solvent shell is highly oriented in the ground state, and the rather specific solvation required for the activated complex in each case will not require too much reorganization of the solvent.

The two slowest reactions are rate-determining protonations of alkenes. In general, nonpolar molecules such as these are not specifically solvated in aqueous solution, but simply fit into cavities in the hydrogen-bonding matrix of the bulk solvent. To the extent that they interrupt the ordering of water molecules, they are destabilized relative to the pure alkene, in contrast to the alcohols, which gain hydrogen-bonding interactions on dissolving in water—hence the relatively smaller activation energies for the alkene reactions, since the transition state will be as highly solvated (and therefore solvent stabilized) as in the alcohol reactions. The entropies of activation also reflect this interpretation; since there is greatly increased ordering of solvent molecules in approaching the carbonium ion-like transition state, a fairly large negative entropy of activation is expected, and indeed observed. The differences between the entropies of activation for these two reactions are small, as would be expected of rate-determining generation of carbonium ions of the same geometric configuration as the starting material.

It is interesting that whereas in the trans system the carbonium ion is the intermediary in the equilibration between alkene and alcohol, in the cis system the corresponding carbonium ion acts as an interceptor, diverting the alkene and alcohol away from equilibration toward isomerization. Naturally, this is a consequence of the relative lifetimes of the two ions. The trans ion was shown[4] to be long lived enough that when generated from optically active **2** or **3** the optical activity was completely lost in the product. Likewise, if $^{18}$O-labeled **2** or **3** were used, the $^{18}$O-labeled water had time to diffuse out of the solvation sphere of the ion before collapse occurred. As has been amply shown here, the average lifetime of the cis ion must be very short indeed. This effect emphasizes once again the great importance to carbonium ion stability of conjugative dispersal of charge along an unsaturated system.

In conclusion, this system is a unique and very interesting one, showing that, even in the field of classical carbonium ions, experimental facts do not always fall along predictable lines.

# Benzocyclobutene Radical Anion[1]

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*Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514.* *Received June 29, 1970*

**Abstract:** The radical anion of benzocyclobutene was prepared by metal and electrolytic reduction. Conclusive evidence is presented showing the fused, four-membered ring remains intact after reduction. An interesting temperature dependence was noted for the epr spectra of the metal-reduced benzocyclobutene. At low temperatures, the four methylene protons are nonequivalent but become equivalent as the temperature is raised. This phenomenon is discussed in terms of an ion pairing process. Finally, the effect of ring strain on spin densities and reduction potentials is discussed.

Since the original report of Mills and Nixon[4] more than 40 years ago, the study of the effects of ring strain on the chemical and physical properties of aromatic hydrocarbons has received considerable attention. Numerous reports have appeared concerning the increased preference for electrophilic attack $\beta$ to the fused ring as strain is increased.[5–9] Markgraf,[10] *et al.*, have reported on the decrease in basicity of the lone pair of electrons of a nitrogen atom $\alpha$ to a fused ring as strain is introduced. Finnegan[11] and Streitwieser, *et al.*,[12] have reported on the increased acidity of the protons $\alpha$ to the fused ring as strain is increased. Another observation[13,14] was the change in spin densities of radical anions of aromatic hydrocarbons with varying amounts of strain in the fused ring. Also, a large shift in half-wave reduction potential with strain has been noted.[15,16]

Several interpretations have been offered to explain these observations.[12,17,18] The argument presented by Streitwieser, *et al.*,[12] rests on a hybridization–polarization effect. This explanation, in contrast to the other

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[1] A preliminary report on this work was presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN-152. In addition, a preliminary communication on this work has appeared: R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, *J. Amer. Chem. Soc.*, **92**, 1418 (1970).

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two advanced, has the advantage of being able to rationalize the changes in physical as well as chemical properties with strain. In this model, the ring juncture carbon atoms containing the fused, strained ring are rehybridized to accommodate the small bond angles; thus, the $\sigma$ bonds in the strained ring have increased p character and the remaining $\sigma$ bonds to the carbon atoms $\alpha$ to the strained ring have more s character. This increase in s character results in an increase in orbital electronegativity which results in a polarization of $\sigma$ electrons away from the $\alpha$-carbon atoms. The decrease in the electron density at the $\alpha$-carbon atoms can explain the decrease in reactivity toward electrophilic reagents, and also rationalizes the acidity and basicity data. The changes in spin densities and the changes in half-wave reduction potentials with strain have been explained using this model within the Hückel framework by making the coulomb integrals for the $\alpha$-carbon atoms more electronegative and making the ring juncture carbon atoms less electronegative with increasing strain.[13–15]

Benzocyclobutene (BCB) has been the subject of several papers which have centered on the effects of the fused, four-membered ring. A recent thermodynamic study[19] has shown that the heat of hydrogenation of benzycyclobutene is essentially that of *o*-xylene, suggesting little ring strain effect on aromatic resonance. Also, a recent report has appeared on the nmr spin–spin coupling constants of BCB.[20]

In this paper, we would like to present some of our observations on the radical anion of BCB and the reduction potential of BCB. The radical anion is shown to be stable and does not undergo an electrocyclic ring opening as recently suggested in the literature.[21] Qualitative molecular orbital arguments are presented to explain the observed ring strain effects on spin densities and reduction potential.

## Experimental Section

Usual high-vacuum procedures employing alkali metals and ethereal solvents were used to prepare the radical anions studied. The initial hydrocarbon concentration was approximately $10^{-2}$ *M* except as noted. Dimethoxyethane (Aldrich) and tetrahydrofuran (MCB) were dried by distillation from lithium aluminum hydride (Alfa), degassed on the vacuum line using the freeze–pump–thaw technique, and distilled under vacuum to solvent bumpers containing sodium–potassium alloy (Unified Science Associates) where they were stored. Hexamethylphosphoramide (Aldrich) was dried by several vacuum distillations from Linde 13X Molecular Sieves (Union Carbide),[22] followed by degassings on the vacuum line prior to use.

Epr spectra were recorded on a Varian E-3 spectrometer with X-band frequencies and an E-3 variable-temperature accessory. Temperatures were checked using a Honeywell Model 2746 potentiometer and copper–constantan thermocouple. Nmr spectra were recorded on a Varian A-60 spectrometer employing an external standard. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 research chromatograph using an 8 ft × ${}^1/_4$ in. column of 10% SE-30 on Chromosorb P. Computer simulations of theoretical epr spectra were done using a Fortran Version IV program for mixtures employing Lorentzian line shapes written by R. Griffin.[23]

**Benzocyclobutene** was prepared by the procedure of Cava and Napier;[24] it was purified by gas chromatography and had the same boiling point and spectral characteristics as reported.[24]

**1-Deuteriobenzocyclobutene.** Magnesium turnings (0.56 g, 0.023 g-atom) were placed in a 100-ml flask under dry nitrogen. Approximately 40 ml of tetrahydrofuran was distilled under nitrogen from LAH into the flask, followed by ethylmagnesium chloride (2 ml, Arapahoe) and 1-chlorobenzocyclobutene[25] (3.22 g, 0.023 mol). The mixture was stirred under nitrogen for 2 hr and then cooled in an ice bath, 10 ml of deuterium oxide (Merck, >99.7%) was added, the mixture was stirred for 20 min, and 40 ml of water was added. The mixture was extracted with ether and washed successively by water, 10% HCl, and water. The extract was dried ($CaCl_2$) and the ether removed, leaving a yellow residue. This was fractionally distilled, followed by gc purification, to give 0.56 g (32%) of 1-deuteriobenzocyclobutene: bp 45–46° (18 mm), lit.[24] (benzocyclobutene) 50–51° (20 mm); mass spectrum *m/e* 105 (93.2%), 104 (6.8%); nmr (neat) $\tau$ 3.62 (m, 4 H), 7.68 (m, 3H), used external standard; ir (neat) 3085, 2950, 2205, 1539, 775, and 750 $cm^{-1}$; same retention time, gc, as authentic benzocyclobutene. Benzocyclobutene-1-carboxylic acid has been prepared by a similar procedure.[26]

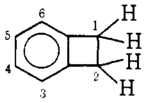
**4-Deuteriobenzocyclobutene.** This was prepared from 1,2-diiodo-4-deuterio- and 1,2-dibromo-4-deuteriobenzocyclobutene[27] by catalytic hydrogenation.[24, 28] The product was purified by gc: mass spectrum *m/e* 105 (68.4%), 104 (31.6%).

***α,α′*-Dibromo-*o*-xylene.** This was obtained from Aldrich and purified by several recrystallizations ($CCl_4$) to give mp 93.5–94° (lit.[29] 93–94°).

## Metal Reduction of Benzocyclobutene

Reduction of BCB with a potassium mirror at −78° in 1,2-dimethoxyethane immediately yielded the 69-line spectrum shown in Figure 1. The spectrum is readily interpreted in terms of the interaction of the electron with four sets of two equivalent nuclei. The hyperfine splitting constants observed are given in Table I. This

**Table I.** Hyperfine Splitting Constants[a] of Benzocyclobutene Radical Anion Prepared with Potassium in DME[b]



| Temp, °C | $A_{\text{methylenes}}$ | | $A_{3,6}$ | $A_{4,5}$ | $A_{\text{K}}$ |
|---|---|---|---|---|---|
| −88 | 5.75 | 5.25 | 7.65 | 1.45 | |
| | (2 H) | (2 H) | (2 H) | (2 H) | |
| −78 | 5.72 | 5.22 | 7.60 | 1.45 | |
| −70 | 5.70 | 5.20 | 7.55 | 1.45 | |
| −60 | 5.67 | 5.20 | 7.50 | 1.45 | |
| −50 | 5.63 | 5.18 | 7.45 | 1.45 | |
| −30 | 5.50 | | 7.38 | 1.45 | 0.11 |
| | (4 H Methylenes equivalent) | | | | |
| −20 | 5.40 | | 7.34 | 1.43 | 0.13 |
| −10 | 5.40 | | 7.28 | 1.42 | 0.18 |
| +20 | 5.30 | | 7.24 | 1.40 | 0.20 |

[a] These values are considered good to ±0.05 G. The temperatures are good to ±1.0°. [b] $A_{\text{H}}$ values are in gauss.

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observation is in direct contrast to the expected 45-line spectrum from the interaction of the electron with two sets of two equivalent nuclei and one set of four equivalent nuclei. The epr spectrum showed an unusual temperature dependence, however, for as the temperature was raised certain lines showed extensive broadening and at higher temperatures collapsed to a new spectrum. The changes in the spectra with temperature are given in Figure 1. One additional feature which was noted was the appearance of metal splittings at approximately −45°. The metal hyperfine splitting gradually increased as the temperature was raised. When the temperature was raised to −10°, the spectrum had collapsed to one which was interpreted as arising by interaction of the electron with two sets of two equivalent nuclei and one set of four equivalent nuclei. We have observed the BCB radical anion up to +20° and found it to be completely reversible with the low-temperature spectrum.

The main difference between the high- and the low-temperature epr spectra is that the low-temperature spectrum has the hyperfine splitting constants 5.20 (2 H) and 5.70 G (2 H) while the high-temperature spectrum has one set of four nuclei with a splitting constant of 5.40 G. This fact, coupled with the alternating line-width effect, suggests an exchange process in which the coupling constants $A_H = 5.20$ G and $A_H = 5.70$ G are being exchanged and in the limit of fast exchange average to one set of four equivalent nuclei. A diagram of the spin states shows that upon exchange of the quantum numbers for these two sets of nuclei all but 27 lines should broaden, as is observed.

Replacement of one of the methylene protons with a deuterium yields the low-temperature spectrum shown in Figure 2. This spectrum can only be simulated as a mixture of two species. A simulated spectrum of a mixture of 1:1 composition, in which one species has a nucleus of splitting constant 5.20 G replaced by a deuterium atom and the second species has one nucleus of 5.67-G splitting constant replaced with a deuterium, matches the observed spectrum. The simulated spectrum is given in Figure 2. As the temperature is raised to −20°, the spectrum collapses to one which can be simulated with three equivalent nuclei of splitiing constant 5.40 G and one of $(^{2}/_{13})$ 5.40 G. The observed and calculated spectra are given in Figure 2. This clearly establishes the 5.20- and the 5.67-G splitting constants as being those associated with the four methylene protons. Replacement of one of the protons meta to the four-membered ring with deuterium gives the spectrum in Figure 3. This establishes the 1.45-G splitting constant as being associated with the 4 and 5 positions. The 7.55-G splitting constant can therefore be assigned to the 3 and 6 positions.

The origin of the nonequivalency of the methylene protons of the radical anion of BCB at low temperatures and the marked temperature dependency of the epr spectra seemed to be due to one of three possibilities. The nonequivalency could arise by ion pairing. A second possibility was that the four-membered ring was skewed and a third possibility was that the four-membered ring had undergone an electrocyclic ring opening to an *o*-xylylene radical anion[21] as suggested in the literature. Line-width alternation and nonequivalency of methylene protons due to ion pairing had been ob-

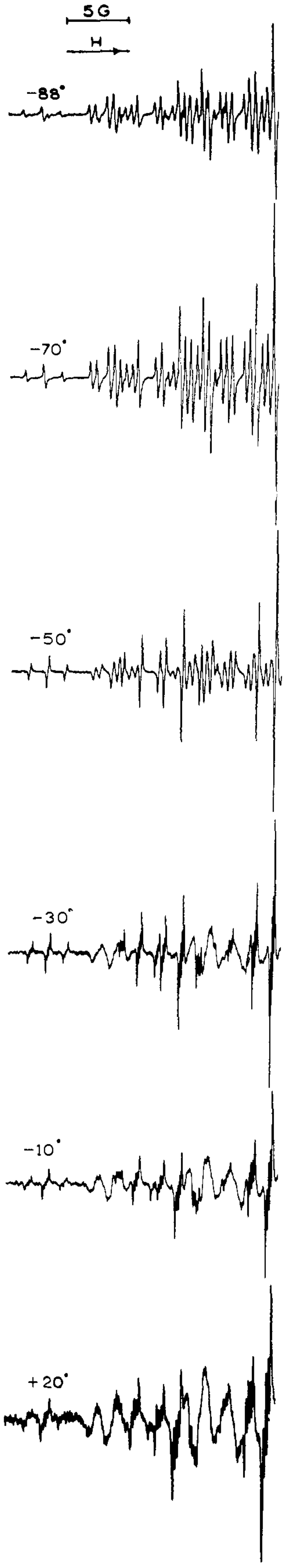

Figure 1. Esr spectra of benzocyclobutene radical anion in DME at various temperatures. The benzocyclobutene concentration was on the order of $10^{-2}$ *M*. The spectrometer gain and modulation amplitude were not kept constant. Therefore, these spectra do not show the changes in relative intensity as a function of temperature.

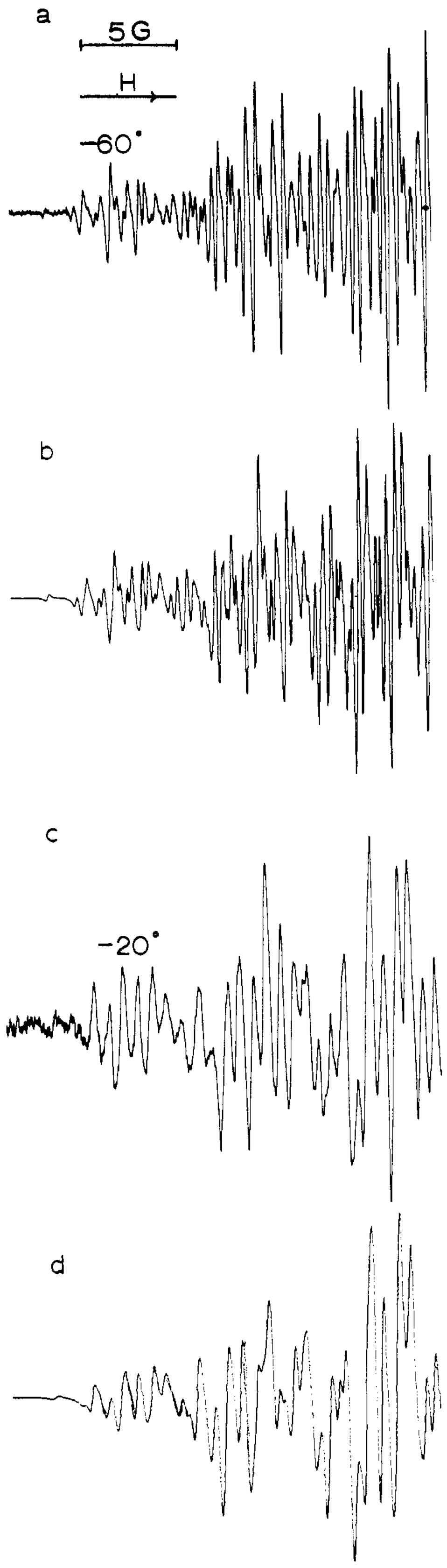

Figure 2. Esr spectra of 1-deuteriobenzocyclobutene radical anion prepared using potassium and DME: (a) experimental spectrum obtained at −60°; (b) calculation of −60° spectrum using a Lorentzian line width of 0.15 G; (c) experimental spectrum obtained at −20°; (d) calculation of −20° spectrum using a Lorentzian line width of 0.30 G.

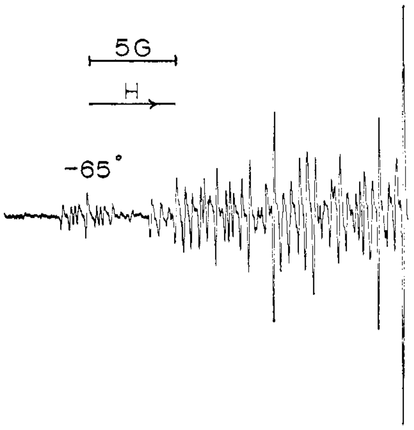

Figure 3. Esr spectrum of a mixture of the radical anions of 4-deuteriobenzocyclobutene and benzocyclobutene, prepared using potassium in DME.

served before in the cases of pyracene radical anion[30] and acenaphthene radical anion.[31] The behavior of these two radical anions was very similar to that of BCB radical anion and suggested that ion pairing was the explanation for the alternating line-width phenomena.

Several experiments were carried out varying solvents and mode of reduction to help elucidate this possibility. The first variation was to produce BCB radical anion in the presence of hexamethylphosphoramide (HMPA). The alkali salts of many radical anions are reported[32] to be completely dissociated in HMPA, so use of this solvent would possibly permit examination of BCB radical anion in the absence of any ion-pairing phenomena. Using a breakseal tube, BCB was reduced first with potassium in DME to give the same spectra for BCB radical anion as shown in Figure 1. HMPA was then added *via* the breakseal to give a volume composition of 10% HMPA and 90% DME with $10^{-2}M$ concentration of BCB. The solution changed from green to dark blue as HMPA was added. The spectrum recorded at −92° is shown in Figure 4, and can only be simulated as arising from the interaction of the unpaired electron with two sets of two equivalent nuclei and one set of four equivalent nuclei, with hyperfine splitting constants of 7.45 (2 H), 1.40 (2 H), and 5.45 G (4 H). Spectra were recorded from −92 to −28°, were reversible, and showed very little temperature dependency; the spectrum width varied no more than 0.40 G over this range. A solvated electron peak was observed at −40°. After several days, during which the BCB radical anion solution had been kept at −78°, a small amount of the ion-paired BCB radical anion could be detected. Metal splittings were never observed after HMPA addition. The concentration of BCB radical anion ion pair was increased by raising the initial BCB concentration to $10^{-1}$ *M* and retaining a volume composition of 10% HMPA and 90% DME. By retaining an initial concentration of $10^{-2}$ *M* BCB and changing the solution to 20% HMPA and 80% DME, the only para-

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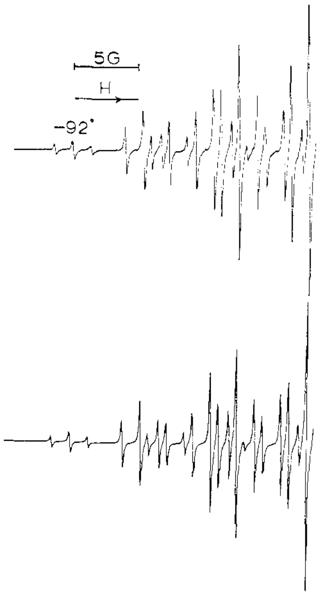

Figure 4. Esr spectrum of benzocyclobutene radical anion prepared using potassium in 10% HMPA and 90% DME (volume composition): upper, experimental spectrum; lower, calculated spectrum using a Lorentzian line width of 0.10 G.

magnetic species appears to be the free BCB radical anion. Spectra could be recorded in this solvent system down to −110°. To lower the temperature range further, a sample was prepared using potassium, $10^{-2}$ $M$ initial BCB, and a solvent of volume composition 20% HMPA and 80% THF. Again, the methylenes were equivalent, even down to −130°. At this temperature anisotropic broadening was observed. These various changes in solvent and concentration produced little effect on the hyperfine coupling constants. Finally, a sample of BCB radical anion was prepared using potassium and DME, followed by the addition of an amount equimolar with initial BCB of a "crown" ether, dicyclohexyl-18-crown-6. The free BCB radical anion with all four methylene protons equivalent was observed as the predominant paramagnetic species, along with a small amount of the ion-paired BCB·⁻. Spectra were reversible from −92° to −12° and the splitting constants were virtually the same as found for the free ion in HMPA solutions, showing little temperature dependency over the temperature range studied.

Close examination of the −88° spectrum in Figure 1 shows an additional species appearing. This ion can now be identified as the free BCB radical anion.

Final proof that the origin of the methylene nonequivalency is arising by ion pairing was the electrolytic reduction of BCB. The electrolytic reduction of BCB was carried out with a platinum electrode in 1,2 dimethoxyethane with tetrabutylammonium perchlorate as electrolyte in an epr cavity at −90°.[33] The observed epr spectrum was identical with the spectra of the free ion obtained in the HMPA and crown ether experiments. This definitely establishes the origin of the nonequivalency as being the formation of an ion pair. This evidence strongly supports the thesis that the four-membered ring is still intact after reduction and also rules out the skewed four-membered ring possibility.

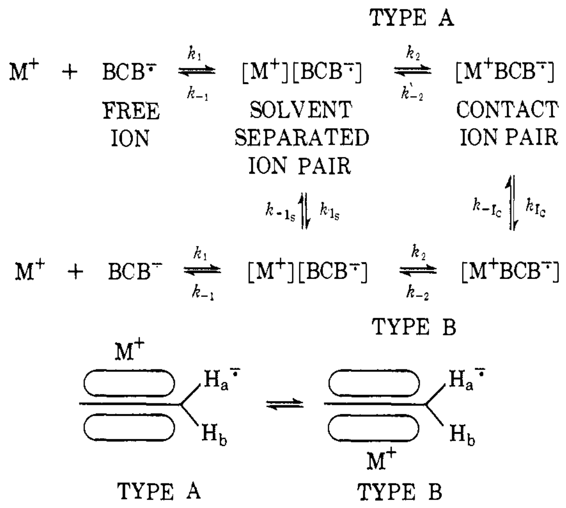

Figure 5. The proposed kinetic scheme for the interconversion of the various benzocyclobutene radical anion ion pairs.

A suggested scheme to explain the temperature dependency of the potassium BCB radical anion in DME is given in Figure 5. The BCB free-radical anion appears to be totally free of the metal cation. In any event, the same species was obtained from the HMPA and crown ether experiments and from the electrolytic reduction. Careful line-width analysis in each of these cases was impossible but hyperfine splitting constants were identical, thus implying that the radical anions were identical. The interconversion of the free ion with the solvent-separated ion pair was slow compared to the epr time scale throughout the temperature ranges studied in this experiment. This places an approximate upper limit on $k_1$ of $10^5$ sec$^{-1}$. The interconversion of the contact ion pair with the solvent-separated ion pair, on the other hand, was fast compared to the epr time scale throughout the temperature range studied, putting an approximate lower limit on $k_2$ of $10^7$ sec$^{-1}$. Thus, the measured epr properties of the ion pairs were weighted averages depending on the equilibrium constants.[34] In contrast to the other two interconversion processes, the interconversion of the two types of ion pairs is comparable to the epr time scale. At temperatures below −50° the interconversion is slow compared to the epr time scale while at temperatures approximately above −10° the interconversion is fast. In the intermediate cases, the lifetime of each type of ion pair is comparable to $[\gamma(a_{\alpha,1} - a_{\alpha,2})]^{-1}$ where $\gamma$ is the gyromagnetic ratio of the electron and $a_{\alpha,1}$ and $a_{\alpha,2}$ are the two different coupling constants for the methylene protons. It is in this temperature range that the alternating line widths are observed. We have no way at the present to decide whether the interconversion of the two types of ion pairs is occurring at the solvent-separated stage or the contact ion stage or both. However, an approximate value of $k_{\text{obsd}}$ can be estimated to be $10^6$ sec$^{-1}$.

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[33] The authors would like to thank Mr. William E. Rich for carrying out the electrolytic reduction of BCB.

[34] The existence of contact and solvent-separated ion pairs has been clearly established.[32,35-37] It appears that in many cases a rapid equilibrium exists between these two types of ions and their measured epr properties depend on the equilibrium constant.

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(37) T. E. Hogen-Esch and J. Smid, *ibid.*, **87**, 669 (1965).

The two types of ion pairs are assumed to be BCB radical anion with a solvated cation above and below the plane of the BCB $\pi$ system. The mode of interconversion cannot be specified. However, the fact that the metal hyperfine splitting remains unbroadened as the temperature is raised to +20° indicates that the exchange process is intramolecular rather than intermolecular.

It should be pointed out that there was no sign of any alternating line-width effects due to oscillation of the metal cation between carbon positions 3 and 6 within a particular type of ion pair. This type of phenomena was observed in the pyracene and acenaphthene radical anions.[30,31] We are continuing to look for conditions under which BCB would also display this process.

**Reduction Potential of BCB.** The proposed electrocyclic ring opening of the anion radical of benzocyclobutene to give the *o*-xylylene anion radical, a transformation similar to the thermal valence isomerization of benzocyclobutene to *o*-xylylene at 200°,[38] was predicated in part upon the lower reduction potential of *o*-xylylene as part of the driving force for this reaction.[21] Empirical correlations of half-wave reduction potentials for aromatic hydrocarbons *vs.* the energies of the lowest vacant molecular orbitals have been derived and are quite good for even-alternate hydrocarbons.[39] *o*-Xylylene, which has its lowest vacant HMO at $E = \alpha - 0.29\beta$, is predicted to have a half-wave reduction potential of approximately −1.50 V.[39] Benzocyclobutene, considered to have benzene-like molecular orbitals (LVHMO, $E = \alpha - 1.00\beta$), should have a reduction potential of about −3.0 V. One method then of elucidating the structure of the anion radical formed upon metal reduction of BCB was to determine its reduction potential.

The polarographic reduction of BCB with a dropping mercury electrode in acetonitrile with tetraethylammonium perchlorate as electrolyte indicated that the reduction potential was more cathodic than the solvent breakdown potential of −2.8 V *vs.* aqueous sce.[40] The reduction potential of the radical anion formed when BCB is treated with potassium metal in DME was determined to be within a certain range of values by adding this radical anion to various hydrocarbons of known reduction potential and noting by epr spectrometry when electron transfer occurred. This was accomplished with the use of a specially designed epr tube with a breakseal attachment whereby the hydrocarbon could be added after reduction of BCB. The tube was constructed so that the metal could be tipped off after reduction of the BCB and before adding the hydrocarbon.

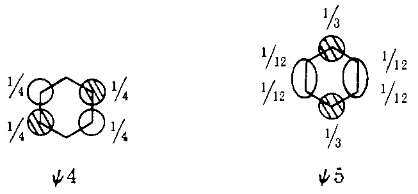
The addition of benzene to the anion radical of BCB did not result in electron transfer. However, the addition of an equimolar quantity of zone-refined biphenyl to a solution of BCB radical anion (initial BCB concentration $4 \times 10^{-3}$ *M*) resulted in the immediate transfer of electrons to form the biphenyl radical anion. Thus the reduction potential of BCB, even after it was reduced, was greater than that of biphenyl or −2.70 V.[39] This is additional proof that upon reduction BCB does not undergo an electrocyclic ring opening to form the *o*-xylylene radical anion.

**Reduction of $\alpha,\alpha'$-Dibromo-*o*-xylene.** Further evidence that the four-membered ring remains intact was obtained from the reduction of $\alpha,\alpha'$-dibromo-*o*-xylene (I). If BCB radical anion underwent a ring opening to form a stable *o*-xylylene radical anion, one would expect that alkali metal reduction of I which gives *o*-xylylene would then be reduced further to the stable radical anion. Compound I was reduced with a potassium mirror in DME under a variety of conditions. In the majority of reductions, only diamagnetic species were produced.[41] In some reductions a complex signal of low intensity was observed, having a spectrum width of *ca.* 27 G. The spectrum showed no sign of BCB radical anion. Further, the dibromide was exhaustively reduced for 3 hr *in situ* in the epr cavity with no sign of any paramagnetic species.[42]

**Stability of Benzocyclobutene Radical Anion.** Sample tubes of BCB radical anion were prepared using potassium and DME and left in contact with excess metal at −78° for up to 8 weeks. The tubes, which showed strong BCB radical anion signals, were then broken open, had dry air bubbled through to remove excess electrons, and then were analyzed by gas chromatography[43] for the parent hydrocarbon. After 1 week, with an initial BCB concentration of $1.20 \times 10^{-2}$ *M*, the BCB concentration was found to be $1.13 \times 10^{-2}$ *M*. No *o*-xylene was detected. After 8 weeks, with an initial BCB concentration of $1.60 \times 10^{-2}$ *M*, it was found that the BCB concentration was $1.65 \times 10^{-2}$ *M*. Again, no *o*-xylene was detected. Therefore, the tubes still contained all the original BCB within experimental error. Isomerization during analysis is ruled out, since pure samples of *o*-xylene and BCB gave two distinct peaks under the analytical conditions employed.

**Ring-Strain Effects on Benzocyclobutene.** The observed spin densities and reduction potential of BCB are readily explained within the models we have developed for ring-strain effects on spin densities and reduction potentials.[13–16] The reduction of BCB adds an electron to one of the two near-degenerate benzene antibonding orbitals shown in Chart I. It has been demonstrated for many substituted benzenes that if the substituent is electron donating the extra electron will

**Chart I.** Near-Degenerate Benzene-Type Orbitals of Benzocyclobutene[a]



[a] The thatched circles represent p orbitals with the plus signs up while the empty circles represent p orbitals with the plus signs down. The number beside each orbital is the square of the coefficient.

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(38) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Lett.*, 15 (1962).

(39) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(40) R. D. Rieke and W. Rich, unpublished results.

(41) The exact nature of this reduction is under continuing investigation.

(42) Reduction was attempted using a Varian Electrolytic Cell V-4556 with mercury electrode and acetonitrile with 0.1 *N* tetraethylammonium perchlorate, $10^{-3}$ *M* in dibromide.

(43) The analytical procedure employed was that of McNair and Bonelli,[44] using standard solutions of BCB and 1,2,3,4-tetrahydronaphthalene.

(44) H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography," Varian Aerograph, 1967, Chapter 7.

prefer the orbital which avoids the substituent. On the other hand, if the substituent is electron attracting, the extra electron will prefer the orbital which places maximum electron density next to the substituent.[45-49] The perturbation is, however, never complete and generally the electron enters an orbital which is an admixture of the two orbitals. In the case of BCB, the extra electron will obviously enter $\psi_5$. This explains the large coupling constants for the 3 and 6 positions. However, the coupling constant for the 3 and 6 positions for *o*-xylene[50] is only 6.95 G while it is approximately 7.50 G for BCB depending on the temperature. We have shown that spin densities of several strained compounds could be correlated and their reduction potentials correlated by making the carbon atoms $\alpha$ to a strained ring more electronegative. Thus in BCB the extra electron enters an antibonding orbital which weighs $\psi_5$ more heavily than in the case of *o*-xylene. In both cases, the substituents are electron donating, causing the electron to prefer $\psi_5$; however, the increased electronegativity of the 3 and 6 positions in BCB results in a heavier weighing of $\psi_5$.[51]

The observed reduction potential of BCB is readily explained by simple perturbation theory. Coulson and Longuet-Higgins[52] have shown that when a coulomb integral is varied in a molecule, the energy of a molecular orbital $\psi_i$ of the $\pi$ system is changed by an amount

$$\delta E_i = C_{ir}^2 \delta\alpha_r$$

and this effect is additive. In this expression the symbols have their usual meaning. Thus, *o*-xylene is expected to have a reduction potential greater than benzene. In the inductive model, the carbon atoms which have the methyls attached will become less electronegative, thus raising the energy of the antibonding orbital causing a cathodic shift in the reduction potential. For BCB the methylene groups will similarly cause positions 1 and 2 to be less electronegative but the ring strain will cause positions 3 and 6 to be more electronegative. Arbitrarily using the parameters found to correlate the reduction potential of naphtho[*b*]cyclobutene,[16] $\alpha_1 = \alpha_2 = \alpha_0 - 0.3\beta$ and $\alpha_3 = \alpha_6 = \alpha_0 + 0.1\beta$, one predicts that the reduction potential of BCB should be more anodic than benzene, as is observed.

## Conclusions

We have shown that the BCB radical anion is stable for relatively long periods of time at low temperatures and does not undergo an electrocyclic ring opening of the fused, four-membered ring. Similar to pyracene[30] and acenaphthene,[31] ion pairing can cause the methylene protons to become nonequivalent. In the case of BCB, however, the nonequivalency is observed even when metal splittings are absent. Finally, the observed spin densities of BCB radical anion and the reduction potential of BCB can be qualitatively explained within the ring strain effect models developed earlier.[13-16]

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