Benzocyclobutadienyl Anion: Formation and Energetics of an Antiaromatic Molecule

Katherine M. Broadus and Steven R. Kass*

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

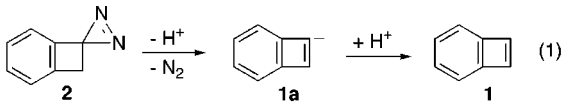
kass@chem.umn.edu

Received May 9, 2000 (Revised Manuscript Received July 24, 2000)

Benzocyclobutadienyl diazirine (**2**) was synthesized and reacted with hydroxide ion in a Fourier transform mass spectrometer to afford the conjugate base of benzocyclobutadiene (**1a**). Authentication of the ion structure was carried out by a derivatization experiment (i.e., **1a** was converted to benzocyclobutenone enolate, which has previously been studied), and its reactivity was explored. Thermochemical data for benzocyclobutadiene (**1**) were obtained ($\Delta H°_{acid}$ (**1**) = 386 ± 3 kcal mol^{-1}, EA(**1r**) = 1.8 ± 0.1 eV, and C−H BDE (**1**) = 114 ± 4 kcal mol^{-1}), compared to MP2 and B3LYP calculations, and contrasted to a series of model compounds. Cyclobutadienyl radical appears to be quite different from benzocyclobutadienyl radical (**1r**) and worth further exploration.

Introduction

Cyclobutadiene and its derivatives have intrigued scientists for decades due to the synthetic challenge, their unusually reactive nature, and various properties associated with antiaromatic molecules.[1−4] Over the past four decades, several highly substituted cyclobutadienes have been synthesized and fully characterized. Benzocyclobutadiene (**1**) has been found to be an unstable derivative that can be detected in a low-temperature argon matrix and as a transient intermediate in a fast-flow NMR experiment.[5,6] Chapman and Trahanovsky, thus, were able to provide the UV, IR, and ^{1}H NMR spectra for **1**. More recently, we have determined the first experimental energetics for benzocyclobutadiene ($\Delta H°_f$)[7] and now wish to extend the known thermochemistry of **1** by reporting its gas-phase acidity ($\Delta H°_{acid}$) and C−H bond dissociation energy. These values were derived from studies of the conjugate base of benzocyclobutadiene (**1a**), which was synthesized in the gas phase by loss of a proton and molecular nitrogen from diazirine **2** (eq 1).



(1)

Hundreds of diazirine derivatives have been prepared, and many serve as stable precursors for carbenes.[8] In addition, the diazirine moiety has been incorporated in biologically active compounds to function as photoaffinity reagents for receptors and as hydrophobic reagents for membrane organization studies.[9−12] Diazirines also enjoy a rich chemistry in the gas phase as precursors for vinyl anions,[13] heterocyclic 4π electron systems,[14] carbynes,[15] and hydrazyl anions.[16]

Despite the wealth of diazirines and diazo compounds reported in the literature, difficulties have been encountered in preparing the diazo derivative of benzocyclobutenone (**3**).[17] Thermolysis of the lithium salt of tosylhydrazone **4** does not lead to recovery of **3**, instead *o*-toluonitrile and benzocyclobutenone are the major products formed (eq 2). Diazo compound **5** has been observed as an intermediate in the photolysis of the hydrazone salt of 4,6-dimethylbenzocyclobutenone by IR and UV analysis (eq 3). The collected carbene dimers, **6** and **7**, provide further evidence for the formation of **5**, but the compound, itself, has not been isolated.[17]

In this paper, we present of the synthesis of benzocyclobutenyl diazirine (**2**) and the conjugate base of benzocyclobutadiene (**1a**). The reactivity, authentication, and thermochemistry and of this ion are reported, and the energetics are compared with density functional and ab initio calculations.

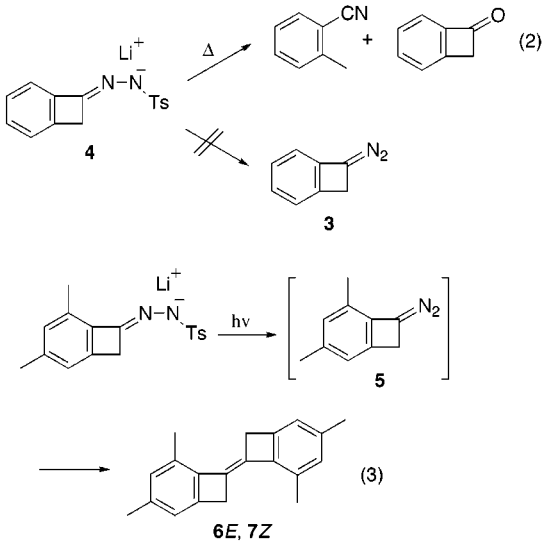
Results and Discussion

Benzocyclobutadiene's reactive nature precludes generating its conjugate base (**1a**) by conventional means

* To whom correspondence shouldbe addressed.

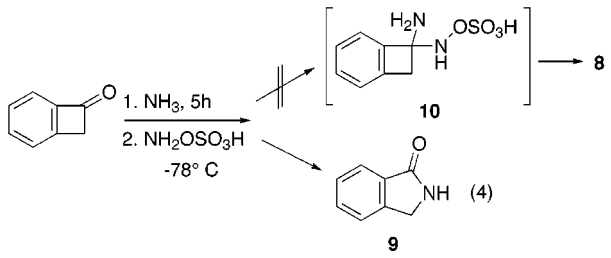
(1) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; Wiley-Interscience: New York, 1994.
(2) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309−332.
(3) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343−370.
(4) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425−490.
(5) Trahanovsky, W. S.; Fischer, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 4971−4972.
(6) Chapman, O. L.; Chang, C. C.; Rosenquist, N. R. *J. Am. Chem. Soc.* **1976**, *98*, 261−262.
(7) Broadus, K. M.; Kass, S. R. Submitted for publication.
(8) Liu, M. T. H. *Chemistry of Diazirines*; CRC Press: Boca Raton, FL, 1987.
(9) Lachaal, M.; Rampal, A. L.; Lee, W.; Shi, Y. W.; Jung, C. Y. *J. Biol. Chem.* **1996**, *271*, 5225−5230.
(10) Kwiattowski, S.; Crocker, P. J.; Chavan, A. J.; Imaj, N. *Tetrahedron Lett.* **1990**, *31*, 2093- 2096.
(11) Meier, E.; Schummer, D.; Sandhoff, K. *Chem. Phys. Lipids* **1990**, *55*, 103−113.
(12) Hatanaka, Y.; Yoshida, E.; Nakayama, H.; Kanaoka, Y. *Bioorg. Chem.* **1989**, *17*, 482−485.
(13) Anderson, K. K.; Kass, S. R. *Tetrahedron Lett.* **1989**, *30*, 3045−3048.
(14) Kroeker, R. L.; Kass, S. R. *J. Am. Chem. Soc.* **1990**, *112*, 9024−9025.
(15) Seburg, R. A.; Hill, B. T.; Jesinger, R. A.; Squires, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 1, 6310−6311.
(16) Broadus, K. M.; Kass, S. R. *Int. J. Mass Spectrom.* **1999**, *187*, 179- 187.
(17) Durr, H.; Nickels, H.; Pacala, L. A.; Jones, J. M. *J. Org. Chem.* **1980**, *45*, 973−980.

10.1021/jo000709o CCC: $19.00
Published on Web 08/31/2000

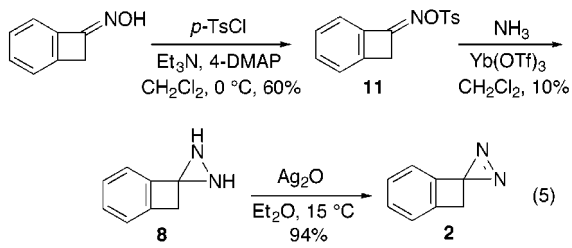


(i.e., deprotonation or fluorodesilylation of a trialkylsilyl derivative). Diazirines have been shown to be powerful sources of vinyl anions in the gas phase, and therefore, we sought to prepare **2** as a precursor for **1a**. These cyclic diazo isomers can be easily synthesized from their corresponding diaziridines using a variety of oxidizing agents. The latter functional group is more difficult to obtain in some instances.[8,18] Diaziridines are generally prepared by reaction of a ketone with ammonia and an aminating reagent such as chloroamine or hydroxylamine-*O*-sulfonic acid. Other reported synthetic routes to diaziridines are based upon modifications of this approach.

Benzocyclobutenyl diazirine (**2**) possesses two components which have been observed as troublesome in the synthesis of diaziridines: an aryl substituent and a four-membered ring.[8,18] To our knowledge, a five-membered ring is the smallest system in which a diaziridine has been introduced successfully. In keeping with this point, we were unable to obtain benzocyclobutenyl diaziridine (**8**) upon reacting benzocyclobutenone with the standard reaction conditions mentioned above, and the lactam **9** was obtained in a reasonable yield (eq 4). Variations of the reaction temperature and order of addition consistently led to the formation of **9** suggesting that benzocyclobutenone is resistant to imine formation with ammonia.



Synthesis of aryl-substituted diaziridines has been achieved in the literature by two routes. Both circumvent the problem with the imine formation step and increase the likelihood of generating the aminated intermediate (**10**) by converting the ketone into its tosyloxime or a benzyl imine prior to treatment with ammonia. In particular, 3-aryl-3-trifluoromethyl substituted diaziridines have been prepared in high yields via their corresponding tosyloximes.[19,20] Initial experiments with **11** under these conditions (stirring for 8 h at room temperature in a sealed apparatus) led to the recovery of starting material. We found, however, that addition of a Lewis acid catalyst, ytterbium(III) trifluoromethanesulfonate, served to activate the tosyloxime,[21] and benzocyclobutenyl diaziridine (**8**) was obtained from **11** after an 18 h reaction period (eq 5). The desired compound also could be generated by heating the tosyloxime and ammonia at 50 °C for 2.5 h. This route was not examined in detail due to the thermal sensitivity of **11**. The second strategy for synthesizing aryl substituted diaziridines (via a benzyl imine precursor) has been successfully applied to acetophenone and other alkyl−aryl ketones.[22,23] Proton NMR results suggest diaziridine **8** can be prepared from the benzyl imine of benzocyclobutenone. The product, however, was never isolated. Difficulties in handling the imine and successful preparation of the target molecule precluded an exhaustive study of this reaction.



Diaziridine **8** was cleanly converted to benzocyclobutenyl diazirine (**2**) in a nearly quantitative yield upon treatment with silver oxide and the product was purified by column chromatography. We have handled this compound without incident and it is stable at room temperature. In most cases the diazirine was prepared and used promptly although we have stored the product at −20 °C in deuterated chloroform for 2 months without significant indication of decomposition.

Benzocyclobutenyl diazirine was found to afford the conjugate base of benzocyclobutadiene (**1a**) by gas-phase anion chemistry. Precursor **2** was introduced into a Fourier transform mass spectrometer (FTMS) and allowed to react with hydroxide which was generated by electron ionization of a methane−nitrous oxide mixture. This reaction affords an M-1 ion (*m*/*z* 129) along with the desired elimination product (**1a**, *m*/*z* 101) (eq 6, Figure 1). The former species can be converted to the latter by sustained off-resonance irradiation (SORI).[24] This technique promotes low energy fragmentation pathways by continually depositing a small amount of kinetic energy (5 eV) into the targeted ion in the presence of an inert collision gas (argon). The conjugate base of benzocyclo-

(18) Church, R. F. R.; Kende, A. S.; Weiss, M. J. *J. Am. Chem. Soc.* **1965**, *87*, 2665−2671.

(19) Hatanaka, Y.; Nakayama, H.; Kanaoka, Y. *Heterocycles* **1993**, *35*, 997−1004.

(20) Baldwin, J. E.; Jesudason, C. D.; Moloney, M. G.; Morgan, D. R.; Pratt, A. J. *Tetrahedron* **1991**, *47*, 5603−5614.

(21) Kobayashi, S.; Nagayama, S. *J. Am. Chem. Soc.* **1997**, *119*, 10049−10053.

(22) Liu, M. T. H.; Jennings, B. M. *Can. J. Chem.* **1977**, *55*, 3596−3601.

(23) Schmitz, E.; Ohme, R. *Chem. Ber.* **1961**, *94*, 2166−2173.

(24) Gauthier, J. W.; Trautman, T. R.; Jacobson, D. B. *Anal. Chim. Acta* **1991**, *246*, 211−225.

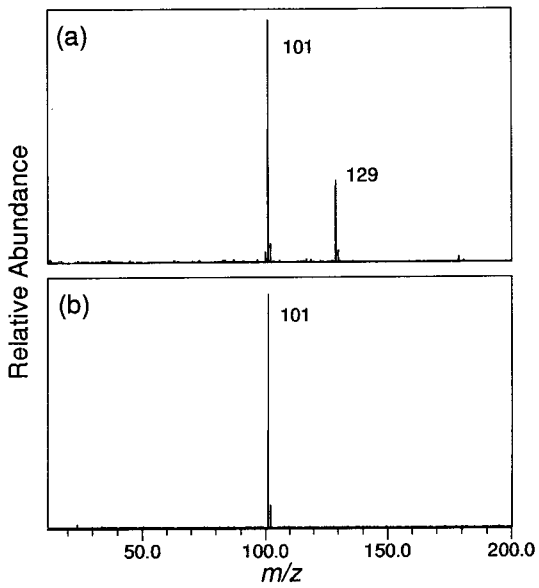


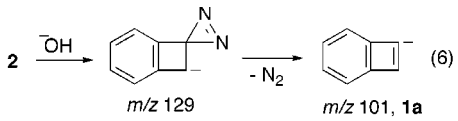
Figure 1. (a) Reaction of benzocyclobutenyl diazirine (**2**) with hydroxide; *m*/*z* 129 arises from deprotonation while subsequent loss of molecular nitrogen affords *m*/*z* 101 (**1a**). (b) Isolation of the conjugate base of benzocyclobutadiene (**1a**, *m*/*z* 101).

Table 1. Summary of Bracketing Experiments of 1a with Various Reference Acids

acid	$\Delta H°_{acid}$ (kcal mol^{-1})[a]	proton/deuteron transfer
deuterium oxide	392.9 ± 0.1	no
fluorobenzene	387.2 ± 2.5	no
pyridazine	385.2 ± 2.5	yes
methanol-*d*	383.5 ± 0.7	yes
ethanol-*d*	378.3 ± 1.0[b]	yes

[a] Acidity values taken from ref 40. [b] Value is for EtOH.

butadiene was then isolated in the FTMS cell by a SWIFT waveform[25] and its thermochemistry and reactivity were probed.



The C−H bond dissociation energy of benzocyclobutadiene can be derived from a thermodynamic cycle which combines the acidity of **1** ($\Delta H°_{acid}$), the known ionization potential of hydrogen atom, (IP (H$^{\bullet}$)), and the electron affinity of benzocyclobutadienyl radical (EA (**1r**)) eq 7.

$$\text{C−H BDE (1)} = \Delta H°_{acid}\text{(1)} - \text{IP (H}^{\bullet}\text{)} + \text{EA (1r)} \quad (7)$$

The acidity of benzocyclobutadiene was measured by titrating its conjugate base with a variety of reference acids. Ion **1a** was found to deprotonate (or abstract a deuteron from) pyridazine, methanol-*Od* and ethanol-*Od*, but not deuterium oxide or fluorobenzene (Table 1). In the case of deuterium oxide, three hydrogen−deuterium exchanges can be observed. The d_1 ion is major (80%) in accord with the structure of benzocyclobutadiene (i.e., two equivalent acidic protons), and additional deuterium incorporation (maximum extent of d_2 17%, d_3 3%) can be explained by the ability of this probe reagent to undergo more than one exchange in a single collision along with the enhanced acidity of the α-position in the aromatic ring.[26,27] Fusion of the strained four-membered ring results in computed MP2 acidities at the α and β positions in benzocyclobutadiene of 392.2 and 397.6 kcal mol^{-1}, respectively, compared to 401.7 ± 0.5 kcal mol^{-1} (expt) and 397.8 kcal mol^{-1} (MP2) for benzene.[28,29] Our observations enable us to assign $\Delta H°_{acid}$ (**1**) = 386 ± 3 kcal mol^{-1} which is in accord with calculated values of 384.0 kcal mol^{-1} (B3LYP) and 383.0 kcal mol^{-1} (MP2).

Table 2. Results for the Electron Affinity Bracketing of Benzocyclobutadienyl Radical (1r)

compound	EA[a] (eV)	electron transfer
sulfur dioxide	1.107 ± 0.087	no
4-nitrobenzaldehyde	1.691 ± 0.087	no
2,5-dimethyl-1,4-benzoquinone	1.761 ± 0.061	no
3,5-di-*tert*-butyl-1,4-benzoquinone	1.804 ± 0.087	no
1,4-naphthoquinone	1.81 ± 0.10	yes
2-methyl-1,4-benzoquinone	1.852 ± 0.087	yes
1,4-benzoquinone	1.91 ± 0.10	yes

[a] Electron affinity values taken from ref 40.

The electron affinity of benzocyclobutadienyl radical (**1r**) was determined in a similar manner. Anion **1a** was allowed to react with reference compounds and the occurrence or nonoccurrence of electron transfer was monitored as a function of time. The conjugate base of benzocyclobutadiene transfers an electron to 1,4-naphthoquinone, 2-methyl-1,4-benzoquinone, and 1,4-benzoquinone, but not to reagents whose radical anions have lower electron affinities (Table 2). These results enable us to assign EA (**1r**) = 1.8 ± 0.1 eV, which is in favorable accord with the computed direct energy difference between **1a** and **1r**, 1.84 eV at the UB3LYP level. This result along with the acidity measurement leads to a carbon−hydrogen bond energy in benzocyclobutadiene of 114 ± 4 kcal mol^{-1} (eq 7).

The reactivity of **1a** was briefly explored. It abstracts a sulfur atom from carbon disulfide as well as carbonyl sulfide (eq 8a) and an oxygen atom from sulfur dioxide and nitrous oxide (eq 8b).[30,31] This latter process provided a means for authenticating the structure of **1a**. In particular, the reactivity and thermochemistry of **12** was compared and found to be identical to that of benzocyclobutenone enolate independently generated via deprotonation of benzocyclobutenone. Specifically, enolate **12** deprotonates 2-trifluoroethanol, but not methanol. Upon reaction with hexafluoropropylene, products arising from carbanion (adduct−HF) and oxy anion (O^-/F exchange) attack are detected. Additionally, **12** slowly affords an adduct−H_2 ion upon reaction with sulfur dioxide. This behavior is the same as we previously reported for benzocyclobutenone enolate.[32]

(25) Wang, T. C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1986**, *58*, 2935−2938.

(26) Glasovac, Z.; Eckert-Maksic, M.; Broadus, K. M.; Hare, M. C.; Kass, S. R. *J. Org. Chem.* **2000**, *65*, 1818−1824.

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

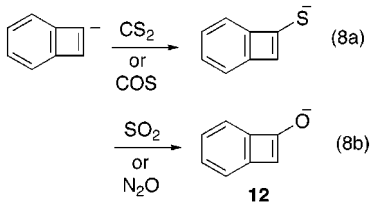
(28) MP2/6-31+G(d) and B3LYP/6-31+G(d) calculations will simply be referred to as MP2 and B3LYP in this paper.

(29) 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.

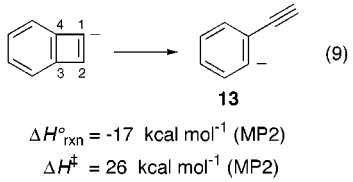
(30) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849- 2851.

(31) DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556−559.

(32) Broadus, K. M.; Kass, S. R. *J. Chem. Soc., Perkin Trans.* 2 **1999**, 2389−2396



The above derivatization experiment and the good agreement between the observed and calculated thermochemistry indicate that the conjugate base of benzocyclobutadiene does not rearrange. One can, however, envision **1a** ring opening to its phenide isomer (**13**, eq 9). Alleviation of the cyclobutadiene interaction as well as a reduction in ring strain (SE (**1**) = 59 kcal mol^{-1})[7] overcomes the energetically unfavorable conversion of a σ bond to a π bond and the process is predicted to be exothermic by 17 kcal mol^{-1} at the MP2 level. It does not occur to a significant extent, if at all, because there is a large activation barrier (26 and 25 kcal mol^{-1} at the MP2 and B3LYP levels, respectively) for the electronic reorganization. An alternative isomerization pathway via the heterolytic cleavage of the C1−C4 bond to afford a vinylidene intermediate is suggested by the geometry change in going from **1** to **1a** (i.e. the bond length increases by 0.052 and 0.055 Å at the MP2 and B3LYP levels of theory, respectively) (Figure 2), but was not explored because of the lack of experimental evidence for **13**.



Examining the thermochemistry of benzocyclobutadiene in the context of reference compounds proved insightful (Table 3). The most striking feature of **1** is its increased acidity (386 kcal mol^{-1}) relative to ethylene, benzene, naphthalene and the 3-position (α vinyl hydrogen) in 6-methylindene. This last difference (6 ± 4 kcal mol^{-1}) can be attributed to the greater percentage of s-character in the C−H bond of **1** (36.0% (**1**) vs 32.4% (6-methylindene))[33] as a result of its increased ring strain. The enhanced acidity of benzocyclobutadiene is counterbalanced by a high electron affinity for its radical (**1r**) so that the C−H bond dissociation energy is comparable to that of ethylene, benzene and naphthalene (ΔBDE = ∼1−3 (±4) kcal mol^{-1}).

Computational results on cyclobutadiene suggest its conjugate base should be stable in the gas phase with respect to electron detachment. The parent is calculated to be 9.9 kcal mol^{-1} more basic than **1** which is slightly larger than the experimental difference observed between naphthalene and benzene, $\Delta\Delta H°_{acid}$ = 7.5 kcal mol^{-1}. A larger disparity in the electron affinities of the corresponding radicals ($\Delta\Delta$EA = 25.1 kcal mol^{-1}) is responsible for the considerably weaker carbon−hydrogen bond in cyclobutadiene ($\Delta\Delta$BDE = 15.5 kcal mol^{-1}). This difference is the result of cyclobutadiene's radical being surprisingly stable and apparently quite distinct from **1r**. For example, **1r** is computed to be planar, the four-membered ring has alternating carbon−carbon bond lengths ranging from 1.347 to 1.531 Å and the spin density is largely (1.35 au) localized at C1 whereas cyclobutadienyl radical is puckered (α = 19.4°, Figure 3), the C−C bond lengths are nearly equivalent (1.43−1.44 Å) and the C1−C3 distance is only 1.85 Å, and the odd electron resides mostly on C2 and C4 (0.66 au each). Further investigation into the cyclobutadienyl radical at higher levels of theory and via experiment would be interesting and is planned.

(33) Hybridization values were determined from Natural Bond Orbital analyses. (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.

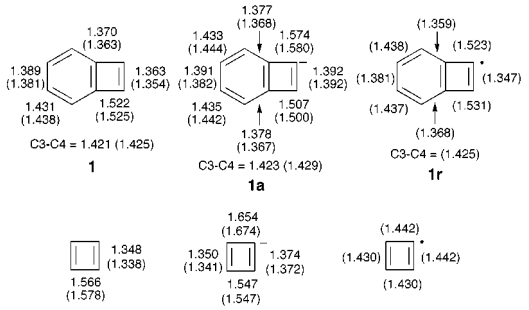


Figure 2. Computed MP2 and B3LYP geometries for benzocyclobutadiene (**1**), its conjugate base (**1a**) and radical (**1r**), and the corresponding cyclobutadiene series. B3LYP results are given in parentheses and all distances are in angstroms.

Table 3. Summary of Thermochemical Comparisons[a]

compound	$\Delta H°_{acid}$ (kcal mol^{-1})	EA (eV)	BDE (kcal mol^{-1})
benzocyclobutadiene	386 ± 3 (384.0)	1.8 ± 0.1 (1.84)	114 ± 4 (112.6)
6-methylindene[b]	392.2 ± 2.9		
benzene[c]	401.7 ± 0.5	1.10 ± 0.01	113.5 ± 0.5
naphthalene[d]	394.2 ± 1.2	1.37 ± 0.02	112.2 ± 1.3
cyclobutadiene	(393.9)	(0.75)	(97.1)
ethylene[c]	409.4 ± 0.6	0.667 ± 0.024	111.2 ± 0.8

[a] Parenthetical numbers correspond to B3LYP results. [b] The acidity corresponds to the 3-position (α-vinyl anion). Broadus, K. M; Han, S.; Kass, S. R. Unpublished work. [c] Thermochemical values come from ref 40. [d] Naphthalene results are reported for the α position and are taken from ref 41.

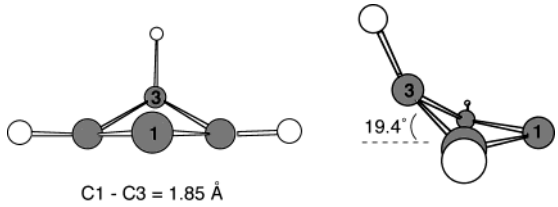


Figure 3. Two views of the optimized UB3LYP/6-31+G(d) structure of cyclobutadienyl radical.

Conclusion

We have prepared the diazirine of benzocyclobutenone (**2**) which is an attractive alternative to the long sought after diazo isomer **3**. In the gas phase, diazirine **2** afforded the conjugate base of benzocyclobutadiene (**1a**). This ion was found to be stable with regard to a unimolecular rearrangement, and its structure was verified by derivatization to benzocyclobutenone enolate. The thermochemistry of **1a** provided the C−H bond energy

(114 ± 4 kcal mol^{-1}) and acidity (386 ± 3 kcal mol^{-1}) of benzocyclobutadiene as well as the electron affinity of its corresponding radical (1.8 ± 0.1 eV). Theoretical calculations suggest the parent, the conjugate base of cyclobutadiene, also should be experimentally accessible and that the corresponding radical is an intriguing species.

Experimental Section

Synthesis. Benzocyclobutenone and its oxime were prepared by published methods.[34,35] All solvents and reagents were purified by standard methods before use.

Benzocyclobutenone *p*-(Tolylsulfonyl)oxime (11). To a solution of benzocyclobutenone oxime (0.95 g, 7 mmol) in 15 mL of methylene chloride were added 4-(dimethylamino)-pyridine (0.08 g, 7 mmol) and triethylamine (1.2 mL). This mixture was cooled to 0 °C, and *p*-toluenesulfonyl chloride (1.6 g, 8 mmol) was added in small portions over a period of 30 min. After an additional 10−15 min at 0 °C, the solution was warmed to room temperature and stirred for 30 min. The product was washed with water, dried with $MgSO_4$, and concentrated by rotary evaporation. In most cases, the tosylate was sufficiently clean to carry on at this point; however, it can be further purified by flash chromatography using methylene chloride (0, 10, 20%) in hexanes as the eluting solvent. The two isomers of **11** were generally obtained as a white solid mixture in a 60% yield (1.2 g). The initial product ratio varied from 1:3 to 1:1.2 depending on the rate of addition of the chloride as well as the reaction temperature: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 4H), 7.2−7.6 (m, 12H), 3.96 (s, 2H, minor isomer), 3.90 (s, 2H, major isomer), 2.44 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 158.6, 145.7, 145.3, 145.2, 144.6, 138.2, 137.4, 134.3, 133.8, 132.6, 132.5, 129.9, 129.8, 129.2, 128.99, 128.97, 127.8, 124.1, 123.6, 123.4, 121.2, 40.1, 39.9, 21.7 (methyl carbons not resolved); IR (KBr)1686, 1598, 1584 cm^{-1}; HRMS-FAB (M + H)$^{\bullet+}$ calcd for $C_{15}H_{14}NO_3S$ 288.0694, obsd 288.0690.

Benzocyclobutenyl Diaziridine (8). Benzocyclobutenone *p*-(tolylsulfonyl)oxime (1.2 g, 4.2 mmol) was dissolved in 10 mL of methylene chloride, and 0.5 g (0.2 equiv) of ytterbium-(III) trifluoromethanesulfonate was added. The mixture was placed in a thick-walled, sidearmed test tube (11 in. × 1 in.) fitted with a vacuum stopcock such that the entire tube could be sealed off. The apparatus was flushed with argon and cooled to −78 °C. Approximately 10 mL of ammonia was then distilled from sodium into the test tube. The stopcock was closed, and the mixture was stirred for ∼18 h at room temperature. During the course of the reaction, a clear red solution was observed. The appearance changed to an orange turbid solution when the reaction was complete. At this point, the test tube was cooled to −78 °C and the stopcock was opened. The solution was allowed to slowly warm to room temperature during which time the residual ammonia evaporated. The mixture was diluted with methylene chloride, washed with sat. NaCl, dried with $MgSO_4$ and concentrated by rotary evaporation. The crude material was purified by column chromatography using ethyl acetate (0, 10, 20, and 40%) in hexanes. Diaziridine **8** was ultimately recrystallized from toluene and recovered as a white solid in a 10% yield (0.055 g), mp 120−122 °C. Alternatively, in place of the Lewis acid catalyst, the tosylate mixture and ammonia can be heated at 50 °C for 2.5 h to afford the diaziridine, but this approach was not examined in detail: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23−7.37 (m, 3H), 7.09 (d, J = 7.5 Hz, 1H), 3.77 (d, J = 14.1 Hz, 1H), 3.59 (d, J = 14.1 Hz, 1H), 2.54 (d, J = 9 Hz, 1H), 2.48 (d, J = 9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 142.7, 130.3, 128.0, 122.7, 120.5, 63.5, 41.6; IR (KBr) 3205 cm^{-1}; HRMS-EI M$^{\bullet+}$ calcd for $C_8H_8N_2$ 132.0687, obsd 132.0699.

Benzocyclobutenyl Diazirine (2). Diaziridine **8** (0.05 g, 0.4 mmol) was dissolved in 8 mL of warm diethyl ether. The solution was cooled to ∼15 °C, and freshly prepared silver oxide (0.15 g, 0.6 mmol) was added in one portion. After stirring for 1.5 h, the solution was filtered and dried over potassium carbonate for several hours. The diazirine was purified by column chromatography (100% pentane). The solvent was removed at 0 °C by rotary evaporation to produce **5** (0.049 g) as a light yellow oil in a 94% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.17 (m, 3H), 6.75 (d, J = 7.2 Hz, 1H), 3.38 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 142.7, 129.1, 128.0, 121.6, 119.6, 40.8, 36.7; IR (neat) 3104, 1639, 1631, 1563, 1548, 1530, 1502 cm^{-1}; HRMS-CI (water−argon) (M + H)$^{\bullet+}$ calcd for $C_8H_7N_2$ 131.0609, obsd 131.0604.

Preparation of Silver Oxide. A sodium hydroxide solution (0.09 g in 1 mL of water) was slowly added to a solution of silver nitrate (0.37 g in 1 mL of water). The precipitated product was collected by suction filtration and washed with water (3 × 1 mL) followed by ether (3 × 1 mL).

1-Isoindolinone (9). Benzocyclobutenone (4.0 g, 0.034 mol) was placed in a 250 mL three-necked round-bottomed flask fitted with a dry ice condenser and addition funnel. Ammonia (∼55 mL) was distilled over sodium into the flask, which was cooled to −78 °C. The reaction was refluxed for 5 h and then cooled to −78 °C. A solution of hydroxylamine-*O*-sulfonic acid (4.5 g, 0.04 mol) in methanol (50 mL) was added over a period of 30 min. After this time, the cooling bath was removed, and the solution was refluxed for 1.5 h. The dry ice condenser was subsequently removed and the ammonia was allowed to evaporate overnight. The crude material was then filtered and washed with generous portions of methanol. The filtrate was concentrated by rotary evaporation, and the solid material was recrystallized with toluene to afford the 2.4 g of **9** (53% yield) as a white solid: mp 149−151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (bs, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.41−7.55 (m, 3H), 4.44 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 143.9, 132.3, 131.7, 128.0, 123.6, 123.3, 46.0; IR (KBr) 3201, 1678 cm^{-1}; HRMS-CI (ammonia) (M + H)$^{\bullet+}$ calcd for C_8H_8NO 134.0606, obsd 134.0617. The spectral data is in agreement with published values.[36]

Gas-Phase Experiments. All work was carried out in a dual cell Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet. Hydroxide was prepared by electron ionization of a 3:1 mixture of methane and nitrous oxide at 3 eV. In general, all ions of interest were isolated in the analyzer cell by ejecting unwanted species with a SWIFT waveform[25] or a chirp broad band excitation for low masses.[37] Ions 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 using Gaussian94[38] installed on IBM and SGI workstations. Geometries were optimized at the HF, MP2, and B3LYP levels of theory with the 6-31+G(d) basis set. The nature of each stationary point was investigated by a full vibrational analysis although in some cases MP2 frequencies were not obtained. Zero-point energy corrections were made using scaling factors of 1.00, 0.9646, and 0.9135 for B3LYP, MP2, and HF results, respectively.[39] Temperature adjustments (0 to 298 K) were made by scaling the frequencies by 0.9427 (MP2), 0.8929 (HF) and 1.00 (B3LYP).[39] All of the computed acidities and electron affinities reported in this work are at 298 and 0 K, respectively.

(34) Teim-Abou, O.; Goodland, M. C.; McOmie, J. F. W. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2659−2662.

(35) Bubb, W. A.; Sternhell, S. *Aust. J. Chem.* **1976**, *29*, 1685−1697.

(36) Norman, M. H.; Minick, D. J.; Rigdon, G. C. *J. Med. Chem.* **1996**, *39*, 149−157.

(37) Marshall, A. G.; Roe, D. C. *J. Chem. Phys.* **1980**, *73*, 1581−1590.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al- Laham, M. A.; Zakrewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, R. 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.

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

Acknowledgment. Support from the National Science Foundation, the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, and the Minnesota Supercomputer Institute are gratefully acknowledged.

(40) Bartmess, J. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Mallard W. G., Linstrom, P. J., Eds.; February 2000, National Institute of Standards and Technology, Gaithersburg MD 20899 (http://webbook.nist.gov).: Gaithersburg, MD, 2000.

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

Supporting Information Available: MP2 and B3LYP energies and *xyz* coordinates along with ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO000709O