Transient [8]Annulenyl Carbanion from the Anion Radical of Bromo-[8]annulene

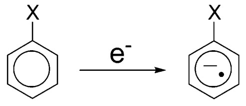
Cheryl D. Stevenson,*,† Matthew K. Kiesewetter,† and Steven J. Peters‡

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160, and Department of Chemistry, California State University, Sacramento, California 95819-6057

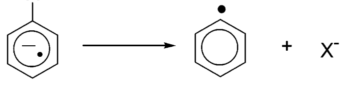
Received: September 18, 2003; In Final Form: December 16, 2003

The anion radical of mono-bromo-[8]annulene was generated in the absence of ion association, and the EPR-measured spin densities can be explained in terms of the odd electron occupying MOs: $\Psi_4' = [2\sqrt{(n^2 + 1)}]^{-1}(\psi_1 + n\psi_2 - \psi_3 - n\psi_4 + \psi_5 + n\psi_6 - \psi_7 - n\psi_8)$ and $\Psi_5' = [2\sqrt{(n^2 + 1)}]^{-1}(\psi_1 - n\psi_2 - \psi_3 + n\psi_4 + \psi_5 - n\psi_6 - \psi_7 + n\psi_8)$ where $n > 1$. This anion radical subsequently disproportionates to its corresponding dianion and neutral molecule. The dianion then undergoes a loss of Br^-, leaving the [8]annulenyl carbanion, which can abstract a proton from either HMPA or liquid ammonia. The pseudo-*ortho*-bromo-[8]annulenyl carbanion also loses Br^- to give [8]annulyne, which can be stabilized in the form of its anion radical. The *g* value of the anion radical of [8]annulyne indicates that the extra strain energy due to the presence of the triple bond causes the two highest occupied MOs (degenerate in the anion radical of [8]annulene) to be slightly split.

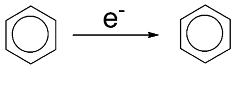
The benzyl ([6]annulenyl) σ radical ($C_6H_5^\bullet$) represents the prototypical aromatic σ radical[1] whose formation, reactivity, and structure have been the subject of numerous studies.[2] A property of particular interest is the positive electron affinity (EA = +27.8 kcal/mol)[2a] of $C_6H_5^\bullet$, as opposed to the negative EA of benzene (EA = −26.6 kcal/mol for C_6H_6).[3a] This, of course, is due to the formation of the carbanion as opposed to the π-delocalized anion radical upon electron addition. One of the most common ways to generate $C_6H_5^\bullet$ in solution involves the dissociative capture of an electron by a [6]annulenyl halide, reactions 1 and 2.[2b] The positive EA of $C_6H_5^\bullet$ renders reaction 3 exothermic in solution and in the gas phase. A series of analogous reactions take place via the capture of an electron by an [8]annulenyl halide, but owing to the very different quantum mechanical situation in [8]annulene (4*n* π electrons) as opposed to that in [6]annulene (4*n* + 2 π electrons), the results are quite different.



(1)



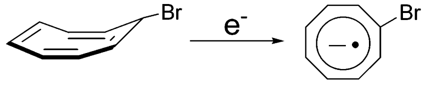
(2)



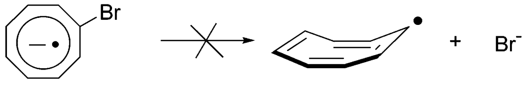
(3)

Over 40 years ago, Eargle[4a] demonstrated that diaryl ether anion radicals can also undergo dissociative cleavage. In particular, dinaphthyl ether can be reduced to its anion radical, which can disproportionate to the corresponding dianion and neutral molecule (Scheme 1). The dianion undergoes an autocleavage reaction to give the alkoxide and the aryl carbanion. The aryl fragment then extracts a proton from the solvent (dimethoxyethane) to give naphthalene. The spontaneous cleavage of the dinaphthyl ether anion radical to a naphthyl radical and an alkoxide also leads to the formation of some β,β'-binaphthyl.

The next (in size) annulenyl σ radical is $C_8H_7^\bullet$, the [8]-annulenyl or cyclooctatetraenyl radical, which we anticipated would form from the anion radical of monobromo-[8]annulene ($Br-C_8H_7^{\bullet-}$). We were surprised, however, to see that $Br-C_8H_7^{\bullet-}$ does endure for several minutes at ambient temperature and that the expected product from $C_8H_7^\bullet$ (biscyclooctatetraenyl)[4b] is not formed, reactions 4 and 5. It was anticipated that the EA of $C_8H_7^\bullet$ would be even greater than that of [8]annulene (C_8H_8) because the EA of [8]annulene is positive (EA = +14 kcal/mol)[3b] and B3LYP/6-31G* calculations on $C_8H_7^-$ predict some delocalization of the negative charge into the eight-π-electron ring system.



(4)



(5)

The anion radical of $Br-C_8H_7$ was unknown, but that of cyano-[8]annulene ($CN-C_8H_7^{\bullet-}$) exhibits a characteristic EPR spectrum for an [8]annulene (C_8H_8) anion radical[4] with an electron-withdrawing substituent.[5] Upon EPR analysis,

---

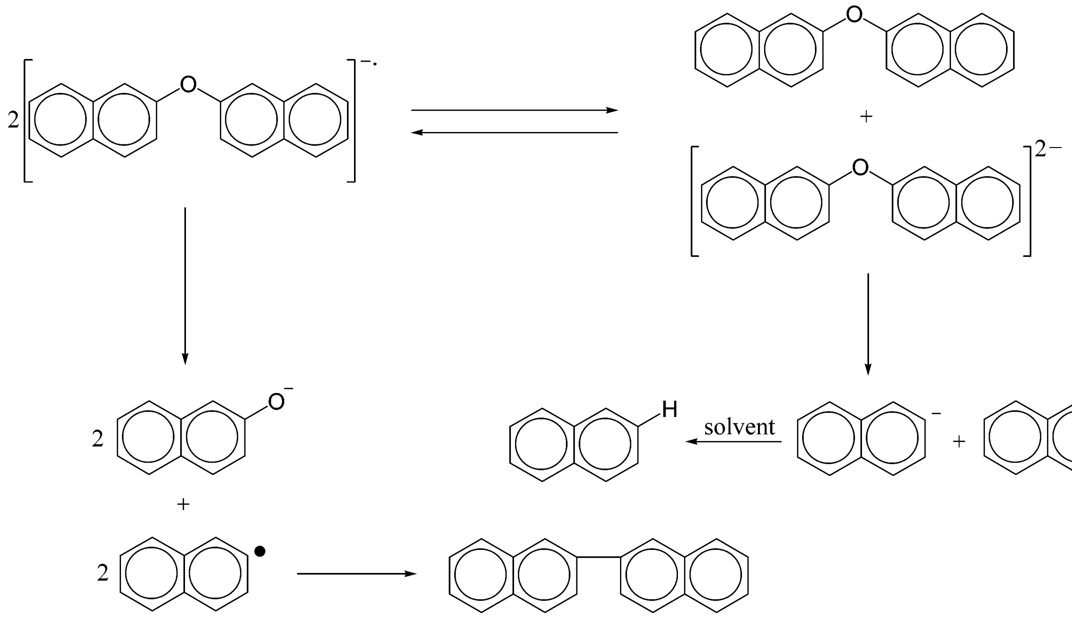
* Corresponding author. E-mail: cdsteve@ilstu.edu.

† Illinois State University.

‡ California State University.

10.1021/jp036801g CCC: $27.50 © 2004 American Chemical Society
Published on Web 02/25/2004

SCHEME 1



$CN{-}C_8H_7^{\bullet-}$ reveals four large proton couplings from the even-numbered carbons, a small a_H is exhibited by the psuedo-para proton, and even smaller splittings arise from the protons on positions 3 and 7.[5] This is consistent with the odd electron residing in the molecular orbitals (Ψs) represented in Figure 1.

There are three electrons in the nonbonding molecular orbitals (NBMOs) of the D_{4h} (with alternating bond lengths) $C_8H_8^{\bullet-}$, which constitute Ψ_4 and Ψ_5 in eqs 6 and 7 when R = H. Ψ_4 and Ψ_5 represent the 1:1 linear combinations of the NBMOs for the D_{4h} equilibrium geometries with alternating bond angles (eqs 8 and 9).[6] That is, $\Psi_4 = (\Phi_4 + \Phi_5)/\sqrt{2}$ and $\Psi_5 = (\Phi_4 - \Phi_5)/\sqrt{2}$.

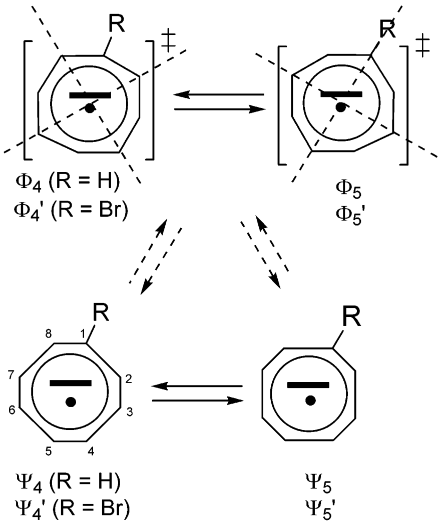


Figure 1. Pictorial representations of the Jahn−Teller distortion of the [8]annulene moiety in the anion radicals of [8]annulene and of Br-[8]annulene to the bond length alternating D_{4h} geometries. The D_{4h} bond angle alternating structures represent the transition states for the exchange from one bond length alternating geometry to the other. The wave functions for the bond length alternating structures (Ψs) are linear combinations of those for the bond angle alternating structures (Φs). The nodal planes in the bond angle alternating structures are denoted with dotted lines.

$$\Psi_4 = \left(\frac{0.5}{\sqrt{2}}\right)(\psi_1 + \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6 - \psi_7 - \psi_8) \quad (6)$$

$$\Psi_5 = \left(\frac{0.5}{\sqrt{2}}\right)(\psi_1 - \psi_2 - \psi_3 + \psi_4 + \psi_5 - \psi_6 - \psi_7 + \psi_8) \quad (7)$$

$$\Phi_4 = \left(\frac{1}{2}\right)(\psi_1 - \psi_3 + \psi_5 - \psi_7) \quad (8)$$

$$\Phi_5 = \left(\frac{1}{2}\right)(\psi_2 - \psi_4 + \psi_6 - \psi_8) \quad (9)$$

The addition of an electron-withdrawing substituent (R = Br) at position 1 lowers the energy of Φ_4' while not perturbing Φ_5', which has a node at position 1. Because there are three nonbonding electrons, the odd electron resides in Ψ_4' and Ψ_5', which are heavy in Φ_5' (eqs 10 and 11 where $n > 1$). The distribution of the odd electron in Ψ_4' and Ψ_5' results in a large EPR coupling constant for the protons in positions 2, 4, 6, and 8 and a small a_H for those in positions 3, 5, and 7.

$$\Psi_4' = \frac{\Phi_4 + n\Phi_5}{2\sqrt{n^2+1}} = [2\sqrt{n^2+1}]^{-1}(\psi_1 + n\psi_2 - \psi_3 - n\psi_4 + \psi_5 + n\psi_6 - \psi_7 - n\psi_8) \quad (10)$$

$$\Psi_5' = \frac{\Phi_4 - n\Phi_5}{2\sqrt{n^2+1}} = [2\sqrt{n^2+1}]^{-1}(\psi_1 - n\psi_2 - \psi_3 + n\psi_4 + \psi_5 - n\psi_6 - \psi_7 + n\psi_8) \quad (11)$$

The one-electron reduction of $Br{-}C_8H_7$ via a freshly sublimed potassium metal mirror in hexamethylphosphoramide (HMPA) under high vacuum, where ion association is not present,[7] yields

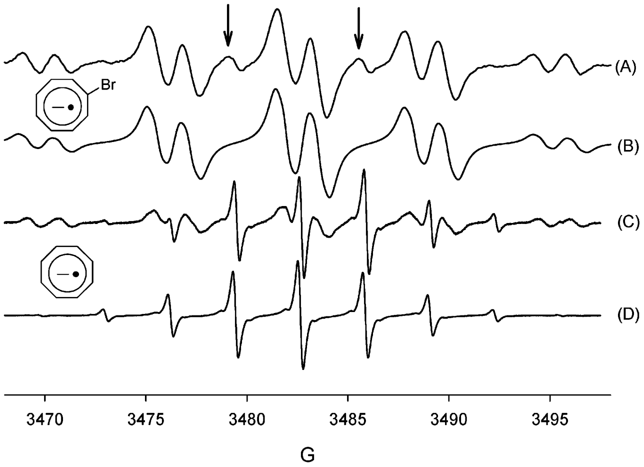


Figure 2. (A) X-band EPR spectrum, recorded at 298 K, immediately after the potassium reduction of $Br-C_8H_7$ in HMPA. The two arrows mark the peaks just to the left and right of central peak of $C_8H_8^{\bullet-}$. (B) Computer generated simulation using a_H's of 6.37 G (4 Hs), and 1.60 G (1 Hs) for $Br-C_8H_7^{\bullet-}$. The peak-to-peak line width (Δw_{pp}) for $Br-C_8H_7^{\bullet-}$ is 0.37 G. This large Δw_{pp} is, in part, due to unresolved splitting from the bromine and the pseudo-meta protons. (C) EPR spectrum of the same solution recorded about 20 min. later. (D) EPR spectrum of the same solution recorded about 40 min. after the recording of spectrum C.

a solution that exhibits an EPR spectrum consistent with this analysis, Figure 2. The observed four large splittings $a_H = 6.37$ G come from the protons on the even-numbered positions and the small a_H from the pseudo-para proton (on position 5). The very small splittings from the protons in the 3 and 7 positions are buried in the line width, which is augmented by the unresolved splitting from the Br, which has a $^3/_2$ nuclear spin. The spin densities observed on positions 3 and 7 are smaller than on position 5 because of proximity effects relative to the large Br substituent.

Further inspection of Figure 2 reveals the presence of the very familiar EPR pattern for the anion radical of [8]annulene, with its nine-line pattern due to the odd electron coupling with eight equivalent protons ($a_H = 3.29$ G). Because the only source of $C_8H_8^{\bullet-}$ (other than impurity) is the substitution of the Br in $Br-C_8H_7$ with a hydrogen (probably from the solvent), we carried out the reduction in a HMPA solution containing 25% HMPA-d_{18}.[6] This leads to an EPR spectrum clearly revealing the presence of $C_8H_7D^{\bullet-}$. The relative concentration ratio of $[C_8H_7D^{\bullet-}]/[C_8H_8^{\bullet-}]$ of 1/33 is eight times smaller than 1/4, which would be observed in the absence of a kinetic isotope effect, this translates to a kinetic isotope effect of $k_H/k_D = 8$. This large primary kinetic isotope effect means that the hydrogen is shared nearly equally between the $C_8H_7^-$ and the HMPA in the transition state.

Because substituted [8]annulene anion radicals undergo efficient disproportionation,[8] it is most likely that the C_8H_7 anion forms from the disporportionation of $Br-C_8H_7^{\bullet-}$ to its corresponding dianion and neutral molecule followed by the elimination of the Br^- from the dianion. This carbanion then extracts a proton from the HMPA or deuterated HMPA to form the [8]-annulenes, which are subsequently reduced to $C_8H_8^{\bullet-}$ and $C_8H_7D^{\bullet-}$, Scheme 2.

By analogy, we assumed that the Li reduction of $Br-C_8H_7$ in THF-d_8 at 150 K would yield a solution of the anion radical of deuterated [8]annulene, but $C_8H_8^{\bullet-}$ is the only paramagnetic species observed. Our assumption, however, did not consider the ammonia, used to form the Li mirror, which was used to carry out the reduction.[9] Repetition of this experiment using a mixture of NH_3 and a preponderance of ND_3 results in the formation of mixture $C_8H_8^{\bullet-}$ and $C_8H_8D^{\bullet-}$, Figure 3. Clearly the [8]annulenyl carbanion cannot extract a proton from THF, but it can from ammonia and HMPA.

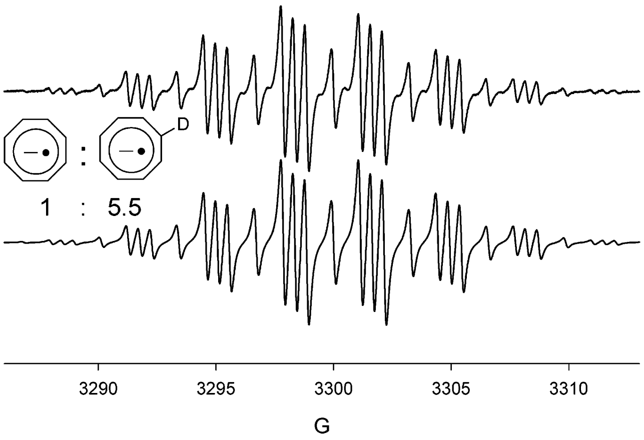
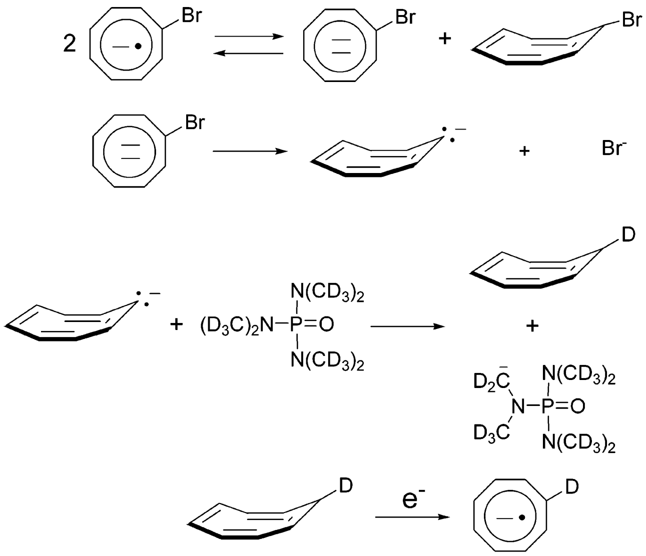
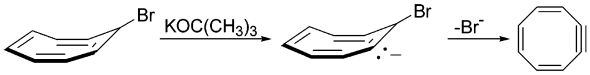


Figure 3. (Upper) X-band EPR spectrum, recorded at 298 K, after the lithium reduction of $Br-C_8H_7$ in tetrahydrofuran containing ND_3 and NH_3 at −120 °C. (Lower) Computer generated simulation using a 5.5:1 mixture of $C_8H_7D^{\bullet-}$ and $C_8H_8^{\bullet-}$ $a_H = 3.29$ G (8 Hs in $C_8H_8^{\bullet-}$ and 7 Hs in $C_8H_7D^{\bullet-}$) and $a_D = 0.50$ G (1D in $C_8H_7D^{\bullet-}$).

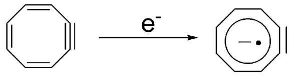
SCHEME 2



Bromo-[8]annulene is known to be dehydrohalogenated by the strong base, potassium *tert*-butoxide, leading to the (nearly planar)[10a] reactive intermediate [8]annulyne, reaction 12.[11] When the lithium reduction of $Br-C_8H_7$ is carried out as describe above, but with the THF + NH_3 containing one equivalent of potassium *tert*-butoxide, two species can be observed via EPR spectroscopy. The major EPR active product is $C_8H_8^{\bullet-}$, and the other product yields a spectrum with the same a_H's as those of the anion radical of [8]annulyne ($C_8H_6^{\bullet-}$),[10b] reactions 12 and 13.



(12)



(13)

Apparently, the [8]annulenyl carbanion quickly extracts a proton from the solvent (either NH_3 or HMPA) to form [8]-annulene, while the pseudo-*ortho*-bromo-[8]annulenyl carbanion releases bromide to form [8]annulyne. Just as insight into the singly occupied MOs of monosubstituted [8]annulenes can be garnished from the EPR splittings, insight into the SOMO of the [8]annulyne anion radical can be obtained from the EPR measured *g* value.[12] The experiment resulting in the simultaneous observation of $C_8H_8^{\bullet-}$ and $C_8H_6^{\bullet-}$ leads to the perfect opportunity for the *g*-shift measurement, which yields valuable insight into the relative energetics of the molecular orbitals.[13]

Since the earliest postulation of the existence of *o*-benzyne ([6]annulyne) over 130 years ago,[14] [6]annulyne has been recognized as a reactive intermediate in base-induced elimination reactions of halobenzenes,[15] and it has been the subject of reviews.[15d] About 110 years after its proposed existence, it was captured via cryogenic (4 K) deposition, and its IR spectrum was recorded.[16] In recent years, the gas-phase anion radical of this highly reactive molecule has been generated ($O^- +$ benzene $\rightarrow H_2O + C_6H_4^{\bullet-}$), which allowed gas-phase PES observation.[17] The next annulyne ([8]annulyne) has received considerably less attention; however, it was observed in the gas phase as its corresponding anion radical $C_8H_6^{\bullet-}$.[10a] We have now observed it in solution under conditions where its *g* value can be readily measured.

The *g* values for most anion radicals are within 1% of that of the free electron (g_o).[13a] Hence, highly accurate methods are required for *g*-value measurements, the best being the use of an internal standard. Because of differences in electron affinities and the reactivity of radicals toward one another, it is usually impossible to observe quantitative *g* shifts with an internal standard. Hence, external standards are usually used, and this leads to laborious measurements with unsatisfying experimental errors.[11,13] The reaction between the [8]annulenyl carbanion and ammonia leading to C_8H_8 coupled with the formation of C_8H_6 from $Br-C_8H_7$ and base afforded a unique opportunity to observe the two respective anion radicals simultaneously. By simply exposing the THF solution of $Br-C_8H_7$ to a stoichiometric deficiency of base and then exposing the resulting mixture ($Br-C_8H_7 + C_8H_6$) to the fresh (from ammonia) lithium metal surface, $C_8H_8^{\bullet-}$ and $C_8H_6^{\bullet-}$ are observed simultaneously. $C_8H_8^{\bullet-}$ serves as the internal standard, and the difference in the two spectral centers could be measured directly and accurately.

Nearly 40 years ago, Stone developed a general theory of *g* values, which, when applied to conjugated hydrocarbons, leads to the simple expression $\Delta g = g_{\mathrm{obsd}} - g_o = [(31.9 \pm 00.4) - (16.6 \pm 1)\lambda] \times 10^{-5}$, where the improved numerical constants were taken from Fraenkel et al.[10b] In the simple HMO model, the energy of the SOMO is given by $E = \alpha + \lambda\beta$. The work of Blois et al.[13a] agrees with this theory quite well, but confirmation by Fraenkel et al.[11b] removed any doubt as to its utility during the early development of MO theory. This interpretation in terms of the Hückel version of Stone's theory is very outdated, but the basic ideas still have utility in modern data interpretation. The data interpretation in the case of the $C_8H_6^{\bullet-}$ system must take account of the locked (short) bond between C_1 and C_8.

The MOs for 1,2-disubstituted COT systems represent the ring in the alternating bond-angle conformations, where (now) the alternating bond-length conformations represent the transition states; see Figure 4.[18] The $C_8H_6^{\bullet-}$ system is a disubstituted COT where the protons are replaced by p orbitals. Hence, the $C_8H_6^{\bullet-}$ system is best represented by alternating bond-angle conformations (Figure 4). Any difference that can be observed between the *g* values of $C_8H_8^{\bullet-}$ and $C_8H_6^{\bullet-}$ represents a splitting in the degeneracy of the two alternating bond-angle structures, shown in Figure 4, due to the presence of the triple bond.

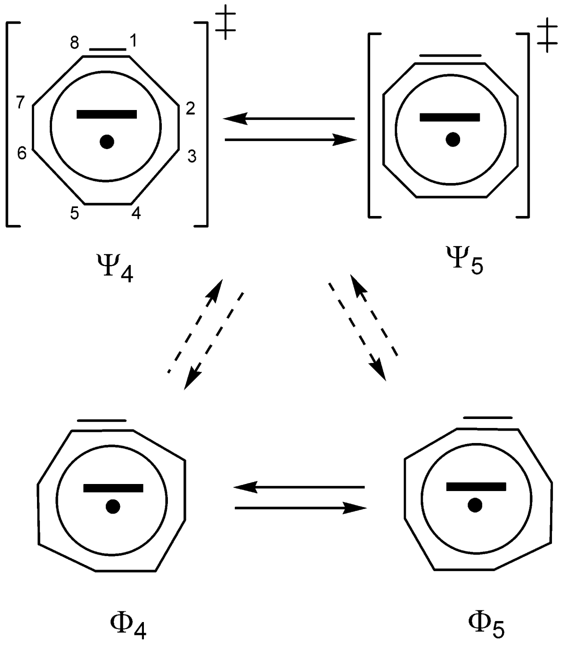


Figure 4. Pictorial representations of the Jahn−Teller distortion (exaggerated) of the [8]annulene moiety in the anion radical of [8]-annulyne. The bond length alternating structures represent the transition states for the exchange from one bond angle alternating geometry to the other.

Careful simulation of the central portion of the EPR spectrum of the $C_8H_8^{\bullet-} + C_8H_6^{\bullet-}$ mixture in THF at 150 K shows that the spectrum of $C_8H_6^{\bullet-}$ is shifted upfield from that of $C_8H_8^{\bullet-}$ by $\Delta B_o = 0.015 \pm 0.003$ G, Figure 5. This translates to a Δg of 4.4×10^{-6}. That is, Φ_4 and Φ_5 are not degenerate in planar dehydro-[8]annulene. This is due to the unequal mixing of Ψ_4 and Ψ_5 to form Φ_4 and Φ_5. This unequal mixing is a result of the shorter triple bond "preferring" the configuration depicted by Ψ_4.

Conclusions

The monoanion of monobromo-[8]annulene can be generated in two ways: an electron can be added to the π system, or a vicinal (to the Br) proton can be subtracted. In the former case, the one-electron reduction leads to an anion radical in which the electron distribution follows the accepted quantum mechanical model.[6] This anion radical disproportionates to its corresponding dianion. The dianion subsequently undergoes reductive elimination of bromide. The resulting [8]annulenyl carbanion can then abstract a proton from slightly protic solvents such as HMPA and ammonia but not from THF.

In the later case, potassium *tert*-butoxide extracts a proton that is in the pseudo-ortho position leading to the corresponding bromocyclooctatetraenyl carbanion, which then loses Br^- to yield [8]annulyne. The unstable [8]annulyne can be "trapped" via the addition of an electron as its corresponding anion radical (as previously published).[19] The EPR resonance of this anion radical is shifted slightly upfield from that of the anion radical of [8]annulene, indicating that the dehydrogenation of the [8]-annulene anion radical splits the degeneracy of Φ_4 and Φ_5 in Figure 4.

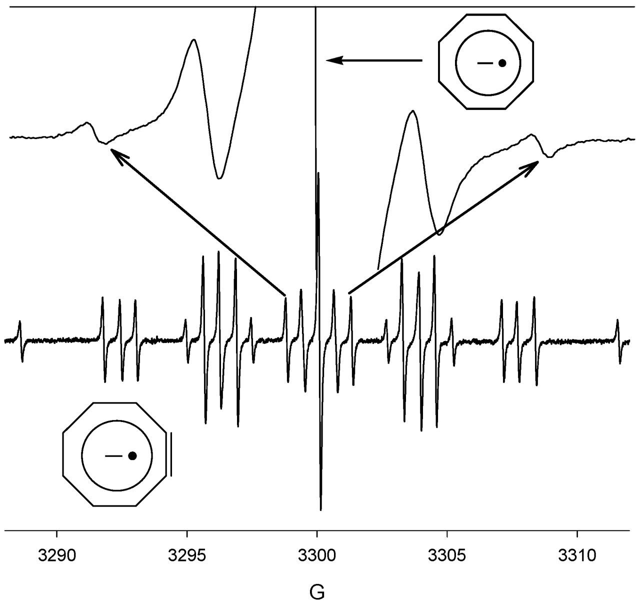


Figure 5. (Upper) A 3.5 G scan of the central portion of the x-band EPR spectrum, recorded at 150 K in THF, of a mixture of the anion radicals of [8]annulene and [8]annulyne. The very large line at spectral center is due to the central resonance of $C_8H_8^{\bullet-}$, and the two lines adjacent to it are due to natural abundance ^{13}C splittings in $C_8H_8^{\bullet-}$. The smaller resonances that appear downfield and upfield of the ^{13}C lines are the 10th and 14th resonances, respectively, in the spectrum of $C_8H_6^{\bullet-}$. (Lower) The complete spectrum of the anion radical of [8]-annulyne, with connecting arrows to the corresponding resonances in the upper spectrum. Note that the spectrum of $C_8H_6^{\bullet-}$ is shifted upfield from that of $C_8H_8^{\bullet-}$ by 15 mG.

Experimental Section

Materials. The synthesis of $Br-C_8H_7$ was carried out as described by Krebs.[11] ND_3 was purchased from Aldrich Chemical Co. The deuterated solvents were purchased from Cambridge Isotopic Laboratories.

Reductions in HMPA. A sealed glass tube (with fragile ends) was charged with 0.1 mmol of $Br-C_8H_7$ and placed into bulb C of the Pyrex glass reaction apparatus shown in Figure 6. A small piece of potassium metal was placed into bulb A, and the apparatus was sealed at point E. The entire apparatus was evacuated, and the potassium metal at A was distilled into bulb B to form a potassium metal mirror. Bulb A was then sealed and cut from the apparatus at point F. HMPA, or a solution of 25% HMPA-d_{18} in HMPA, (~4 mL) was distilled under vacuum from a separate bulb, containing potassium metal, directly into bulb C. The evacuated apparatus was sealed from the vacuum line at point G. The apparatus was shaken to break the sealed glass tube and dissolve the $Br-C_8H_7$. The solution was then touched to the metal mirror.

In dehydrohalogenation reactions (in either HMPA or THF solvent), 0.1 mmol of potassium *tert*-butoxide was placed into bulb C coincidentally with the sealed glass tube containing $Br-C_8H_7$. Also, after being sealed from the vacuum line, the apparatus was shaken gently to dissolve the *tert*-butoxide before the sealed glass tube was broken.

The EPR spectra were recorded immediately by placing the 3-mm tube D into the EPR cavity. The apparatus could be removed from the EPR cavity to expose the solution to more metal, and the spectrum could be recorded again; this process was continued until the best signal-to-noise ratio was achieved.

Reductions in THF. Reductions of $Br-C_8H_7$ in THF were executed in a manner similar to those carried out in HMPA. Rather than HMPA, THF (or THF-d_8) was condensed into bulb C from a separate bulb. The reduction of the THF solution was done with lithium metal. Because it is very difficult to sublime lithium metal under vacuum in Pyrex glass (because lithium undergoes an ion-exchange reaction with sodium within the matrix of the glass), the lithium was dissolved in NH_3 (~5 mL). The ammonia was subsequently removed under high vacuum, and a lithium mirror remained. In reactions involving ND_3, the lithium mirror was formed with NH_3, and ND_3 (~1 mL) was condensed into the THF solvent from a gas cylinder.

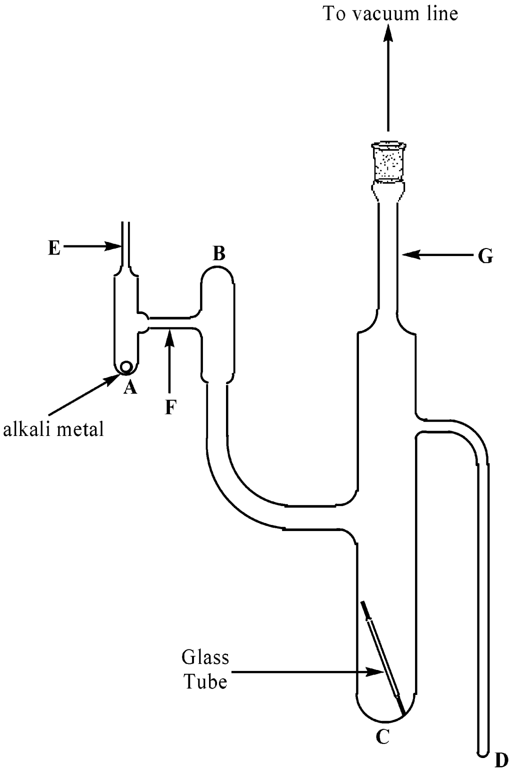


Figure 6. Apparatus used to generate the anion radicals used in the EPR analyses.

Acknowledgment. We thank the National Science Foundation (CHE-9617066), The Petroleum Research Fund, administered by the American Chemical Society, and the Camille and Henry Dreyfus Foundation for supporting this work.

References and Notes

(1) Friderichsen, A. V.; Radziszewski, J. G.; Nimios, M. R.; Winter, P. R.; Dayton, D. C.; David, D. E.; Ellison G. B. *J. Am. Chem. Soc.* **2001**, *123*, 1977.

(2) (a) Nicolaides, A.; Smith, D. M.; Jensen, F.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 8083. (b) Kimura, N.; Takamuku, S. *J. Am. Chem. Soc.* **1995**, *117*, 8023.

(3) (a) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295. (b) Wentworth, W. E.; Ristau, W. *J. Phys. Chem.* **1969**, *73*, 2126. (c) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456.

(4) (a) Eargle, D. H. *J. Am. Chem. Soc.* **1963**, *28*, 1703. (b) Stevenson. C. D.; Concepcion, J. D. ***J.** Am. Chem Soc.* **1973**, *95*, 5692.

(5) Hammons, J. H.; Bernstein, M.; Myers, R. J. ***J.** Phys. Chem.* **1979**, *83*, 2034.

(6) Hammons, J. H.; D. A. Hrovat, Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500.

(7) Ion association is absent with anion radicals in HMPA. See (a) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268. (b) Stevenson, C. D.; Echegoyen, L.; Lizardi, L. R. *J. Phys. Chem.* **1972**, *76*, 1439.

(8) (a) Stevenson, C. D.; Ocasio, I. *J. Am. Chem. Soc.* **1976**, *98*, 890. (b) Stevenson, C. D.; Concepcion, J. G.; Echegoyen, L. *J. Am. Chem. Soc.* **1974**, *96*, 5452.

(9) Lithium metal is usually dissolved in liquid ammonia, which is subsequently removed under vacuum to produce Li mirrors. See Experimental Section.

(10) (a) Wenthold, P. G.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 7772. (b) Stevenson, C. D.; Colon, M.; Concepcion, J. G.; Block, A. *J. Am. Chem. Soc*. **1974**, *96*, 2283.

(11) Krebs, A. *Angew. Chem.* **1965**, *77*, 1966. (b) Krebs, A.; Byrd, D. *Liebigs Ann. Chem.* **1967**, *707*, 66.

(12) (a) Stone, A. J. *Mol. Phys.* **1963**, *6*, 509. (b) Segal, B. G.; Kaplan, M.; Fraenkel, G. K. *J. Chem. Phys.* **1965**, *43*, 4191.

(13) For example, see (a) Astashkin, A. V.; Raitsimring, A. M.; Walker, F. A.; *J. Am. Chem. Soc.* **2001**, *123*, 1905. (b) Kurth, T. L.; Brown, E. C.; Smirnov, A. I.; Reiter, R. C.; Stevenson, C. D. *J. Phys. Chem. A* **1999**, *103*, 8566.

(14) (a) Blois, M. S.; Brown, H. W.; Mailing, J. E. *Arch. Sci. (Geneva)* **1960**, *13*, 243. (b) Stevenson, C. D.; Alegria, A. E. *J. Am. Chem. Soc*. **1975**, *97*, 4859. (c) Stevenson, C. D.; Alegria, A. E. *J. Phys. Chem.* **1975**, *79*, 1042.

(15) (a) Kauffman, T.; Wirthwein, R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 20. (b) Bryce, M. R.; Vernon, J. M. *Adv. Heterocycl. Chem.* **1981**, *28*, 183. (c) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. (d) Heaney, H. *Chem. Rev.* **1962**, *62*, 81.

(16) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pecansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134.

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

(18) Stevenson, C. D.; Kim, Y. S. *J. Am. Chem. Soc*. **2000**, *122*, 3211.

(19) (a) Peters, S. J.; Turk, M. R.; Kiesewetter, M, K.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 11212. (b) Peters, S. J.; Turk, M. R.; Kiesewetter, M, K.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 11264.