Contrasting Free Energies of Electron Transfer from [6]- and [8]Annulenes to Their Perdeuteriated and Per-13C Analogues

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A very large equilibrium isotope effect (confirmed via physical separation of the isotopes involved) was observed via the EPR analysis of a mixture of benzene and perdeuteriated-per-13C-benzene competing for a deficient number of electrons in tetrahydrofuran (THF) in the presence of 18-crown-6 (18C6). The K_{eq} for the reaction $C_6H_6^{\bullet-},K^+(18C6) + {}^{13}C_6D_6 = C_6H_6 + {}^{13}C_6D_6^{\bullet-},K^+(18C6)$ is 0.096 ± 0.008 at −100 °C. An analogous competition for electrons exists between [8]annulene and perdeuteriated-per-13C-[8]annulene. In contrast to the benzene system the K_{eq} for the reaction $C_8H_8^{\bullet-},Na^+ + {}^{13}C_8D_8 = C_8H_8 + {}^{13}C_8D_8^{\bullet-},Na^+$ in liquid ammonia is 1.20 ± 0.04 at −100 °C. Similar contrasting results (but smaller in magnitude) were observed for the benzene and cyclooctatetraene perdeuteriated and per-13C systems. The results are interpreted in terms of the divergence of the [6]annulene system from aromatic character upon electron addition and the convergence of the [8]annulene system toward aromatic character upon electron addition.

Introduction

The most important properties that we can determine about any molecular system are its structure and energy, and the addition or subtraction of π electrons to or from conjugated organic systems can have a most profound effect upon both of these, as in the case of [8]annulene,[1a] or to a lesser degree [6]annulene.[1b] The extensive interest in structural perturbations due to π electron addition is accounted for by its importance to the understanding of conjugation and aromaticity.[1] Since Kekule's original vision of "resonating" structures,[2] there have been a number of empirical and theoretical definitions of aromaticity.[3,4] However, the one tried and true concept to which all theoretical models and experimental tests are ultimately compared is Hückel's $4n + 2$ rule.[5] Aromaticity in a Hückel sense is based upon the number of π electrons that exist in a conjugated system. It follows that experimental tests of conjugation and aromatic character might best be based upon the addition or subtraction of π electrons to form ion radicals.[6] Here we wish to propose a direct probe (EPR) into bonding changes upon π electron addition.

Over the years EPR has proven to be an accurate analytical tool for evaluation of relative concentrations of radicals,[7] and nearly two decades ago, free energy changes for electron transfer as small as 500 cal/mol were measured with a reported experimental error of only about 10 cal/mol.[8] These facts along with the advances in EPR computer simulation processes make "the EPR technique"[9]

extremely viable for the study of electron transfer reactions of the type shown in reaction 1.[9]

$$A^{\bullet-} + B = A + B^{\bullet-} \tag{1}$$
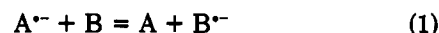
More recently, we have made use of this EPR approach to investigate the free energy changes involved in reaction 1 when A and B are isotopic isomers. Specifically, when A represents benzene and B its perdeuteriated analogue (reaction 2), K_{eq} was found to be 0.26 ± 0.01 at −100 °C.[7f]

 (2)
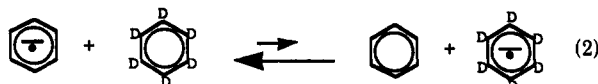
The nonunity value for the equilibrium constant necessarily means that any separation of the neutral molecule from anion radical will result in a partial separation of the isotopic isomers. In fact, separation of the neutral benzenes (labeled phase I) from the benzene anion radicals, which were subsequently reoxidized back to benzenes and labeled phase 2, did yield the expected partial separation of C_6H_6 (enriched in phase 2) from C_6D_6 (enriched in phase 1).[10]

Wolfsberg et al.[11] have pointed out that the *empirically* derived magnitudes of the carbon and nitrogen isotope effects in reaction 1 are at variance with conclusions based upon statistical mechanical calculations. Therefore, the viability of the use of the EPR technique to obtain the equilibrium constants for reaction 1 when A and B represent isotopic isomers involving polarizable systems and isotopes heavier than H and D has been questioned.[11] However, the long history of the technique for nonisotopic systems,[9] the agreement between the EPR measured K_{eq}'s and the separation data,[10,12] the fact that the H and D cyclic voltammetry data[13a,b] are in good agreement with the EPR data, and the agreement with the effect of deuteriation upon electron-promoted bond cleavage[14] leaves no reasonable doubt that the technique yields valid and very useful results, at least for the H and D systems.

The point remains, however, that the inclusion of solvent effects for polarizable ionic systems may not be straight-

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forward. It should be noted that the D/H effects and the $^{13}C/^{12}C$ effect in benzene (a nonpolarizable system) were specifically described as *not* being excessive in Wolfsberg's critique, and it is these systems that are the subject of this report.

The lower solution electron affinity of C_6D_6 relative to that for C_6H_6 is explained in terms of zero point energy changes and the general bond loosening that takes place when an electron is added to the benzene system.[1a,15] The bond loosening can be thought of as a consequence of the divergence of the [6]annulene system from aromatic character that takes place as a consequence of electron addition.[16] The resulting thermodynamic destabilization upon electron addition is greater for the heavier isotopic isomer (C_6D_6). For a truly antiaromatic system, electron addition should result in a convergence upon aromatic character and consequent bond tightening. It is predicted that the solution electron affinity of the isotopically heavy isomer would be greater than that of the isotopically light under these conditions. Thus, we were motivated to investigate the possibility of utilizing the difference in stability of ring deuteriated and undeuteriated annulenes as a probe into deviations from aromatic character upon electron addition. The procedure is analogous to the way Guthrie et al.[14] used the difference in stability of ring deuteriated and undeuteriated naphthylmethyl phenyl ethers and naphthyl benzyl ethers to probe the transition states for anion radical cleavage reactions.

Results and Discussion

When liquid ammonia solutions containing 0.069 mmol of [8]annulene and 0.091 mmol of perdeuteriated-per-^{13}C [8]annulene are reduced with a very deficient number of millimoles ($<10^{-2}$) of sodium metal, both anion radicals are generated and are in rapid equilibrium, reaction 3. EPR

$$\Delta G^\circ = -267 \text{ J/mol} \qquad (3)$$
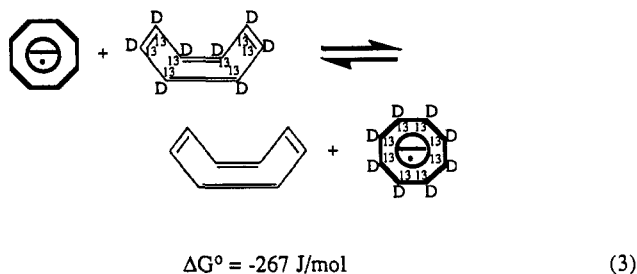
analyses of these solutions show that $[^{13}C_8D_8{}^{\bullet-}]/[^{12}C_8H_8{}^{\bullet-}]$ is close to $[^{13}C_8D_8]/[^{12}C_8H_8]$ and $K_{eq} = 1.17 \pm 0.04$ at 205 K, Figure 1.

In dramatic contrast, when analogous equilibrium constants were measured for the [6]annulene systems, a very large equilibrium isotope effect was realized, reaction 4.

$$\Delta G^\circ = +3.4 \text{ kJ/mol} \qquad (4)$$
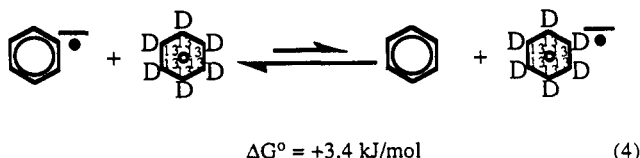
The exposure of a solution containing 0.1578 mmol of $^{13}C_6D_6$ in tetrahydrofuran (THF) containing a molar deficient amount of 18-crown-6 (0.0254 mmol) to a potassium mirror under high vacuum results in the formation of the corresponding anion radical. The extent of formation of

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(16) Stevenson, G. R.; Schock, L. E.; Reiter, R. C. *J. Phys. Chem.* **1983**, *87*, 4004.
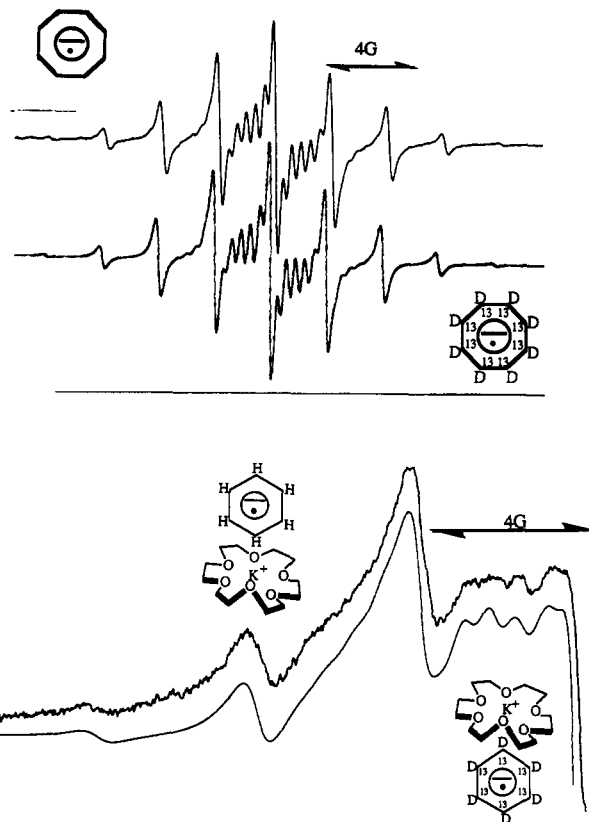
Figure 1. (Lower) Low-field half of the EPR spectrum (recorded at 173 K) of a 93/1 mixture of $^{13}C_6D_6$ and C_6H_6 reduced with a very deficient amount of potassium metal in THF containing crown ether. The computer simulation (below) was generated using a ratio of $[^{13}C_6D_6{}^{\bullet-}]/[C_6H_6{}^{\bullet-}] = 8.2$. This particular experiment corresponds to an K_{eq} of 0.088 and a ΔG° for reaction 4 of 3.5 kJ/mol. Several such experiments yielded an average value for ΔG° of 3.4 kJ/mol. (Upper) EPR spectrum at 205 K and recorded after the reduction with a very deficient amount of potassium metal of a 0.76/1 mixture of C_8H_8 and $^{13}C_8D_8$ in liquid ammonia. The computer simulation (below) was generated by assuming a ratio of $[C_8H_8{}^{\bullet-}]/[^{13}C_8D_8{}^{\bullet-}] = 0.65$ ($A_D = 0.51$ G and $A_{13C} = 1.07$ G). These data are consistent with an equilibrium constant of 1.17 for reaction 3.

the anion radical is controlled by the amount of crown ether present. The addition of 0.0141 mmol of $^{12}C_6H_6$ to this solution results in the complete replacement of $^{13}C_6D_6{}^{\bullet-}$ by $^{12}C_6H_6{}^{\bullet-}$. However, when only 0.001 69 mmol of $^{12}C_6H_6$ is added to the $^{13}C_6D_6{}^{\bullet-}$ solution, the EPR signals of both anion radicals can be observed simultaneously at 173 K, Figure 1, and the relative concentrations of the two are controlled by reaction 4. The resulting EPR spectrum is best simulated using a ratio of $[^{13}C_6D_6{}^{\bullet-}]/[^{12}C_6H_6{}^{\bullet-}] = 8.2$, Figure 1. If the solution electron affinities of $^{13}C_6D_6$ and $^{12}C_6D_6$ were identical, this anion radical ratio would have been the same as $[^{13}C_6D_6]/[^{12}C_6H_6]$ or 93. Thus, the equilibrium constant for reaction 4 that best fits this experiment is 0.088. From several independent experiments K_{eq} was found to be 0.095 ± 0.008, $\Delta G^\circ = +3.4$ kJ/mol. This value is actually within experimental error of the 3.1 kJ/mol that is predicted by simply adding the reported[7f,17] free energy changes for reaction 2 (1.94 kJ/mol) and the analogous exchange between benzene and per-^{13}C-benzene (1.12 kJ/mol).

It has been pointed out that the EPR technique as used here is not reliable when K_{eq} is greater than 250 or less than $1/250 = 0.004$ due to the necessity of using an enormous

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Table I. Free Energy Change and Equilibrium Constant for Electron Transfer from the Annulene Anion Radical to the ^{13}C and/or D Isotopically Labeled Annulene

annulene	no. of ^{13}C's	no. of ^{2}H's	$\Delta G°$ (J/mol)	K_{eq} (-100 °C)
(hexagon)	0	0	0.00	1.00
	0	6	1937 ± 67	0.26 ± 0.02
	6	0	1117 ± 344	0.46 ± 0.12
	6	6	3386 ± 65	0.095 ± 0.008
(octagon)	0	0	0.00	1.00
	0	8	-208 ± 20	1.16 ± 0.02
	8	0	52 ± 30	0.97 ± 0.03
	8	8	-267 ± 25	1.20 ± 0.04

excess of one of the materials.[9b] The K_{eq} for reaction 4 is very small for an equilibrium isotope effect but well within the limits for a reliable EPR determined electron transfer (reaction 1) equilibrium constant.

Physical separation of the anion radicals from the neutral molecules followed by reoxidation of the anion radical phase yields two isotopic mixtures of benzenes. That is, separation of the liquid solution from the metal followed by distillation of the neutral benzenes (collected as phase 1) under reduced pressure leaves the solid (dark red) K(18C6)$^+$, anion radical salt (phase 2). This anion radical salt was left exposed to a high vacuum (10^{-6} Torr) to ensure complete removal of the neutral benzenes. Phase 1 had the same isotopic ratio as did the initial mixture, since only a small fraction of the benzenes was reduced to anion radical. The neutral hydrocarbons were recovered from phase 2 via reoxidation with iodine (2A$^{•-}$ + I$_2$ → 2I$^-$ + 2A). The solid-phase equilibrium constant is the mole ratio of the heavy to light isotopic isomers in phase 1 divided by that in phase 2. This same quantity is often called the separation factor eq 5.

$$K_{eq(s)} = \frac{([^*R]/[R])_{phase\,1}}{([^*R]/[R])_{phase\,2}} = \alpha \qquad (5)$$

From three separate measurements this ratio of ratios (as determined from the room-temperature separations) is 0.26 ± 0.06. Assuming that $\Delta G° = \Delta H°$, this corresponds to a K_{eq} of 0.098 at -100 °C. The value obtained from the EPR data yields a K_{eq} of 0.095 ± 0.008. Thus, mass spectral analysis of the two mixtures shows that the isotopic separation is consistent with a free energy of electron transfer of 3.4 kJ/mol.

The equilibrium constants for both reactions 3 and 4 are controlled by the vibrational partition functions,[17,18] which demand that the electron preferentially occupies the isotopic isomer that is least destabilized by its presence. The dramatic contrast in the two isotope effects is due to the fact that the [8]annulene system has $4n$ π electrons, is nonaromatic, and approaches planar aromatic character upon the addition of nonbonding electrons.[19] On the other hand, [6]annulene has $4n + 2$ π electrons, is aromatic, and diverges from aromatic character upon the addition of the antibonding electron. The destabilization of [6]annulene upon electron addition is more extensive for the heavy isotopic isomer.

Similar contrasts in equilibrium isotope effects, but smaller in magnitude, were observed when identical studies were carried out with [8]annulene and [6]annulene systems that were less extensively isotopically substituted, Table I and Figure 2. For instance, the reduction of solutions
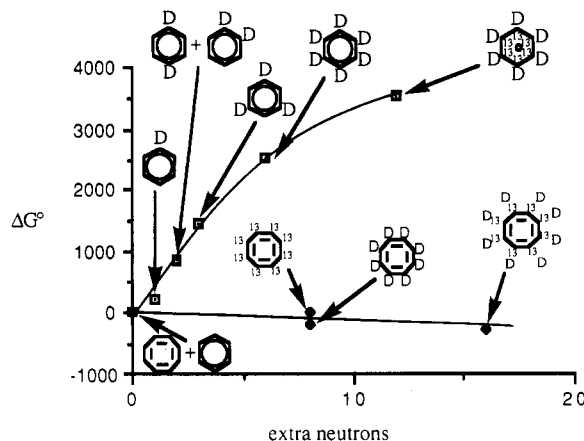
Figure 2. Plot of the free energy of electron transfer in J/mol from the light isotopic isomer to the heavy vs the number of "extra" neutrons in the form of deuteriums and/or ^{13}C's.

Scheme I (gas phase)
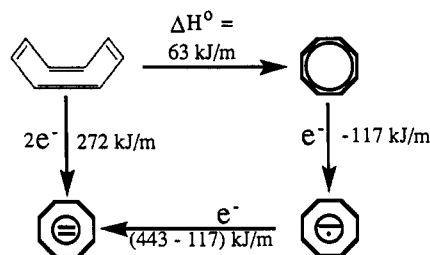
of carefully weighed portions of perdeuteriated [8]annulene and normal [8]annulene in liquid ammonia with very deficient amounts of sodium metal yields anion radical solutions that exhibit EPR spectra of the two anion radicals in ratios consistent with an equilibrium constant for reaction 6 of 1.13 ± 0.02 at 205 K, Figure 3. A K_{eq} that is

$$\Delta G° = -208 \text{ J/mol} \qquad (6)$$
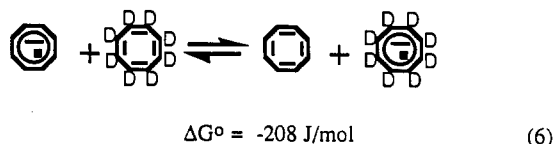
within experimental error of unity was obtained for the per-^{13}C [8]annulene system, Table I. Coupling constants of $A_{13C} = 1.19$ and $A_H = 3.23$ G were used to simulate the EPR spectrum of $^{13}C_8H_8{}^{•-}$.

The free energy for reaction 7 will be much greater than zero when R represents an aromatic system, near zero when R represents a nonaromatic system, and should be much less than zero if R were to represent a symmetric planar antiaromatic (D_{8h}) system. The magnitude of the isotope effect can be controlled by the degree of substitution, Figure 2. An increase in the magnitude of an isotope effect with increased deuterium substitution was predicted by Bigeleisen.[20] In general, the equilibrium constant for reaction 7 should be less than unity whenever

$$R^{•-} + {}^*R = {}^*R^{•-} + R \qquad (7)$$
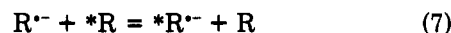
bond loosening occurs upon electron addition and greater than unity whenever bond tightening occurs upon electron addition. The test comprises a direct probe into the bonding changes resulting from electron addition.

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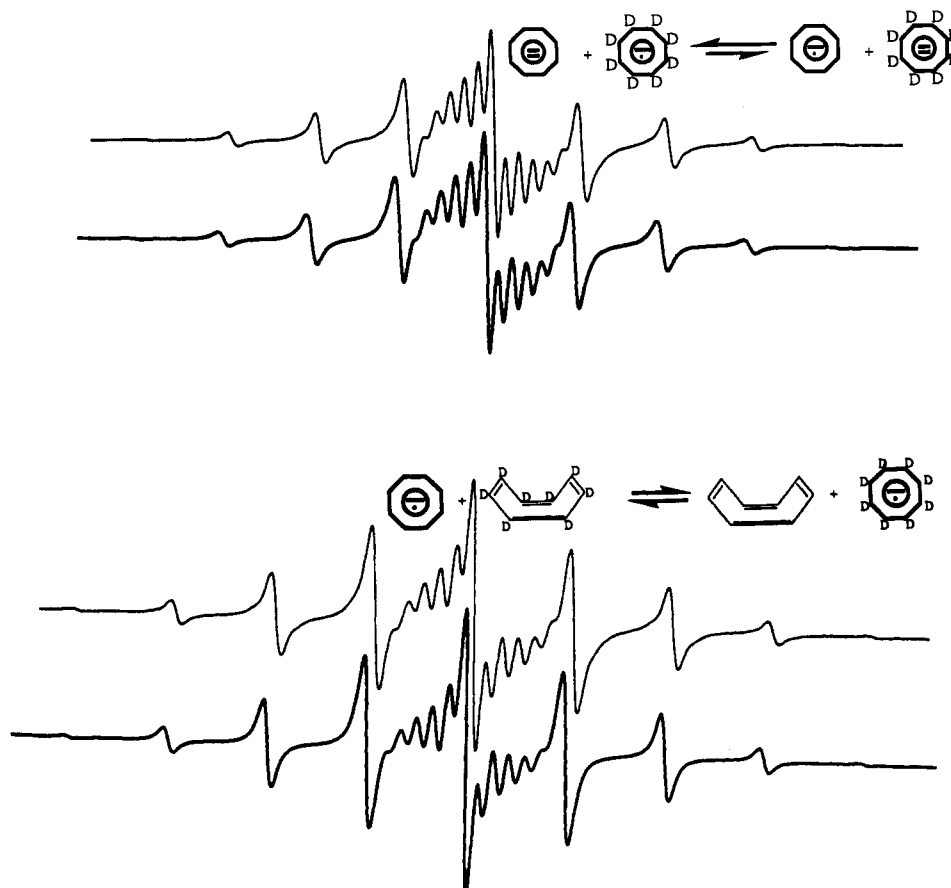
Figure 3. (Upper) EPR spectrum (liquid ammonia at 205 K) after a near exhaustive reduction of C_8H_8, C_8D_8, and C_8D_7H in a ratio of 1.0:1.77:0.35 respectively. Below this is the computer simulation generated using a ratio 1.0:2.16:0.43 for $[C_8H_8{}^{\cdot-}]:[C_8D_8{}^{\cdot-}]:[C_8D_7H{}^{\cdot-}]$. These data indicate a K_{eq} for reaction 9 of 0.82. (Lower) EPR of $C_8H_8{}^{\cdot-} + C_8D_8{}^{\cdot-} + C_8D_7H{}^{\cdot-}$ after the reduction of a mixture of C_8H_8, C_8D_8, and C_8D_7H in the ratio 1.0:0.97:0.18, respectively, with a very deficient amount of sodium metal, $[Na^+] \ll [C_8H_8]$, in liquid ammonia at 205 K. The C_8D_7H was present in the C_8D_8 as an impurity. Below this is the computer simulation, which was generated using a respective ratio of 1.0:0.89:0.17. The data are consistent with an equilibrium constant for reaction 6 of 1.09. Several such experiments yield an average K_{eq} of 1.13.

Since both anion radical and dianion are planar, the geometrical changes that occur upon the addition of the second electron to the [8]annulene system are quite different from those associated with the first electron addition. In contrast to the [6]annulene reduction case, it is relatively easy to add a second π electron to the [8]-annulene anion radical. In fact, the enthalpy change for disproportionation of the anion radical (reaction 8) is less
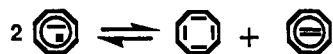
$\Delta H° = -4.6$ in HMPA[21] with K^+ and $+380$ kJ/m in gas phase[22]   (8)

than zero in many solvent systems.[1a,19] This is the case in spite of the fact that the electron–electron repulsion energy in the dianion is 443 kJ/mol rendering the formation of the dianion in the gas phase very energetically unfavorable (endothermic by 272 kJ/mol), Scheme I.[5,23] The destabilizing effect of the electron–electron repulsion energy in the dianion of [8]annulene must manifest itself in the zero point bond vibrational energies and is expected to render the electron affinity of the perdeuteriated anion radical less than that of the isotopically light material. That is, the perdeuteriated system favors the addition of the first electron and the perprotiated system should preferentially accept the second electron. This is the situation that was, in fact, observed.

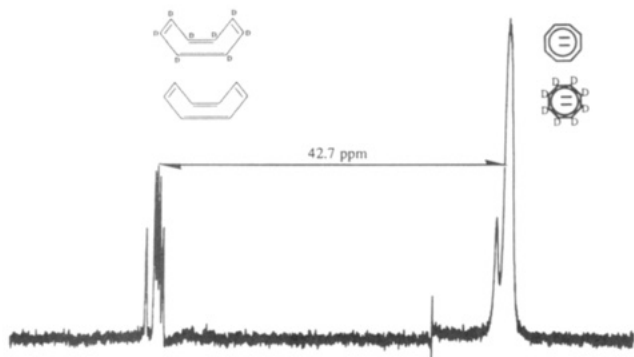(23) Stevenson, G. R.; Zigler, S. S.; Reiter, R. C. *J. Am. Chem. Soc.* 1981, *103*, 6057.

Exhaustive reduction of [8]annulene by exposure to sodium metal in THF led to the formation of the dianion in the absence of anion radical (not detectable via EPR). Removal of the solvent under reduced pressure left the solid dianion salt.[23] This salt was then dissolved in liquid ammonia and a very small fraction of it reoxidized to produce a recordable EPR signal of the two anion radicals, concentrations of which are controlled by reaction 9.


$\Delta G° = 359$ J/mol   (9)
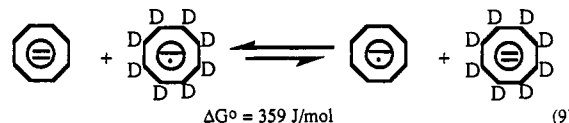
The exhaustive reduction of a mixture of C_8H_8 and C_8D_8, solvent removal, ammonia dissolution, and partial reoxidation yields an EPR signal at 205 K exhibiting both $C_8H_8{}^{\cdot-}$ and $C_8D_8{}^{\cdot-}$, Figure 3. Since the ratio of dianions $([C_8H_8{}^{2-}]/[C_8D_8{}^{2-}])$ is the same as that of the neutral molecules used to produce the mixture, computer simulation of the EPR spectrum yields K_{eq} for reaction 9. Several such experiments show K_{eq} to be 0.81 ± 0.2.

The reduction of a mixture of C_8H_8 and C_8D_8 with 1 mol of potassium metal per mol of total [8]annulene in THF yields a solution that contains mostly neutral and dianionic materials. Due to the very large equilibrium constant for disproportionation (ca. 10^9)[1a] there is very little anion radical present in solution. Thus, any separation of the anionic materials from the neutral materials is in net effect a separation of the dianionic and neutral materials. Further, the ratios of isotopic isomers in the two phases

Figure 4. 300-MHz NMR of a THF solution of neutral molecule and dianion of [8]annulene. Qualitative information concerning the relative concentrations of $C_8D_8^{2-}$, $C_8H_8^{2-}$, C_8D_8, and C_8H_8 is difficult to obtain due to very different relaxation times, but a separation and reoxidation followed by an NMR analysis of the two phases should yield this information (see Figure 5).
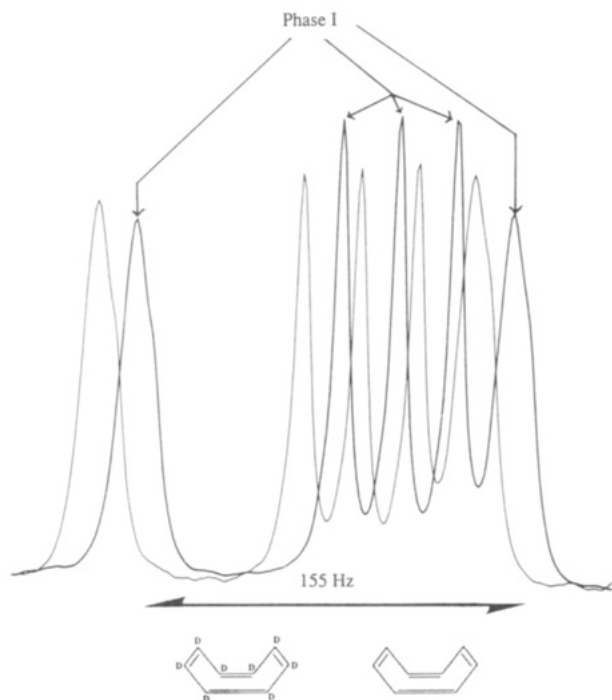

Figure 5. After the partial potassium reduction of a mixture of 2.40 mmol of [8]annulene and 6.66 mmol of perdeuteriated [8]-annulene the neutral phase and dianion phase were separated. The dianions were reoxidized to neutral material (phase 2) and the ^{13}C NMR (300-MHz, proton) spectra of each phase were recorded. That of phase 1 is shown shifted slightly to the right. Note that phase 1 is enriched in C_8D_8 and depleted in C_8H_8 relative to phase 2. This is due to the fact that the electrons "prefer" the isotopically light material ($K_{eq} < 1.0$ for reaction 10). Both spectra were recorded under identical conditions (not proton decoupled, 8700 scans, 6-s pulse delay, 6-μs pulse width, same lock signal power, etc.).

are controlled by the equilibrium constant for reaction 10 which must be $0.81 \times 1.13 = 0.92$ at 205 K.

$$\Delta G^\circ = 142 \text{ J/mol} \tag{10}$$
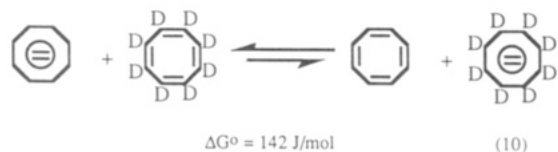
A mixture of 2.40 mmol of C_8H_8 and 6.66 mmol of C_8D_8 was reduced by about 7 mmol of potassium metal at room temperature in THF, Figure 4. The solvent and neutral [8]annulenes were removed under reduced pressure (phase 1) and the remaining solid dianion salt reoxidized with
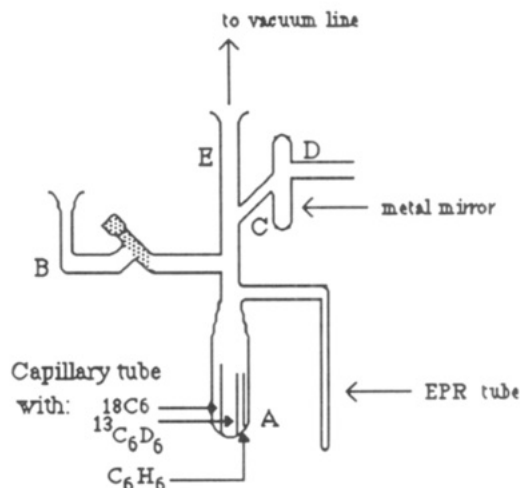
Figure 6. Apparatus used for the physical separations of benzene anion radical from benzene and cyclooctatetraene from its dianion.
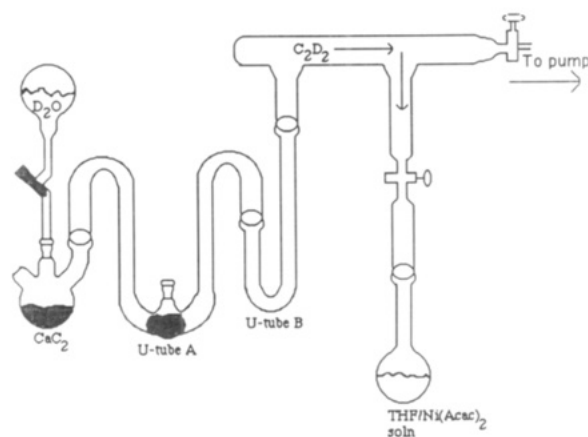
Figure 7. Apparatus used for the production of perdeuteriated cyclooctatetraene.

iodine (i.e., $I_2 + K^+{}_2C_8H_8^{2-} \rightarrow C_8H_8 + 2I^-$) and labeled phase 2. The [8]annulenes from both phases were distilled under vacuum and submitted to NMR analysis, Figure 5. The nondecoupled ^{13}C NMR spectra clearly show the predominance of the perdeuteriated material in phase 1 and perprotiated material in phase 2.

Experimental Section

Separations. The apparatus shown in Figure 6 was used for the physical separation experiments involving the C_6H_6 and $^{13}C_6D_6$. Two of the three capillary tubes were charged with 0.0191 g (0.2122 mmol) and 0.0166 g (0.2128 mmol) of $^{13}C_6D_6$ and C_6H_6, respectively. The third capillary tube was charged with 0.1111 g (0.4208 mmol) of 18-crown-6. An excess of potassium metal was placed into side arm D, which was subsequently sealed shut. The entire system was evacuated, and the potassium was then distilled from point D into bulb C, and side arm D was sealed from the apparatus. Four mL of tetrahydrofuran (THF) was distilled from a bulb containing NaK$_2$ directly into tube A, which was cooled in a dry ice/acetone mixture. The apparatus was then sealed from the vacuum line at point E. Agitation of the apparatus ruptured the three capillary tubes. After complete dissolution of their contents, the apparatus was tilted to expose the solution to the potassium mirror. The amount of potassium used in the reaction was controlled by the time of contact with the solution. This reaction time was kept short enough to avoid complete reduction of the benzenes. The reaction mixture could be submitted to EPR spectral analysis by pouring a small portion of the anion radical into the EPR tube. The apparatus was reconnected to the vacuum line via side arm B. The stopcock was then opened and the volatile contents (THF + neutral benzenes) were exhaustively removed under high vacuum and collected in a separate chilled flask and

labeled phase I. The solid potassium-crown-benzene anion radical salt was left in tube A. 0.0980 g of I_2 was sublimed into tube A and 0.5 mL of THF distilled into tube A to act as a medium for reoxidation. The contents of bulb A were then labeled phase II. Both phases were submitted to a GC-mass spectral analysis using a Hewlett-Packard Model 5970 spectrometer connected with a 5790A gas chromatograph.

The possibility that changes in solvent/salt/solute ratios or that successive phase equilibrations during distillation may be partially responsible for observed isotopic enrichment is counterindicated by the following facts. First, under conditions of hard vacuum the distillation does not proceed by a series of equilibrium steps, and isotopic separation could not occur to a significant extent. Second, the distillations were exhaustive yielding no separation of liquids. Third, any separation that did so occur would involve preferential vaporization of the lighter isotopic isomer—the opposite of our observation. Further, the empirical separation factor is very close to that predicted by the EPR measured equilibrium constant for reaction 4.

The following column conditions resulted in complete separation of the benzenes from the THF: column = 30 m, 0.25-mm i.d. capillary of methylphenylsilicone; column temperature ramp = 40–200 °C at 10 deg/min; solvent delay = 2.3 min. The mass spectrometer was set in the ion selective mode focusing on the parent ions for calculation of the isotopic ratios. The average peak abundances were recorded for the benzene peaks (retention time 2.8–3.1 min).

The equilibrium constant for electron transfer ($C_6H_6^{\cdot-} + {}^{13}C_6D_6 = C_6H_6 + {}^{13}C_6D_6^{\cdot-}$) was evaluated from

$$K_{eq} = [\text{abund of } m/z = 90 \text{ (phase II)}]/[\text{abund of } m/z = 78 \text{ (phase II)}]/[\text{abund of } m/z = 90 \text{ (phase I)}]/[\text{abund of } m/z = 78 \text{ (phase I)}]$$

The apparatus shown in Figure 6 was also used for the physical separation experiments involving the C_8H_8 and C_8D_8. Two of the three capillary tubes were charged with carefully weighed portions of $^{13}C_8D_8$ and C_8H_8. The third capillary tube was not used in these experiments. An excess of potassium metal was, as before, placed into side arm D, which was subsequently sealed shut. The solutions of [8]annulene were exposed to the metal mirror. The THF and neutral cyclooctatetraenes were removed under reduced pressure and collected in a separate chilled flask and labeled phase I. The solid potassium [8]annulene dianions were left in tube A and were subsequently reoxidized with I_2 in THF. The contents of bulb A were then labeled phase II. Both phases were dissolved in diethyl ether, washed with water and sodium thiosulfate, and concentrated via rotoevaporation. The [8]annulenes were vacuum distilled and submitted to NMR analysis, Figure 5.

Electron Exchange Measurements. Carefully weighed mixtures of [8]annulene and isotopically substituted [8]annulene were placed into separate capillary tubes which were in turn sealed. The tubes containing the [8]annulenes were placed into bulb A of the apparatus shown in Figure 6. After evacuation of the entire apparatus, a freshly distilled potassium mirror was deposited into bulb C from the side tube, which was subsequently sealed from the apparatus. Dry liquid ammonia was then distilled from a storage bulb containing potassium, directly into bulb A. The entire apparatus was then sealed from the vacuum system. The apparatus was then shaken to break the tubes containing the [8]-annulenes. A very small amount of ammonia was allowed to condense in tube C by cooling it with a cold cotton swab. This allowed a very small amount of the dissolved potassium metal to drip into bulb A containing the bulk of the solution. A sample of this resulting anion radical solution was then poured into the EPR tube and subjected to EPR analysis. The relative amounts of the two anion radicals in solution were accurately obtained from computer simulations of the EPR spectra as previously described.[7f,12]

The experiments involving the [6]annulene system were carried out in essentially the same way. However, in this case the capillary containing 18C6 was used, and the apparatus was then shaken in such a manner as to break the tubes containing the $^{13}C_6D_6$ and 18C6 only. The amount of anion radical formed was controlled by the amount of 18C6 (the limiting reagent) present in the solution. A sample of this resulting anion radical solution was

then poured into the EPR tube and subjected to EPR analysis. This resulting EPR signal exhibited $^{13}C_6D_6^{\cdot-}$ only. The apparatus was then removed from the spectrometer and shaken to rupture the capillary tube containing the benzene. This benzene was then allowed to fully mix with the already formed anion radical solution, and a second EPR analysis was obtained. The second EPR spectrum always exhibited the presence of both the anion radical of $^{13}C_6D_6$ and C_6H_6. The relative amounts of the two anion radicals in solution were accurately obtained from computer simulations of the EPR spectra.[7f,12]

Instrumentation. The EPR spectra were recorded at −100 °C on an IBM (Bruker) ER-200D spectrometer equipped with an IBM variable-temperature unit. The 300-MHz NMR spectra of these samples were recorded on a Varian (Gemini) 300-MHz NMR spectrometer. Mass spectral data were collected using a Hewlett-Packard Model 5970 spectrometer connected using a 5790A gas chromatograph.

Synthesis. The procedures for the production of [8]annulene have been widely (Reppe synthesis) published.[24] However, there were some differences in the procedures used in our laboratory to generate the isotopically labeled materials.

A 50-mL round-bottom bulb was charged with about 0.85 g of $Ni(Acac)_2$, and the bulb was connected to the vacuum line and evacuated. 30 mL of dry THF was then distilled into the round-bottom bulb using a dry ice/acetone solution (−70 °C). The bulb was then kept in the dry ice/acetone solution so that the acetylene would condense into the THF solution. The production of deuteriated acetylene was performed on the same vacuum line by dripping approximately 50 mL of D_2O onto 100 g of CaC_2, resulting in the production of 1.25 mol of acetylene which was condensed into the 50-mL bulb. The apparatus used for the production of deuteriated acetylene is shown in Figure 7. The chemical reaction between water and calcium carbide is very exothermic. Therefore, some unreacted water will vaporize and possibly condense in the reaction bulb. To eliminate this possibility two U-tubes were placed between the reaction bulb and the three-neck flask where the CaC_2/D_2O reaction was taking place. U-tube A was submerged in an ice bath and was charged with CaC_2 to convert any vaporized D_2O to acetylene. To condense any residual D_2O, U-tube B was submerged in an acetone bath which had been cooled to approximately −50 °C. When the THF solution became saturated with acetylene, the bulb was submerged in liquid N_2 to condense any residual acetylene. Once all the acetylene was condensed and the solution frozen solid, the bulb was sealed from the line and enclosed in a 500-mL steel bomb. The bomb was submerged in a 90 °C oil bath for 15 h and shaken periodically. The bomb was then cooled in an ice bath and opened. The materials in the bomb were removed and dissolved in about 300 mL of diethyl ether. The solution was dried with magnesium sulfate and gravity filtered. The ether was evaporated under a stream of dry nitrogen. The remaining dark liquid was then vacuum distilled at 30 Torr. A yellow liquid was collected over a temperature range of 40–50 °C. Mass spectra analysis is consistent with perdeuteriated [8]annulene (93% isotopic purity) mixed with heptadeuteriated [8]annulene (7% isotopic purity).

The production of per-^{13}C [8]annulene and per-^{13}C perdeuteriated [8]annulene was carried out in the same manner except that commercial dideuteriodi-^{13}C-acetylene (Cambridge Isotopes) and di-^{13}C-acetylene (Cambridge Isotopes) replaced the homemade C_2D_2. After the polymerization reaction, all of the volatile materials, including THF, [8]annulene, and other by-products, were distilled under vacuum. The [8]annulene analogues were separated from the unwanted materials and collected using preparatory gas chromatography. Mass spectral analysis confirmed the isotopic purity (>99%) of the [8]annulene analogues.

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(24) Perdeuteriated, per-^{13}C, and perdeuteriated-per-^{13}C-[8]annulenes are easily synthesized via the Reppe synthesis using appropriately labeled acetylene (MSD isotopes) see: (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Ann.* 1948, *560*, 1. (b) Lippincott, E. R.; Lord, R. C.; McDonald, R. C. *J. Am. Chem. Soc.* 1951, *73*, 3370.