Isotopic Exchange Involving the [8]Annulene Anion Radical and Its Dimerization to the [16]Annulene Anion Radical

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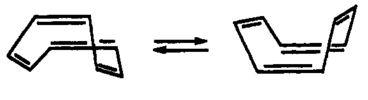
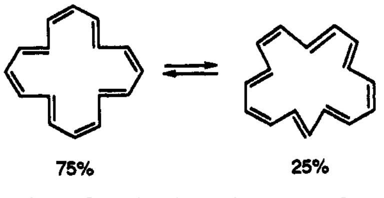
The addition of D_2O to hexamethylphosphoramide solutions of the potassium salt of the [8]annulene anion radical results in the slow (days) formation of the monodeuteriated anion radical ($C_8H_7D^{\bullet-}$). However, several days after a similar addition to the sodium salt solution, no $C_8H_7D^{\bullet-}$ is present. Instead, the anion radical of [16]annulene is found. These observations led to EPR and NMR studies, which have revealed the mechanism of each process. The mechanisms are based upon the facts that ion association is necessary for the isotope exchange reaction and the absence of ion association is required for the dimerization. Solutions of deuteriated [8]annulene anion radical, [8]annulene dianion, [16]annulene anion radical, and [16]annulene dianion can be readily generated from reduced solutions of [8]annulene for EPR, NMR, etc. studies by making use of the isotopic exchange and dimerization mentioned above.

Introduction

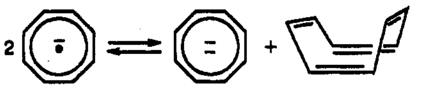
[8]Annulene, the first nonbenzoid cyclic system with alternating double and single bonds, was first described in 1911 by Willstatter and Waser who obtained it from an alkaloid from the bark of a pomegranate tree.[1] Even though it was the only 4n π-electron annulene known for some time, it was not the center of much research activity until the discovery of the Reppe synthesis in 1948.[2] Since that time, and especially after its commercial availability, [8]annulene (along with its respective anions) has become one of the most widely studied organic compounds. Indeed, an entire book has been devoted to this compound and its derivatives.[3] The intense interest in [8]annulene is clearly due to the fact that it sits in a position analogous to that of benzene (the only readily available 4n + 2 annulene) as it is the only readily available 4n π-electron annulene. The lack of thermodynamic stability and thus availability of [10], [12], and [14]annulenes is due to the extreme crowding of the internal protons.[4] [16]Annulene is the first annulene (other than [8]annulene and benzene) for which this problem is relieved to the point of its having sufficient thermodynamic and kinetic stability for routine use. Unlike [8]annulene, which exists in a tub conformation (reaction 1), [16]annulene has been shown to exist in a dynamic equilibrium between two interconverting configurations (reaction 2), each having double and single bond alternation.[5]


(1)



(2)

The reduction chemistries of [8]annulene and [16]annulene are similar. For both systems the addition of one and two electrons affords the planar anion radical and dianion, which are in equilibrium with the neutral species through the disproportionation of the anion radical (reactions 3 and 4).



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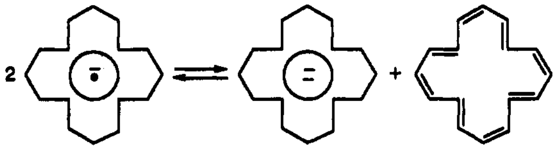

(4)

Literally hundreds of articles have been published concerning the anions of [8]annulene and its derivatives. [16]Annulene has some very interesting features that are quite unlike those of [8]annulene. However, there are only a few reports on the chemistry of this system. This is undoubtedly due, at least in part, to the laborious synthetic procedure[6] required for the production of this compound (a process this senior author has been through several times).[7] The synthesis of [16]annulene involves first the thermal dimerization of [8]annulene, which affords a low yield of both the 2 + 2 and more complex dimers. These dimers, of equal molecular weight, must be separated and the 2 + 2 dimer photolyzed to produce [16]annulene. A further complication arises from the fact that neutral [16]annulene decomposes above -10 °C and cannot be routinely handled in the laboratory.[6] Solutions of its anions have, on the other hand, persisted for years on our shelves. A convenient source of the anions of [16]annulene should open the door to a vast amount of chemistry, as one did for the analogous [8]annulene system.

[†] This author previously published under the name of Gerald R. Stevenson.

[•] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

(1) (a) Willstatter, R.; Waser, E. *Ber.* **1911,** *44,* 3423. (b) Willstatter, R.; Heidelberger, M. *Ber* **1913,** *46,* 517.

(2) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Ann.* **1948,** *560,* 1.

(3) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclo-octatetraene and its Derivatives*; Cambridge University Press: New York, 1978.

(4) Garratt, P. J. *Aromaticity*; John Wiley & Sons: New York, 1986; Chapter 4.

(5) Oth, J. F. M.; Gilles, J. M. *Tetrahedron Lett.* **1968,** 6259.

(6) (a) Sondheimer, F.; Gaoni, Y. *J. Am. Chem. Soc.* **1961,** 83, 4863. (b) Oth, J. F.; Bauman, H.; Gilles, J. M.; Schroder, G. *J. Am. Chem. Soc.* **1972,** *94,* 3498.

(7) (a) Stevenson, G. R.; Forch, B. E. *J. Am. Chem. Soc.* **1980,** *102,* 5985. (b) See also ref 13.

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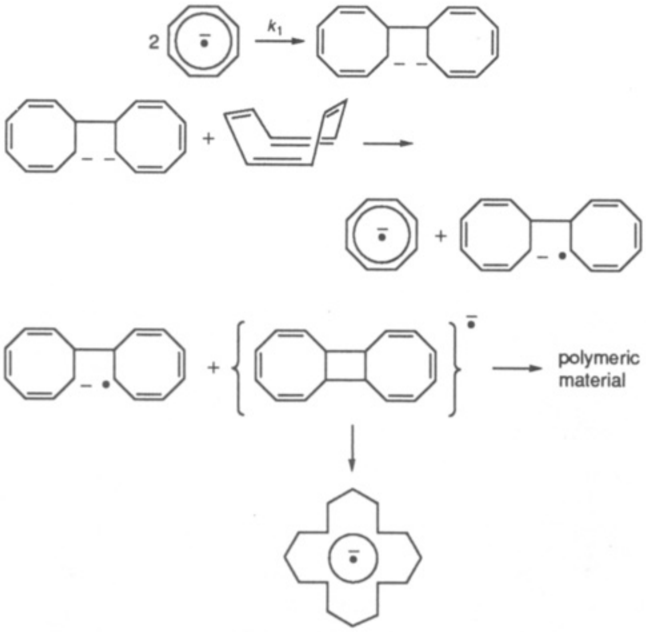
Scheme I



Several years ago, we reported that the sodium [8]annulene anion radical salt in hexamethylphosphoramide (HMPA) readily dimerizes to form the anion radical of [16]annulene.[8,9] At ambient temperatures this dimerization results in solutions that are devoid of the anion radical of [8]annulene and where the anion radical of [16]annulene is the only observable radical in solution (see Figure 1 in ref 8). Kinetic studies revealed that the reaction is second order in the [8]annulene anion radical, and a mechanism was proposed, Scheme I.[8] The possibility of utilizing this dimerization as a useful synthetic procedure for [16]annulene was discounted 6 years ago due to polymerization problems.[8] However, recent results have revitalized this possibility. Further, with the use of isotopically substituted [8]annulenes, the dimerization process becomes a potential source of isotopically substituted [16]annulenes.

In order to investigate the possible effects of isotopic substitution upon the molecular orbitals of [16]annulene ($C_{16}H_{16}$) in a manner that is analogous to that of earlier benzene and [8]annulene (C_8H_8) studies,[10,11] we became interested in generating the anion radical of monodeuteriated [16]annulene ($C_{16}H_{15}D^{\bullet-}$) and analyzing its EPR spectrum.

Results and Discussion

Exposure of dilute (0.01–0.5 M) solutions of [8]annulene in HMPA to freshly distilled potassium metal mirrors results in the formation of the respective dianion and anion radical. The addition of molar-deficient amounts of deuteriated water to the potassium salt of the anion radical of [8]annulene ($C_8H_8^{\bullet-}$) in HMPA results in an immediate reduction in the anion radical concentration. After about 10 h, the presence of the anion radical of monodeuteriated [8]annulene can be observed simultaneously with $C_8H_8^{\bullet-}$ upon EPR analysis, Figure 1. The concentration of $C_8H_7D^{\bullet-}$ continues to grow for several days, and after about 36 h the presence of polydeuteriated [8]annulene anion radicals can also be detected. This reaction represents a rather convenient source of the deuteriated anion radical, and it is a simple matter to obtain a concentration of $C_8H_7D^{\bullet-}$ that is larger than that of $C_8H_8^{\bullet-}$, Figure 1. The exchange has also been demonstrated to take place with T_2O.[10] The isotopically substituted anion radical can be further reduced to the respective dianion for NMR studies, and the dianion can be oxidized to the neutral molecule with iodine ($C_8H_7D^{2-} + I_2 \rightarrow 2I^- + C_8H_7D$).[12]

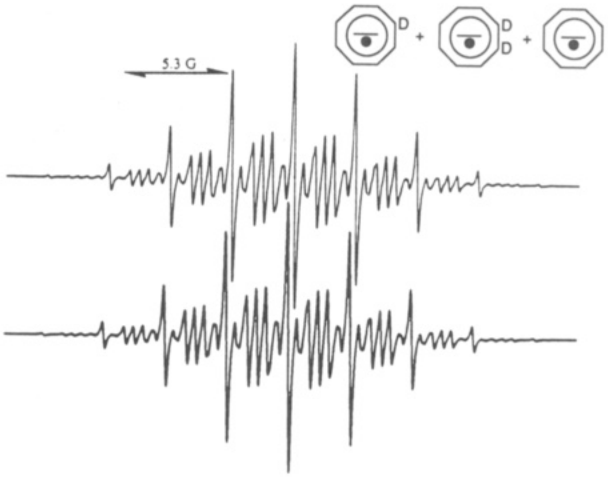


Figure 1. (Top) room-temperature EPR spectrum of the solution resulting from the potassium reduction of [8]annulene. This spectrum was recorded 48 h after the addition of 2 μL of D_2O to the solution. The moles of D_2O are less than the total number of moles of potassium salts in the sample tube. (Bottom) A computer simulation generated using the spectra of $C_8H_8^{\bullet-}$, $C_8H_7D^{\bullet-}$, and $C_8H_6D_2^{\bullet-}$ in a ratio of 1.0:1.3:0.86, respectively. Both dideuterio isomers are present, and they yield identical EPR patterns.

In light of the above work it occurred to us that we could avoid developing a synthetic procedure to produce the unknown monodeuteriated [16]annulene by taking advantage of both the deuterium exchange reaction and the dimerization of $C_8H_8^{\bullet-}$ discussed in the Introduction. Thus, it was our original intent to simply generate the anion radical of [8]annulene in HMPA, add a small quantity of D_2O to this solution to yield $C_8H_7D^{\bullet-}$, and then let the solution stand until the anion radical of deuteriated [16]annulene was exhibited upon EPR analysis.

The addition of deuteriated water to solutions of the sodium salt of $C_8H_8^{\bullet-}$ in HMPA does result in the expected decrease in the anion radical concentration, but EPR analysis of the resulting solution never exhibits the presence of the deuteriated [8]annulene anion radical ($C_8H_7D^{\bullet-}$). Further, if the HMPA solution is allowed to stand until $C_{16}H_{16}^{\bullet-}$ is the dominant EPR-active species and *then* the D_2O is added, $C_{16}H_{15}D^{\bullet-}$ is still not formed in a concentration detectable via EPR analysis. In contrast, when potassium metal serves as the reducing agent, the addition of D_2O gives rise to the formation of detectable amounts of $C_8H_7D^{\bullet-}$ within a few hours. However, allowing the potassium solution to stand at room temperature for 1 week does not result in the formation of $C_{16}H_{16}^{\bullet-}$. Some $C_{16}H_{16}^{\bullet-}$ is eventually formed in these

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[8] Stevenson, G. R.; Nebgen, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 5501.

[9] Stevenson, G. R.; Reiter, R. C.; Sedgwick, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 6521.

[10] Stevenson, G. R.; Peters, S. J. *J. Org. Chem.* **1991**, *56*, 3468.

[11] Carrington, A.; Longuet-Higgins, H. C.; Moss, R. E.; Todd, P. F. *Mol. Phys.* **1965**, *9*, 187.

[12] (a) Stevenson, G. R.; Hashim, R. T. *J. Phys. Chem.* **1986**, *90*, 1896. (b) Stevenson, G. R.; Sturgeon, B. E.; Vines, K. S.; Peters, S. J. *J. Phys. Chem.* **1988**, *92*, 6850.

solutions, but the reaction is at least 1 order of magnitude slower than in the case of the sodium reduction, and the concentration of $C_{16}H_{16}^{\bullet-}$ is always very low.

The potassium cation will not form ion pairs with $C_8H_8^{\bullet-}$ but it will ion associate with the corresponding dianion $C_8H_8^{2-}$ in HMPA, and the dianion exists as $C_8H_8^{2-}$, K^+ + K^+.[13] The sodium cation, on the other hand, ion associates with neither the anion radical nor the dianion, and the sodium salt of the dianion is best described as $C_8H_8^{2-}$ + $2Na^+$.[13] Thus, the formation of $C_8H_7D^{\bullet-}$ after D_2O addition to the anion radical solution must proceed through the ion associated dianion.

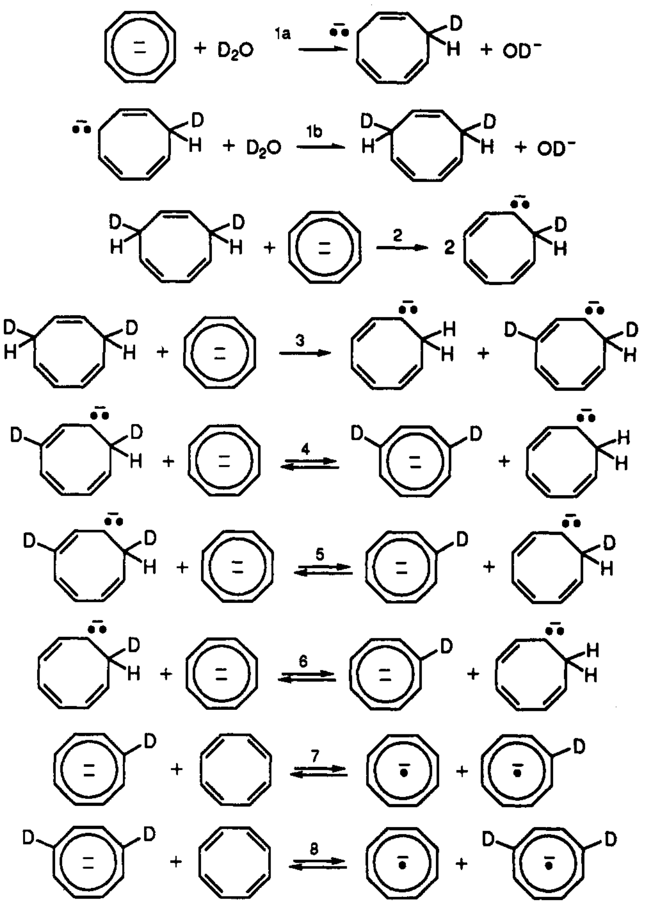
The EPR spectrum of $C_8H_7D^{\bullet-}$ was never visible until at least 6 h after the addition of the D_2O. However, Krapcho and Bothner-By[14a] have found the half-lives for most Birch reductions to be on the order of milliseconds. Thus, if the reaction of the dianion with D_2O to form the deuteriated carbanion, followed by extraction of a proton and electron transfer, were responsible for the formation of the $C_8H_7D^{\bullet-}$, then its formation should have been very fast. Therefore, the formation of $C_8H_7D^{\bullet-}$ must proceed through a less acidic deuterium donor, and the only viable candidate in the solution is deuteriated cyclooctatriene. Indeed, the addition of a mixture of 7,8-dideuterio-1,3,5-cyclooctatriene and 5,8-dideuterio-1,3,6-cyclooctatriene, recovered from the addition of D_2O to $C_8H_8^{2-}$,[14b] to the $C_8H_8^{\bullet-}$ + K^+ solutions leads to the formation of $C_8H_7D^{\bullet-}$ in the same time frame as does the addition of D_2O.

Scheme II accounts for these results (the potassium ions and the other dideuteriated isomer[14b] are not shown). The formation of the $C_8H_8D_2$ most likely involves two steps (1a and 1b in Scheme II) as opposed to being a termolecular process. Yet, if the $C_8H_8D^-$ is in rapid equilibrium with the monodeuteriated anion radical of [8]annulene via reactions 6 and 7 of Scheme II, then the deprotonation of $C_8H_8D_3$ (step 3) can be the rate-determining step in the formation of $C_8H_7D^{\bullet-}$ only if $C_8H_8D^-$ partitions cleanly in the direction of the $C_8H_8D_2$ (step 1b proceeds very rapidly). However, more likely and still consistent with the observations is that the deprotonation of $C_8H_8D^-$ (step 6) is rate determining and the deprotonation of $C_8H_8D_2$ (step 3) is fast. This latter mechanism is also consistent with the formation of the anion radicals of the mono- and dideuteriated [8]annulene anion radicals in similar time frames.

The situation is different in the case of the sodium reduction. The resulting unassociated dianion simply generates the Birch reduction products (dideuterio-1,3,5-cyclooctatriene and -1,3,6-cyclooctatriene), and they are not, for the most part, involved in step 2 in Scheme II.

Since the [16]annulene dianion and anion radical are also free of ion association with the sodium cation in HMPA,[13] it is understandable that the addition of D_2O to HMPA solutions of $C_{16}H_{16}^{\bullet-}$ + Na^+ does not give rise to $C_{16}H_{15}D^{\bullet-}$. Ion pairing must be present for this to happen. On the other hand, $C_{16}H_{16}^{2-}$ does ion pair with K^+, and $C_{16}H_{15}D^{\bullet-}$ should, consequently, result from the addition of D_2O to the $C_{16}H_{16}^{\bullet-}$, K^+–HMPA solutions. Unfortunately, this system cannot be generated via simple $C_8H_8^{\bullet-}$ dimerization.

Scheme II



Given Scheme I, there is no obvious reason that the potassium-reduced solutions will not give rise to the [16]-annulene anion radical. Still, HMPA solutions of $C_8H_8^{\bullet-}$ generated from K reduction and those generated from sodium reduction after the addition of a molar excess of potassium iodide do not lead to the formation of $C_{16}H_{16}^{\bullet-}$. This suggests that ion association involving the [8]-annulene dianion inhibits the formation of the anions of [16]annulene. Only the free solvated [8]annulene dianion is involved in the formation of $C_{16}H_{16}^{\bullet-}$, and only the ion-associated species ($C_8H_8^{2-}$,K^+) is involved in the formation of $C_8H_7D^{\bullet-}$. A reviewer suggested that crown ether or a cryptand be added to the potassium solution after the formation of deuteriated [8]annulene. The cation complexing agent might free the dianion from ion association and then the dimerization might be realized. The addition of 2.2.2 cryptand to the potassium reduced solution, however, did not result in the hoped for dimerization. This is probably due to the fact that the potassium–crypt complex is still capable of ion association,[15] and further, it has been reported that crown ether addition to HMPA solutions of the nitrobenzene anion radical altered neither the metal ion coupling constants nor the ratio of free solvated ion to ion pair.[16] HMPA is a very strong cation binding solvent, and crowns and crypts do not compete effectively with it.[16]

Deuteration of $C_8H_8^{2-}$, K^+ by $C_8H_8D_2$ must, due to the proximity of the cation, result in the formation of the ion-paired carbanion ($C_8H_8D^-$,K^+). This ion-associated species

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[13] Wiedrich, C. R.; Catlett, D. L., Jr.; Sedgwick, J. B.; Stevenson, G. R. *J. Phys. Chem.* **1983**, *87*, 578.

[14] (a) Bothner-By, A. A.; Krapcho, A. P. *J. Am. Chem. Soc.* **1959**, *81*, 3658. (b) The dideuteriocycloocta-1,3,5-triene and cycloocta-1,3,6-triene are both formed upon the addition of deuterium oxide to the dianion as explained in: Roth, W. R. *Ann.* **1964**, *671*, 25.

[15] Watts, M. T.; Lu, M. L.; Chen, R. C.; Eastman, M. P. *J. Phys. Chem.* **1973**, *77*, 2959.

[16] Echegoyen, L.; Hidalgo, H.; Stevenson, G. R. *J. Phys. Chem.* **1973**, *77*, 2649.

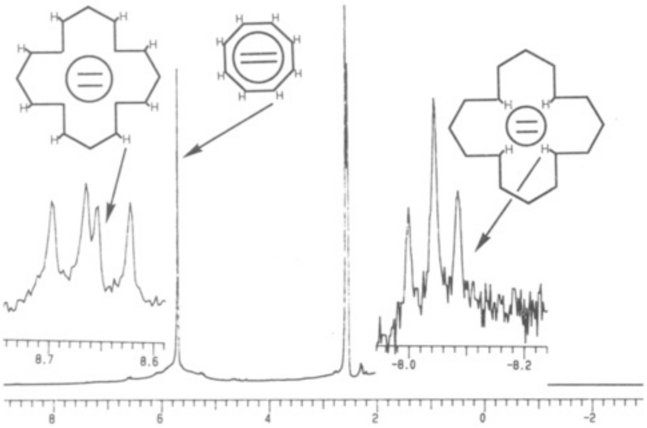
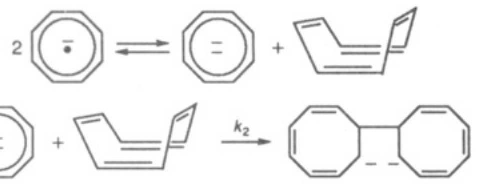


Figure 2. ^{1}H-NMR (300-MHz) spectrum of a perdeuteriated HMPA solution of the [8]annulene anion radical recorded 1 week after its formation and immediately following the addition of sufficiently more sodium metal to ensure full reduction of the annulenes to their respective dianions.

Scheme III



is much more approachable by the dianion for proton transfer and consequent formation of the monodeuteriated [8]annulene anion radical than is the unassociated carbanion. Hence, ion association enhances the formation of $C_8H_7D^{\bullet-}$.

While kinetic studies have previously shown that the dimerization is second order in $C_8H_8^{\bullet-}$,[8] the first step must be more complicated than indicated in Scheme I. This first step, written in a slightly more complicated manner as shown in Scheme III, still accounts for the reaction order ($-d[C_8H_8^{\bullet-}]/dt = k_2K_{eq}[C_8H_8^{\bullet-}]^2 = k_1[C_8H_8^{\bullet-}]^2$), while involving the unassociated dianion (originating from the disproportionation of $C_8H_8^{\bullet-}$). This mechanism also eliminates the awkward need for the intimate approach of two negative species. The remainder of the mechanism proceeds as shown in Scheme I.

The previously noted inhibitory effect of ion association upon dimerization is a consequence of decreased reactivity (attenuation of k_2) of the dianion in its ability to attack the neutral [8]annulene and form the $C_{16}H_{16}^{2-}$. With Scheme III in mind, tractable amounts of [16]annulene might be synthesized by utilizing high concentrations of neutral [8]annulene. A 0.5 M C_8H_8 solution in perdeuteriated HMPA was partially (ca. 10%) reduced with sodium metal. The resulting solution was allowed to stand at room temperature for 2 weeks. During this time the reaction progress was monitored via EPR. After 2 weeks the solution was again exposed to sodium metal until the EPR signal disappeared. At this point both annulenes were in the form of their respective dianions. A sample of this solution was then poured into an NMR tube, which was subsequently sealed from the apparatus. The ^{1}H-NMR of this solution clearly exhibits the presence of the [16]annulene dianion, Figure 2. Integration of the NMR spectrum indicates that the yield of $C_{16}H_{16}^{2-}$ is only about 10% based upon total [8]annulene used. Still, this is a very convenient source of dilute solutions of the [16]annulene dianion for "immediate" research purposes. Further, the [16]annulene dianion can be stored for long periods of time at room temperature, while neutral molecule is labile toward polymerization. Thus, it is convenient to store [16]annulene as its dianion. This can later be oxidized with I_2 to $C_{16}H_{16}$ as needed.[12]

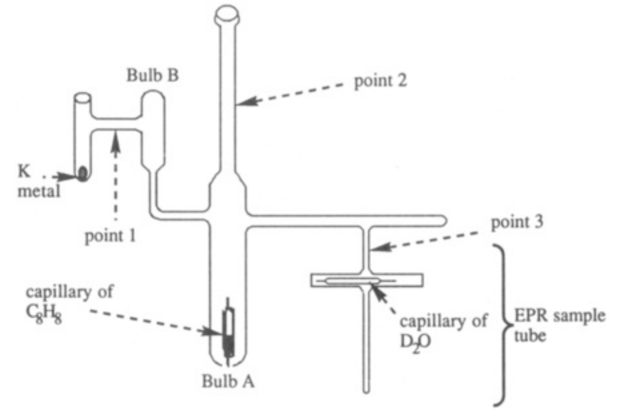


Figure 3. Apparatus used for the study of the dimerization and isotopic exchange involving the [8]annulene anion radical.

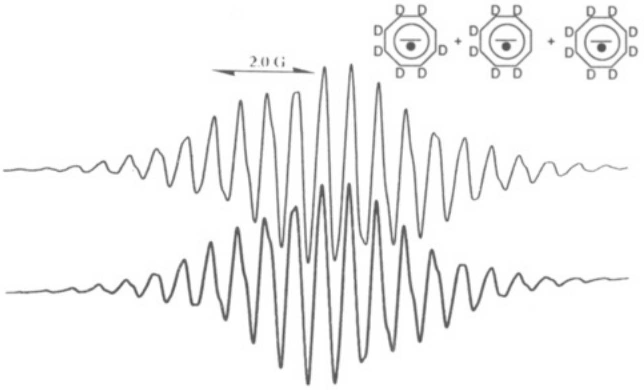


Figure 4. (Top) Room-temperature EPR spectrum of the solution resulting from the potassium reduction of perdeuteriated [8]annulene. This spectrum was recorded 24 h after the addition of 2 μL of H_2O to the solution. The moles of H_2O are less than the total number of moles of potassium salts in the sample tube. (Bottom) A computer simulation generated using a mixture of $C_8D_8^{\bullet-}$, $C_8D_7H^{\bullet-}$, and $C_8D_6H_2^{\bullet-}$ in a ratio of 1.0:0.81:0.23, respectively.

Experimental Section

Deuterium Exchange. A capillary tube containing [8]annulene was placed into bulb A of the apparatus shown in Figure 3. The entire apparatus was placed on the vacuum line and evacuated. Potassium metal was distilled from a side tube into bulb B; the side tube was then sealed at point 1. HMPA was distilled from potassium metal under high vacuum directly into bulb A of the apparatus, at which time the apparatus was sealed from the vacuum line at point 2. The capillary of [8]annulene was broken, and the resulting solution was poured into bulb B, where it was exposed to the metal mirror. A 0.5–1-mL portion of this anion-radical solution was then poured into the EPR tube, which was subsequently sealed from the apparatus at point 3. The EPR spectrum of the [8]annulene anion radical was then recorded. The EPR sample tube was then agitated horizontally so as to break the sealed tube containing the D_2O, and after thorough mixing of the heavy water with anion radical solution, the EPR spectrum was periodically recorded. This is a very convenient source of the deuteriated anion radical. The previous standard synthesis involved the bromination of [8]annulene followed by the dehydrohalogenation of the dibromocyclooctatetraene to obtain monobromoclooctatetraene, which is thermally unstable and rearranges to bromostyrene.[11,17] The Grignard of this could then be used to obtain the deuteriated [8]annulene. Reactions using dideuteriocyclooctatriene as the donor were carried out in the same manner except that this material was placed into the horizontal capillary tube in place of D_2O.

Identical procedures were carried out for the exchange of hydrogen onto the perdeuteriated [8]annulene ring,[18] with H_2O being added to the anion radical of perdeuteriated [8]annulene, Figure 4. It should be noted that while the addition of water to dilute solutions of the [8]annulene dianion proceeds safely, exposure of the solid dianion salt to either water or air produces an explosive reaction.

Dimerizations. The anion radical solutions were generated in the same manner as described above for the exchange reactions except that no D_2O was added to the solution, and sodium metal was used as the reducing agent. Spectra of the resulting mixtures of [8]annulene and [16]annulene anion radicals have been published.[8] Due to the "catch 22" situation of ion association being necessary for isotope exchange and ion association prohibiting [8]annulene anion radical dimerization, we were unable to generate deuteriated [16]annulene anion radicals in situ from $C_8H_8^{\bullet-}$. However, we have generated the deuteriated [16]annulene anion radicals via the dimerization of separately isolated deuteriated [8]annulene. The EPR spectra of these anion radical solutions are very complex as there are three nonequivalent sites for deuterium substitution in the monodeuteriated [16]annulene anion radical and this anion radical is presumably mixed with those of the nonsubstituted anion radical, the dideuteriated anion radical, and the anion radical of the deuteriated [8]annulene. We will eventually be able to sort these simultaneously observed EPR spectra out via the synthesis of specifically deuteriated materials. Hopefully, this will be the topic of a future report.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE-9011801) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(17) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclo-octatetraene and its Derivatives*; Cambridge University Press, New York, 1978; pp 83 and 100.

(18) Perdeuteriated [8]annulene was synthesized as described in: Stevenson, G. R.; Burton, R. D.; Reiter, R. C. *J. Am. Chem. Soc.* **1992**, *114*, 399.