjustment was used for the DFT results.²³

The computed structures are interpreted by making use of simple qualitative bond indices such as hybridization parameters²⁴ and Coulson's π -bond orders.²⁵ For this purpose, the amount of s-character was calculated by natural bond orbital (NBO) analysis.²⁶ Bader's topological parameters were used to address the electron density distribution.²⁷ Furthermore, atomic charges, π -electron densities and π -bond orders were obtained using density partitioning based on symmetric Löwdin's orthogonalization.²⁸

Results and Discussion

To address the question of enhanced reactivity in proton abstraction reactions at the α position of benzocyclobutene, we have measured the gas-phase acidities of the aromatic positions in **1H** using a kinetic method

(18) (a) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 11890–11897. (b) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; pp 92–118.

(19) *Gaussian 94*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian, Inc.*: Pittsburgh, PA, 1995.

(20) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *GAMESS. J. Comput. Chem.* **1993**, *14*, 1347–1363.

(21) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(22) (a) Chandrasekar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609–5612. (b) Gao, J.; Garner, D. S.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4784–4790. (c) Siggel, M. R. F.; Thomas, D. T.; Saethre, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 91–96.

(23) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345–350.

(24) (a) Maksic, Z. B. In *Theoretical Models of Chemical Bonding*; Maksic, Z. B., Ed.; Springer-Verlag: Berlin-Heidelberg, 1991; Vol. 2, p 137. (b) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367–1400.

(25) McWeeny, R. *Coulson's Valence*, 3rd ed.; Oxford University: Oxford, 1979.

(26) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926. (b) Weinhold, F.; Carpenter, J. E. In *The Structure of Small Molecules and Ions*; Naaman, R.; Vager, Z., Eds.; Plenum: New York, 1988; p 227. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736–1740. (e) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066–4073. (f) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.

(27) (a) Bader, R. F. W. In *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990. (b) The implementation in Gaussian 94 is due to Cioslowski and co-workers. See: Cioslowski, J.; Nanayakkara, A.; Challacombe, M. *Chem. Phys. Lett.* **1993**, *203*, 137–142 and the Gaussian 94 manual for more details.

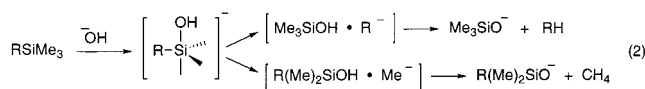
(28) Löwdin, P. O. *J. Chem. Phys.* **1950**, *18*, 365–375.

Table 1. Data for the DePuy Kinetic Acidity Measurement^a

R-TMS	Me ₃ SiO ⁻ / R(Me) ₂ SiO ^{-b}	ln(3*ratio)	Δ <i>H</i> _{acid} (RH, kcal mol ⁻¹)
ethyl	0.122	-1.01	420.1 ± 2.0
methyl	1.00	0.000	416.7 ± 0.7
cyclopropyl	0.876	0.966	411.5 ± 2.0
vinyl	2.32	1.94	409.4 ± 0.6
phenyl	8.84	3.28	401.7 ± 0.5
α-benzocyclobutenyl	21.5	4.17	398.5 ± 1.6
β-benzocyclobutenyl	12.3	3.61	400.9 ± 1.8

^a Acidity values for calibrant species are taken from refs 29, 30, and 44. ^b Ratios are isotopically corrected.

developed by DePuy and co-workers.²⁹ Attempts to bracket the acidity of the aromatic isomers were unsuccessful because these ions readily rearrange to the more stable benzylic anion (**1**) upon reaction with ND₃, EtNH₂, Me₂NH, or D₂O. In this approach an unknown's acidity is determined relative to that of methane on the basis of the fragmentation of a pentacoordinate silicate anion (eq 2). Following reaction of an alkylsilane with hydrox-



ide, the resulting intermediate can fragment either by loss of CH₃⁻ or R⁻. The incipient ions then deprotonate the hydroxysilane, generating R(Me)₂SiO⁻ or Me₃SiO⁻. The natural logarithm of the statistically corrected ratio of these two product ions has been shown to correlate linearly with gas-phase acidities. In our study, a calibration curve was constructed with various substituted trimethylsilanes to yield the following equation: Δ*H*_{acid}⁻(RH) = -4.29 × ln(Me₃SiO⁻/R(Me)₂SiO⁻) + 416.3, *r*² = 0.984. A complete listing of the data is given in Table 1. When the α- and β-trimethylsilylbenzocyclobutenes (**2α** and **2β**) are allowed to react with hydroxide ion, not only are the two siloxides of interest formed but deprotonation also takes place (35%). A small correction for the M-1 ion (*m/z* 175) is necessary as a result of the overlap of its ¹³C, ²⁹Si, and ³⁰Si isotopes with the R(Me)₂SiO⁻ ion at *m/z* 177. This adjustment was made by subtracting natural isotope abundances of the M-1 signal from the observed siloxide intensity at *m/z* 177. The resulting ratios for **2α** and **2β** afford acidities of 398.5 ± 1.6 and 400.9 ± 1.8 kcal mol⁻¹ for the α and β positions of benzocyclobutene, respectively. Comparison of these values with that for benzene (Δ*H*_{acid}⁻ = 401.7 ± 0.5 kcal mol⁻¹)³⁰ reveals that the fused cyclobutane ring acidifies the α site of **1H** by 3.2 ± 1.7 kcal mol⁻¹; the β position is relatively unaffected since a possible difference (0.8 ± 1.9 kcal mol⁻¹) lies within the range of experimental error.

Our experimental results are in modest absolute numerical agreement with 298 K calculations carried out at the MP2/6-31+G(d) level of theory (i.e., ΔΔ*H*_{acid}⁻ = -4.6 (α) and -2.0 (β) kcal mol⁻¹, Table 2). A similar discrepancy at this level is also found for benzene (ΔΔ*H*_{acid}⁻ = -3.5 kcal mol⁻¹), suggesting that the error is not an experimental problem related to the use of a kinetic method since benzene's acidity was determined by an equilibrium measurement. Therefore, the acidity

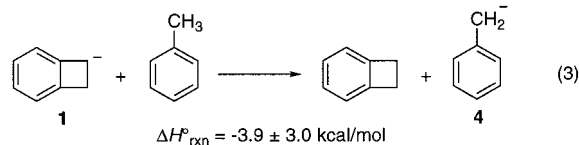
(29) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968–1973.

(30) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590–2599.

values were reinvestigated using additional polarization functions on the hydrogen atoms, MP2/6-31+G(d,p)//MP2/6-31+G(d), and the results are in better accord with experiment (i.e., Δ*H*_{acid}⁻ = 397.1 (α, -1.4), 402.4 (β, +1.5), and 402.2 (benzene, +0.5) kcal mol⁻¹). These estimates are within the limits of the experimental accuracy. This improvement is consistent with an earlier study of polysubstituted benzene acidities and an intuitive notion that hydrogen atoms need to be well described in carbon–hydrogen bond breaking.³¹ It is interesting to mention that DFT calculations using the B3LYP hybrid functional yield acidity values close to those predicted by the MP2/6-31+G(d,p)//MP2/6-31+G(d) results (Δ*H*_{acid}⁻ = 395.1 (α), 399.3 (β), and 396.8 (benzene) kcal mol⁻¹).³² Other approaches to estimating acidities, such as correlating the amount of s-character in the C–H bond or using the ¹³C–H coupling constant (*J*_{13C-H}) have been described in the literature.^{33,34} In this case, the ordering and difference in magnitude between the α and β sites (ΔΔ*H*_{acid}⁻ = 1.8 kcal mol⁻¹) are correctly predicted using ¹³C–H coupling constants, but the absolute acidities are too weak (i.e., 408.5 and 410.3 kcal mol⁻¹ for the α and β positions, respectively).³⁵

The acidity of the benzylic position in **1H** also was examined. In this case the bracketing technique was used, and the occurrence or nonoccurrence of proton transfer between **1** and a series of reference acids was observed (Table 3). Anion **1** was found to deprotonate pyridazine and methanol-OD but not less acidic compounds such as fluorobenzene, deuterium oxide, and ammonia-*d*₃. In the reverse direction, **1H** was deprotonated by fluorophenide, OD⁻, and NH₂⁻ but not weaker bases such as 1,3-diazinide and methoxide ions. In accord with these observations, **1** incorporates three deuterium atoms upon reaction with ammonia-*d*₃ and five deuterium atoms with deuterium oxide.³⁶ These results allow us to assign Δ*H*_{acid}⁻(**1H**) = 386.2 ± 3.0 kcal mol⁻¹, which is in good agreement with calculated values of 387.5 kcal mol⁻¹ (MP2/6-31+G(d)) and 385.5 kcal mol⁻¹ (B3LYP/6-31+G(d)).

The benzylic position in **1H** is slightly less acidic than toluene³⁷ (ΔΔ*H*_{acid}⁻ = 3.9 ± 3.0 kcal mol⁻¹, eq 3). This



finding is in accord with the generally accepted view put forth by Eaborn et al., which states that the increased s-character in the benzylic C–H bond of **1H** is counterbalanced by less effective delocalization in the resulting

(31) Maksic, Z. B.; Kovacek, D.; Eckert-Maksic, M.; Zrinski, I. *J. Org. Chem.* **1996**, *61*, 6717–6719.

(32) The B3LYP data are available in the Supporting Information.

(33) The acidity of certain positions can be estimated from the corresponding s-character according to the following relationship: p*K* = 83.12 - 1.33(%s). (a) Maksic, Z. B.; Eckert-Maksic, M. *Tetrahedron* **1969**, *25*, 5113–5126. (b) Merrill, G. N.; Kass, S. R. *J. Phys. Chem.* **1996**, *100*, 17465–17471.

(34) Kass S. R.; Chou P. K. *J. Am. Chem. Soc.* **1988**, *110*, 7899–7900.

(35) Acidities are calculated using the correlation Δ*H*_{acid}⁻ = -0.296 *J*_{13C-H} + 455.3, which is taken from ref 33.

(36) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185–5192.

(37) Ellison, G. B.; Davico, G. E.; Bierbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrom. Ion Processes* **1996**, *156*, 109–131.

Table 2. Experimental and Calculated Acidities for the Different Positions in Benzocyclobutene and Absolute Energies and Scaled Zero-Point Vibrational Energies for the Different Species

compound	energy (au)		$\Delta H_{\text{acid}}^{\text{P}} (\text{kcal mol}^{-1})^a$		
	MP2/6-31+G(d) (MP2/6-31+G(d,p)) ^a	ZPVE ^b	0 K	298 K	experiment
1H	-308.59723 (-308.65848)	0.13057			
1	-307.96641 (-308.02325)	0.11454	385.6 (388.4)	387.5 (390.3)	386.2 ± 3.0
1α	-307.95756 (-308.01372)	0.11633	392.5 (395.7)	393.9 (397.1)	398.5 ± 1.6
1β	-307.94989 (-308.00562)	0.11651	397.4 (400.9)	398.9 (402.4)	400.9 ± 1.8
C ₆ H ₆	-231.47203 ^c (-231.51906)	0.09570 ^c			
C ₆ H ₅ ⁻	-230.82593 ^c (-230.86655)	0.08188 ^c	396.8 (400.8)	398.2 (402.2)	401.7 ± 0.5 ^d
C ₆ H ₅ CH ₃	-270.64417 ^c (-270.70717)	0.12322 ^c			
C ₆ H ₅ CH ₂ ⁻	-270.01874 ^c (-270.07659)	0.10777 ^c	382.8 (386.0)	384.3 (387.5)	382.3 ± 0.3 ^e

^a Parenthetical values correspond to MP2/6-31+G(d,p) single point energies on MP2/6-31+G(d) geometries. ^b ZPVEs are scaled by 0.9646. ^c Values are taken from ref 7. ^d Reference 30. ^e Reference 37.

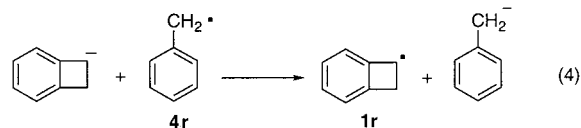
Table 3. ΔH_{acid} Bracketing Results for Benzocyclobutene

HA	$\Delta H_{\text{acid}}^{\text{P}} (\text{kcal/mol})^a$	proton transfer ^b		H/D exchange
		forward	reverse	
ND ₃	403.6 ± 0.8 ^c	no	yes	3
D ₂ O	392.9 ± 0.1	no	yes	5
PhF	387.2 ± 2.5	no	yes	
pyridazine	385.2 ± 2.5	yes	no	
MeOD	383.5 ± 0.7	yes	no	no

^a Values are taken from ref 45. ^b The forward and reverse directions correspond to the reactions of **1** with different acids and **1H** with different bases, respectively. ^c The acidity for NH₃ was used.

anion.⁴ More specifically, in this case it appears that delocalization into the aromatic π system is the dominant factor. This point is illustrated by considering the *s*-character in the C–H bonds of **1H** and toluene (25.4% vs 23.9%) in comparison to the Ar–C π -bond orders, 0.69 (**4**) vs 0.61 (**1**).³⁸

The stability of benzocyclobutenyl anion **1** can be further probed by examining the electron affinity of its corresponding radical (**1r**). This quantity was measured by monitoring electron transfer between **1** and a variety of standard reference compounds (Table 4). In particular, electron transfer was observed with perfluorotoluene and sulfur dioxide but not with the other reagents. These observations lead to a bracketed electron affinity of 0.84 ± 0.11 eV for **1r**. Our experimental electron affinity results can be compared with a predicted value of 0.75 eV at the UB3LYP/6-31+G(d) level of theory.³⁹ An isogyric reaction with benzyl anion should afford a more reliable number, 0.82 eV, eq 4. Benzyl radical has an



$$\text{EA}(\mathbf{1r}) = \Delta H_{\text{rxn}}^{\text{P}}(\text{UB3LYP}/6\text{-}31\text{+G(d)}) + \text{EA}(\mathbf{4r}) = 0.82 \text{ eV}$$

(38) Glasovac, Z.; Eckert-Maksic, M., unpublished results.

(39) MP2 calculations were not carried out because they typically give poor results for electron affinities, whereas B3LYP values are usually quite good. For example, see Merrill, G. N.; Kass S. R. *J. Am. Chem. Soc.* **1997**, *119*, 12322–12337.

Table 4. Electron Affinity Bracketing Results for Benzocyclobutenyl Radical (1r**)**

compound	EA (eV) ^a	electron transfer	other products
CS ₂	0.51 ± 0.10	no	see text
<i>m</i> -CF ₃ C ₆ H ₄ CN	0.67 ± 0.10	no	M-1, cluster ^b
perfluoropyridine	0.68 ± 0.11	no	adduct - HF
1-naphthaldehyde	0.68 ± 0.10	no	adduct ^c
<i>p</i> -CF ₃ C ₆ H ₄ CN	0.76 ± 0.10	no	adduct - CHF ₃ , -CN, M-1 ^d
<i>p,p'</i> -difluorobenzophenone	0.78 ± 0.05	no	adduct - HF
C ₆ F ₅ Cl	0.82 ± 0.11	no	adduct - HF, C ₆ F ₅ ⁻ , Cl ⁻
C ₆ F ₅ CF ₃	0.86 ± 0.11	yes	adduct - HF
SO ₂	1.107 ± 0.008	yes	oxygen-atom transfer

^a Electron affinity values from ref 45. ^b Collision-induced dissociation (CID) of the cluster gives ⁻CN and *m*-CF₃C₆H₄CN⁻ as the major products and *m*-CF₃C₆H₄CN^{•-} and **1** as minor ones. ^c CID of the adduct gives **1** as the dominant ion. ^d *p*-CF₃C₆H₄CN^{•-} is also observed in this reaction, but double-resonance experiments suggest that it does not arise from **1**.

electron affinity of 0.912 ± 0.006 eV,³⁷ and thus the less effective conjugation in the benzocyclobutene system results in a 0.1 eV lower electron binding energy.

The benzyl C–H bond dissociation energy for **1H** can be determined by combining our measured electron affinity and acidity for **1r** and **1H** in a thermodynamic cycle (eq 5). A bond energy of 92 ± 4 kcal mol⁻¹ is

$$\text{C-H BDE}(\mathbf{1H}) = \Delta H_{\text{acid}}^{\text{P}}(\mathbf{1H}) - \text{IP}(\mathbf{H}^{\bullet}) + \text{EA}(\mathbf{1r}) \quad (5)$$

obtained, which is 2 kcal mol⁻¹ greater than for toluene (C–H BDE = 89.8 ± 0.6 kcal mol⁻¹).³⁷ The relatively small difference in the BDEs is the result of the weaker acidity for **1H**, which in turn is largely canceled by the lower electron affinity for **1r**.

In addition to their thermochemical differences, the three benzocyclobutenyl isomers exhibit unique reactivity with some probe reagents (Table 5). The reaction between **1** and carbon disulfide gives HS⁻ as the major product along with C₉H₇⁻ (adduct-S₂), C₉H₆S⁻ (adduct-HS), and a small amount of sulfur-atom transfer. In contrast, the major pathway for both phenide isomers is sulfur-atom abstraction. All three ions react with carbonyl sulfide to give HS⁻, sulfur-atom transfer, and an adduct, but the

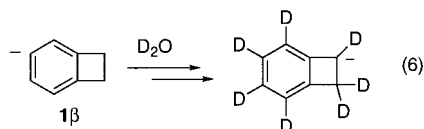
Table 5. Summary of Products Obtained upon Reaction of 1, 1 α , and 1 β with CS₂, COS, SO₂, and MeSSMe^{a,b}

reagent	1	1α	1β
CS ₂	HS ⁻ (71%) adduct - S ₂ (9%) adduct - HS (13%) SAT (7%)	HS ⁻ (14%) SAT (86%)	HS ⁻ (13%) SAT (82%) adduct (6%)
COS	HS ⁻ (73%) SAT (25%) adduct (2%)	HS ⁻ (48%) SAT (52%) adduct (trace)	HS ⁻ (51%) SAT (35%) adduct (14%)
SO ₂	SO ₂ ⁻ (91%) OAT (9%)	SO ₂ ⁻ (32%) OAT (42%) adduct (26%)	SO ₂ ⁻ (49%) OAT (38%) adduct (13%)
MeSSMe	MeS ⁻ (maj) MeSCH ₂ S ⁻ (min)	MeS ⁻ (maj) MeSCH ₂ S ⁻ (min)	MeS ⁻ (maj) MeSCH ₂ S ⁻ (min)

^a Reported percentages are taken from data points at different reaction times and should be considered as estimates (i.e., $\pm 5\%$)
^b SAT and OAT stand for sulfur-atom and oxygen-atom transfer, respectively.

product ratios differ somewhat. Sulfur dioxide reacts with **1 α** and **1 β** via electron transfer, oxygen-atom abstraction, and adduct formation, whereas the benzylic ion largely gives SO₂⁻, and only a small amount of oxygen-atom abstraction takes place. Similar behavior among the isomers is observed with dimethyl disulfide; MeS⁻ and MeSCH₂S⁻ are the major and minor products, respectively.

Hydrogen–deuterium exchange of the isomers with D₂O illustrates some divergent behavior. Under similar reaction conditions (~ 7 s, 1×10^{-7} Torr D₂O), **1** was observed to undergo five exchanges in comparison to six for **1 α** and seven for **1 β** (eq 6). A few comments can be

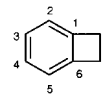


made regarding the exchange process. Ion **1-d₀** is consumed roughly at the same rate as **1 α -d₁** and **1 β -d₁**, which supports the rapid isomerization of the phenide ions to **1**. The benzylic sites appear to exchange more rapidly than the aryl ones, as suggested by the lifetimes of the **1-d₁** and **1-d₂** ions. Last, **1 β** can incorporate deuteriums at C3 and C4 more easily than **1 α** ; presumably the latter isomerizes more readily to the benzylic anion.

Geometries and Electronic Structures. With an understanding of the benzocyclobutenyl anions' experimental thermochemistries and reactivities, we explored their structures and electron distributions computationally. The key geometric parameters of the MP2/6-31+G(d) optimized structures are summarized in Table 6. The calculated structure of **1H** was found to be in good agreement with published X-ray data.⁴⁰

It is worth commenting on a few important features. Formation of phenyl anions **1 α** and **1 β** induces hybridization changes at the deprotonation sites, which are marked by decreased C–C–C bond angles (-8.3° for C1–C2–C3 (α) and -8.1° for C2–C3–C4 (β)). To accommodate these large perturbations, angular distortions occur elsewhere in the ring, primarily at the adjacent carbon atoms. The bonds emanating from the anionic site

(40) Böse, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304–305.

Table 6. Geometric Parameters of Benzocyclobutene (1H) and Its Anions 1, 1 α , and 1 β Calculated at the MP2/6-31+G(d) Level of Theory^{a,b}

bond or angle	1H	1	1α	1β
C1–C6	1.398 (1.391)	1.436	1.409	1.396
C1–C2	1.392 (1.385)	1.422	1.404	1.401
C2–C3	1.406 (1.400)	1.407	1.429	1.427
C3–C4	1.408 (1.399)	1.410	1.420	1.431
C4–C5	1.406 (1.400)	1.425	1.409	1.418
C5–C6	1.392 (1.385)	1.378	1.393	1.393
C1–C8	1.520 (1.518)	1.420	1.532	1.529
C6–C7	1.520 (1.518)	1.529	1.519	1.521
C7–C8	1.576 (1.576)	1.548	1.576	1.578
C6–C1–C8	93.3	93.8	92.1	93.0
C1–C6–C7	93.3	90.4	94.1	93.7
C1–C2–C3	115.7	116.9	107.4	120.7
C2–C3–C4	121.8	123.4	126.6	113.7
C3–C4–C5	121.8	119.7	121.7	127.0
C4–C5–C6	115.7	116.7	114.1	115.2
C5–C6–C1	122.4	124.0	121.4	121.0
C6–C1–C2	122.4	118.3	128.6	122.2
C1–C8–H	115.5	131.0	115.5	116.3
C6–C7–H	115.5	115.3; 112.6	116.2	116.3
C6–C1–C8–H	± 115.6	149.2	± 115.9	± 115.4

^a Bond lengths and angles are in angstroms and degrees, respectively. Parenthetical values correspond to experimental data taken from ref 40 ^b The indicated numbering scheme is used in all cases (e.g., the carbanion centers in **1**, **1 α** , and **1 β** are C8, C2, and C3).

lengthen by 0.012–0.023 Å. These structural changes are consistent with increased s-content of the lone pair and the accompanying decrease in the s-character of the carbon–carbon bonds, decreased ellipticities (ϵ) and less negative Laplacians ($\nabla^2\rho_C$) (Table 7).⁴¹ Although π -atomic orbitals cannot mix with the σ orbital of the anionic lone pair because of symmetry, a strong shift of π electrons away from the deprotonation site is observed. The α and β position π -densities are depleted by 0.22 and 0.21 e⁻, respectively, and concomitant increases are noted in the *meta* and *para* carbon atoms (0.06–0.07 for α ; 0.05–0.07 for β).

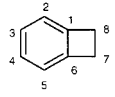



Deprotonation of the benzylic site produces significant distortions in both rings.⁴² These changes involve elongation of the annelated (C1–C6) and *ortho* (C1–C2) bonds, while the bonds emanating from the anionic center and the C5–C6 bond shorten. As expected, the C1–C8 bond undergoes the largest contraction (0.1 Å), and the remaining hydrogen at C8 is displaced out of the C1–C8–C7 plane by 33.5° because the lone pair favors participation of the s-orbital in its hybrid. It is interesting to note that the B3LYP functional predicts **1** to have a planar structure.³² This dihedral angle is the only major discrepancy between the DFT and MP2 computed structures and should be considered as a serious drawback of the former approach.⁴³

Concomitant with the above structural changes in forming **1**, the π -electron density increases in the aro-

(41) (a) Alcamí, M.; Mó, O.; Yañez, M.; Abboud, J. L. M.; Elguero, J. *Chem. Phys. Lett.* **1990**, *172*, 471–477. (b) Alcamí, M.; Mó, O.; Yañez, M.; Abboud, J. L. M. *J. Phys. Org. Chem.* **1990**, *4*, 177–191. (c) Abboud, J. L. M.; Cañada, T.; Homan, H.; Notario, R.; Cativiela, C.; Diaz de Villegas, M. D.; Bordejé, M. C.; Mó, O.; Yañez, M. *J. Am. Chem. Soc.* **1992**, *114*, 4728–4736.

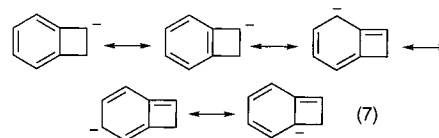
(42) For consistency sake, we have used the same numbering scheme for **1** as for **1H**, **1 α** , and **1 β** . As a result, C8 is the anionic carbon in **1**.

Table 7. Bader's Topological Parameters (ρ_c , $\nabla^2\rho_c$, and ϵ) and Löwdin's π -bond Orders, Atomic Charges, and π -Densities for **1H, **1**, **1 α** , and **1 β** Computed from MP2/6-31+G(d) Structures and Wavefunctions; Natural Bond Orbital Hybridization Parameters Are Calculated at the MP2/6-31G(d)//MP2/6-31+G(d) Level of Theory^a**

cmpd	bond	NBO s-char. %	Bader's topological params. ^b			Löwdin population analysis			
			ρ_c	$\nabla^2\rho_c$	ϵ	π -b.o.	atom	charge	π -den.
1H 	C1-C6	30.7-30.7	0.318	-0.876	0.217	0.59	C1	-0.12	0.96
	C1-C2	38.4-34.8	0.310	-0.842	0.199	0.61	C2	-0.22	0.99
	C2-C3	34.7-35.2	0.303	-0.808	0.211	0.62	C3	-0.24	0.99
	C3-C4	35.3-35.3	0.303	-0.805	0.209	0.62	C4	-0.24	0.99
	C4-C5	35.2-34.7	0.303	-0.808	0.211	0.62	C5	-0.22	0.99
	C5-C6	34.8-38.4	0.310	-0.842	0.199	0.61	C6	-0.12	0.96
	C1-C8	30.7-25.4	0.246	-0.559	0.025	0.20	C7	-0.37	1.16
	C6-C7	30.7-25.4	0.246	-0.559	0.025	0.20	C8	-0.37	1.16
	C7-C8	23.6-23.6	0.225	-0.477	0.002	0.13	-	-	-
	C8-H	25.5	0.268	-0.906	0.008	-	-	-	-
1 	C1-C6	27.2-29.8	0.295	-0.766	0.148	0.45	C1	-0.13	0.96
	C1-C2	36.7-34.9	0.291	-0.756	0.158	0.48	C2	-0.34	1.12
	C2-C3	35.5-36.2	0.300	-0.781	0.258	0.64	C3	-0.29	1.04
	C3-C4	36.0-35.6	0.299	-0.776	0.245	0.61	C4	-0.38	1.15
	C4-C5	34.8-34.9	0.290	-0.744	0.210	0.53	C5	-0.29	1.06
	C5-C6	36.2-39.6	0.314	-0.844	0.264	0.69	C6	-0.16	1.00
	C1-C8	35.7-35.5	0.288	-0.695	0.295	0.60	C7	-0.39	1.12
	C6-C7	30.3-24.6	0.240	-0.529	0.015	0.19	C8	-0.54	1.39
	C7-C8	26.5-28.9	0.231	-0.478	0.095	0.19	-	-	-
	C8-H	34.5	0.260	-0.844	0.073	-	-	-	-
1α 	C1-C6	31.6-31.7	0.310	-0.827	0.227	0.60	C1	-0.21	0.97
	C1-C2	41.1-33.6	0.303	-0.817	0.044	0.59	C2	-0.33	0.77
	C2-C3	32.0-37.9	0.288	-0.728	0.057	0.60	C3	-0.34	0.99
	C3-C4	35.1-36.7	0.294	-0.758	0.206	0.62	C4	-0.32	1.05
	C4-C5	35.1-35.2	0.300	-0.790	0.224	0.62	C5	-0.29	1.05
	C5-C6	35.2-38.3	0.307	-0.822	0.217	0.60	C6	-0.18	1.02
	C1-C8	27.1-27.3	0.244	-0.548	0.036	0.19	C7	-0.41	1.14
	C6-C7	29.8-26.6	0.245	-0.545	0.023	0.20	C8	-0.42	1.14
	C7-C8	24.1-23.3	0.224	-0.469	0.016	0.13	-	-	-
	C8-H	24.7	0.264	-0.867	0.011	-	-	-	-
1β 	C1-C6	31.0-31.2	0.319	-0.878	0.248	0.59	C1	-0.18	1.02
	C1-C2	39.9-34.6	0.302	-0.799	0.194	0.61	C2	-0.32	0.99
	C2-C3	37.4-32.6	0.289	-0.738	0.060	0.61	C3	-0.36	0.78
	C3-C4	32.8-38.1	0.287	-0.730	0.054	0.59	C4	-0.33	0.98
	C4-C5	34.9-36.1	0.295	-0.759	0.206	0.63	C5	-0.32	1.06
	C5-C6	34.7-39.1	0.307	-0.825	0.215	0.60	C6	-0.17	1.01
	C1-C8	28.8-26.8	0.241	-0.528	0.031	0.20	C7	-0.40	1.14
	C6-C7	29.6-26.7	0.244	-0.545	0.030	0.21	C8	-0.40	1.14
	C7-C8	23.8-23.5	0.224	-0.468	0.013	0.13	-	-	-
	C8-H	24.8	0.264	-0.867	0.005	-	-	-	-

^a NBO analyses for **1H** and **1** at the MP2 level with the 6-31+G(d) basis set give virtually identical results to those reported here, but problems arose when using diffuse functions in the calculations for **1 β** and **2 β** . ^b ρ is in atomic units (i.e., electrons/bohr³).

matic ring. Löwdin analysis reveals the following increments: C4 (0.16 e⁻), C2 (0.13 e⁻), and C6 (0.04 e⁻) in comparison to 0.23 e⁻ at C8 (Table 7, eq 7). The changes



(43) This is further supported by MP3/6-31+G(d) calculations which predict a displacement of the benzylic hydrogen (27.1°) similar to that found in the MP2/6-31+G(d) optimized structure. Glasovac, Z.; Eckert-Maksic, M., unpublished results.

(44) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744–2765.

(45) All thermodynamic data, unless otherwise noted, comes from Bartmess, J. E. *Negative Ion Energetics Data in Secondary Negative Ion Energetic Data*; National Institute of Standards and Technology: Gaithersburg, MD 20899, 1998 (<http://webbook.nist.gov>).

in the carbon–carbon bond distances described above are consistent with the resonance structures in eq 7. Analysis of the Laplacian ($\nabla^2\rho_c$) and ellipticity (ϵ) values derived from topological analysis of the electron density distribution further support these observations. For example, there is a substantial increase in $\nabla^2\rho_c$ (−0.876 vs −0.766)

for the fused bond upon deprotonation of benzocyclobutene at C8. A shift in the electron density, ρ_c , is observed, although to a smaller extent. The ellipticity changes also reflect reduced π bond character. Comparable perturbations occur in the C1–C2 bond. As for the C1–C8 bond, opposite effects are noted; the Laplacian decreases and the ellipticity undergoes a significant change, increasing from 0.025 to 0.295, once again indicating considerable conjugation with the aromatic fragment.

Conclusion

The gas-phase acidities and reactivities of the three positions in benzocyclobutene were explored in a Fourier transform mass spectrometer. The thermochemistry of **1H** reveals that the fused cyclobutane ring has a slight acidifying effect at the α position ($\Delta H_{\text{acid}}^{\circ} = 398.5 \pm 1.6$ kcal mol⁻¹) in contrast to the β site ($\Delta H_{\text{acid}}^{\circ} = 400.9 \pm 1.8$ kcal mol⁻¹). The benzylic ion (**1**) is the most stable of the three anions and gives rise to the following thermodynamic data: $\Delta H_{\text{acid}}^{\circ} = 386.2 \pm 3.0$ kcal mol⁻¹, EA = 0.84 ± 0.11 eV, and C–H BDE = 92 ± 4 kcal mol⁻¹.

Reactivity differences between **1**, **1 α** , and **1 β** were observed with carbon disulfide, carbonyl sulfide, and sulfur dioxide. Ab initio calculations provided geometries of the anions, as well as insight into their electronic structures. In addition, the computed acidities are in good accord with experimental data.

Acknowledgment. Support from the National Science Foundation, the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the Minnesota Supercomputer Institute is gratefully acknowledged. The work in Zagreb (M.E.M. and Z.G.) has been supported by the Ministry of Science and Technology of Croatia through project 00980801 and HR-US project JF 143. M.E.M and Z.G. also thank the Center for Advanced Computing at the University of Zagreb for computer time.

Supporting Information Available: The energies and xyz coordinates for benzocyclobutene and its anions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO991825Y