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Reactions Involving Di-*trans*-[12]Annulenes

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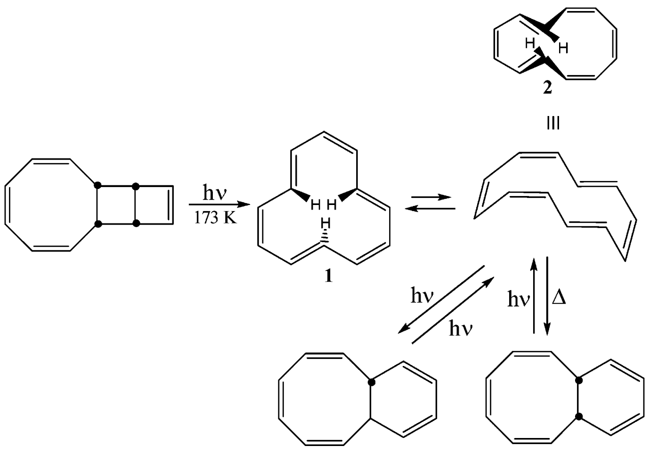
Abstract: The low temperature complete dehydrohalogenation of pentabromocyclododecene ($C_{12}H_{17}Br_5$) with potassium *tert*-butoxide in THF followed by exposure to potassium metal leads to the formation of the anion radical of 1,5-di-*trans*-[12]annulene, which loses hydrogen and undergoes ring closure to form the anion radical of 11,12-dihydro-[8]annuleno-[6]annulene. This product can, in turn, be isolated as its neutral molecule via reoxidation with iodine. A [12]annulene obtained via the dimerization of 1,5-hexadiyne in the presence of 18-crown-6 and potassium *tert*-butoxide undergoes ring closure, with concomitant loss of hydrogen, to yield the heptalene anion radical. It follows that the heptalene anion radical precursor was the 1,7-di-*trans* isomer of [12]annulene.

Introduction

Unlike [6]annulene, which is ubiquitous in our universe,[1] [12]-annulene was not reported until 1970. Oth and co-workers reported the synthesis (Scheme 1) of sym-tri-*trans*-[12]annulene (**1**)[2] and found that it could undergo photochemical or thermal ring closure to yield different isomers of [6.4.0]bicyclododecapentaene. This report did not convince all concerned that an isomer of [12]annulene had been synthesized, and a leading worker in this area wrote the following: "The 4*n* π-electron-[12]annulene has received little study and does not appear to have been prepared."[3a] The coexisting destabilizing forces from the sterically interacting internal protons (e.g., see **1** in Scheme 1), bond angle strain, and the presence of 4n π-electrons were thought to leave[12]annulene with insufficient thermodynamic stability for convenient synthesis.[3a]

A recent extensive theoretical study of the [12]annulene system now leaves almost no doubt that Oth and co-workers actually did synthesize sym-tri-*trans*-[12]annulene (**1**).[3b] Castro's, Karney's, and co-workers' calculations also predict that the 1,7-di-*trans*-[12]annulene (**3**) is less stable than the originally synthesized tri-*trans* system, but by only about 1 kcal/mol. Further, the 1,5-di-*trans*-[12]annulene (**2**) is higher in energy (relative to **3**) by about 4 kcal/mol,[3b] and the all-*cis*-[12]annulene isomer has an energy that is comparable to that of the 1,7-di-*trans* isomer at the CCSD(T)/cc-pVDZ//BHH/6-311+G** level of theory. In spite of this, NMR data for any isomer, other than that of the sym-tri-*trans*-[12]annulene system, are unknown.

Scheme 1



Since the lack of experimental information originates (in part) from the electron count rule, we were motivated to find simple synthetic (one pot) procedures, analogous to that shown in Scheme 2, for the syntheses and immediate "entrapment" via electron transfer of [12]annulenes. For all isomers with internal protons, the steric interactions and angle strain act synergistically (in a destabilizing manner) with the 4*n* π-electron count in the [12]annulenes. This steric crowding is partially alleviated in the dehydro-[12]annulyne system. Hence, dehydrogenation and electron addition are stabilizing in the [12]annulene system. On the other hand, in the [6]annulene system, which has a $4n + 2$ π-electron count and only *cis* double bonds, both are destabilizing.[4]

The 107 year history of *o*-benzyne ([6]annulyne), wherein it has proven to be a remarkably interesting and useful reactive intermediate,[5] stimulated our interest in the small annulynes and

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(1) Chan, K.; Roellig, T. L.; Onaka, T.; Mizutani, M.; Okumura, K.; Yamamura, I.; Tanabe, T.; Shibai, H.; Nakagawa, T.; Okuda, H. *Astrophys. J.* **2001**, *546*, 273.

(2) (a) Oth, J. F. M.; Röttele, H.; Schröder, G. *Tetrahedron Lett.* **1970**, *1*, 61. (b) Oth, J. M.; Schröder, G. *J. Chem. Soc. B* **1971**, 904.

(3) (a) Wiberg, K. B. *Chem. Rev.* **2001**, *101*, 1317. (b) Castro, C.; Karney, W. L.; Vu, C. M. H.; Burkhardt, S. E.; Valencia, M. A. *J. Org. Chem.* **2004**, *70*, 3602.

(4) The electron affinity of benzene is −26.5 kcal/mol; see: Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 7189.

(5) The heating of bromobenzene and sodium amide, with a Bunsen burner, lead to aniline and undoubtedly involved the benzyne intermediate: Haeussermann, C. *Ber.* **1899**, *32*, 1912.

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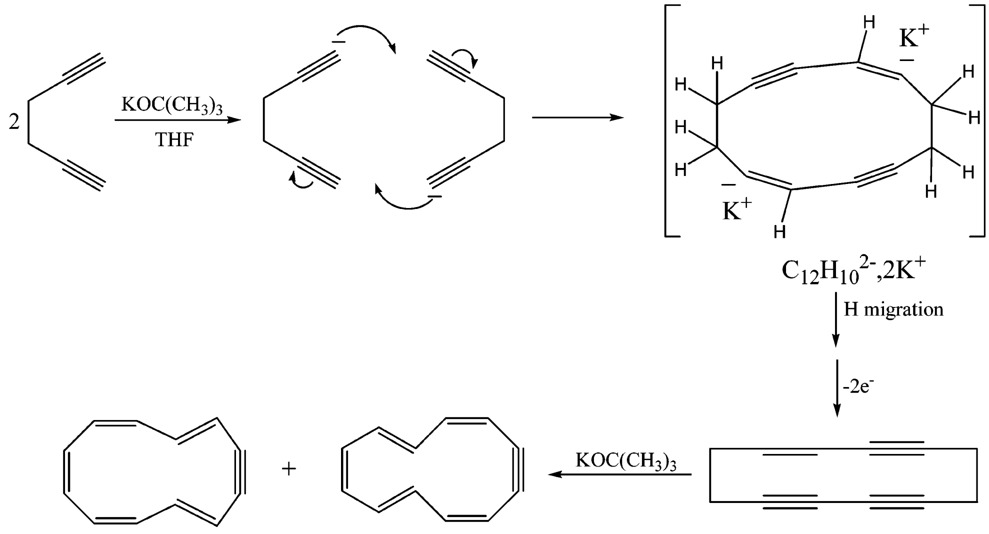
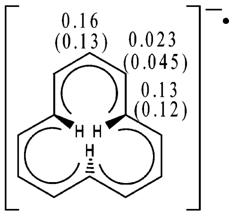
Scheme 2



led to investigations into the properties of [8]annulyne[6] and [12]annulyne.[7] Although [8]annulyne appears to be stable only as its corresponding anion radical ($C_8H_6^{\bullet-}$), a mixture of the two isomers of neutral [12]annulyne proved to be remarkably facile to synthesize. It is formed spontaneously when, commercially available, 1,5-hexadiyne is exposed to potassium *tert*-butoxide in THF, Scheme 2, and its ability to endure at ambient temperature allowed complete understanding of its ^{1}H and ^{13}C NMR spectra.[7]

As in the case of C_8H_6,[6] the addition of an extra electron to [12]annulene attenuates the destabilizing effects of the electron count rule.[8] When the final synthetic step (the photolysis shown in Scheme 1) of Oth's original synthesis of **1** is followed immediately by exposure to potassium metal, the EPR spectrum of the anion radical ($\mathbf{1}^{\bullet-}$) can be recorded.[8] The resulting EPR pattern has an extremely narrow width of only 9.84 G, which is the signature of a highly strained nonplanar system. Typically total spectral widths are in the 22−27 G range for planar annulene anion radicals. For example, it is 25.6 G for the [8]-annulene anion radical.[6,9] Anion radical nonplanarity results in poor spin transfer from the π-system to the C−H σ-bonds resulting in smaller hydrogen 1s spin densities and smaller a_H values.[6]



$\mathbf{1}^{\bullet-}$

B3LYP/6-31G* calculations indicate that two internal protons lie above the plane of the ring and one below,[10] and the p_z spin densities (ρ's), obtained from these calculations (shown in parenthesis), are in reasonable agreement with those obtained via EPR measurement.[10] Since there are no negative spin densities, the total spectral width is identical to the Q value, and the measured a_H's can be converted to ρ's using the simple McConnell relationship ($a_H = Q\rho$).[9]

The anion radical of 1,7-di-*trans*-[12]annulene ($\mathbf{3}^{\bullet-}$) yields a well resolved EPR spectrum, which has been analyzed.[10] This EPR pattern also has a very small total spectral width of only 13.5 G. The narrow spectral pattern for the tri-*trans* system strongly suggests that it deviates more from planarity than does the sym-di-*trans* anion radical system. This is in contrast to the relative planarities of the respective dianions.[2] Coupling constants for planar anion radicals can be accurately predicted via B3LYP/6-31G* calculations coupled with the McConnell relationship.[6,11,5]

The B3LYP/6-31G* structure of lowest energy for $\mathbf{3}^{\bullet-}$ predicts that one side of the molecule lies in a plane, while the other side is twisted.[10] The anion radical undergoes pseudorotation around a "Mexican hat" in a manner that is analogous to that found in the anion radicals of [6]annulene ($C_6H_6^{\bullet-}$), [8]-annulene ($C_8H_8^{\bullet-}$), and [18]annulene ($C_{18}H_{18}^{\bullet-}$), depicted with exaggerated distortions in Scheme 3 for the smaller annulene systems.[11,12] In the case of $\mathbf{3}^{\bullet-}$ the transition state remains unknown, and only in the case of $C_6H_6^{\bullet-}$ is the pseudo-rotation too fast for its effects to be observable in the EPR spectra.[12b]

Due to the proximity of carbons 1 and 7 (1.589 Å apart), ring closure, resulting in the formation of the heptalene anion radical, occurs when $\mathbf{3}^{\bullet-}$ is allowed to warm to ambient temperature. Our simple "one pot" synthesis of one of the two isomers of dehydro-[12]annulene,[7] and the tremendous interest in the elusive [12]annulene system,[2,3] prompted us to investigate the reactions leading to the [12]annulenes and [12]annulynes,

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[6] For a pertinent example, see: Peters, S. J.; Turk, M. R.; Kiesewetter, M. K.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 11264.

[7] Gard, M. N.; Kiesewetter, M. K.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2005**, *127*, 16143.

[8] Stevenson, C. D.; Concepcion, R.; Reiter, R. C. *J. Org. Chem.* **1983**, *48*, 2777.

[9] (a) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*; John Wiley and Sons: New York, 1994; p 241. (b) The successful theoretical interpretation appears in: Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500. (c) Q for the cyclooctatetraene anion radical is 25.6 G.

[10] Gard, M. N.; Reiter, R. C.; Stevenson, C. D. *Org. Lett.* **2004**, *6*, 393.

[11] Stevenson, C. D.; Kim, Y. S. *J. Am. Chem. Soc.* **2000**, *122*, 3211.

[12] (a) Hrovat, D. A.; Hammons, J. A.; Stevenson, C. D.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 9523. (b) Kurth, T. L.; Brown, E. C.; Hattan, C. M.; Reiter, R. C.; Stevenson, C. D. *J. Phys. Chem. A* **2002**, *106*, 478.

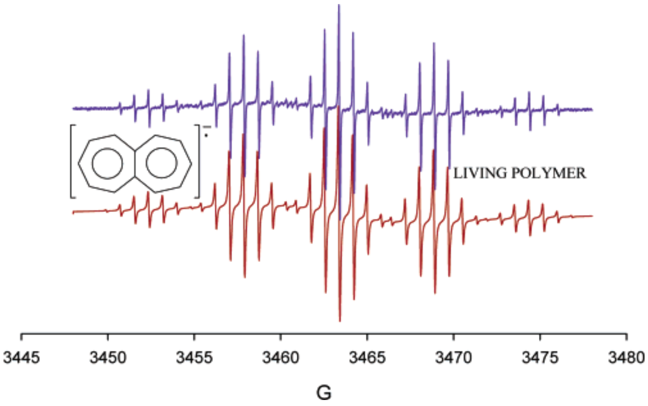
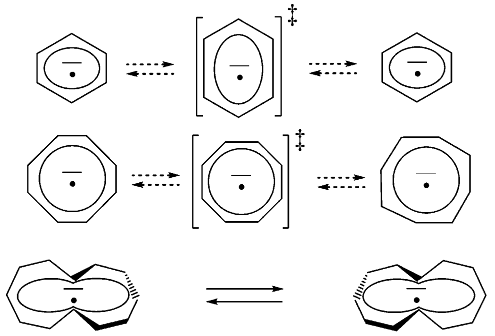


Figure 1. (Upper) X-band EPR spectrum resulting from the reaction of 1,5-hexadiyne with potassium *tert*-butoxide in THF containing 18-crown-6, recorded at 198 K. This spectrum is simulated using coupling constants of 5.510 G (4 H's) and 0.827 G (6 H's); the peak-to-peak line width is 0.06 G. Note that the spectrum for the heptalene anion radical sits on top of a very broad resonance from a "living polymer," included in the simulation.

Scheme 3



with the hope of unraveling more of the interesting [12]annulene chemistry and perhaps generating new isomers of [12]annulene.

Results and Discussion

The intermediate ($C_{12}H_{10}^{2-}$,$2K^+$) produced during the reaction of 1,5-hexadiyne with potassium *tert*-butoxide is a very tightly ion associated dianion (Scheme 2). It seemed reasonable to us that if this intermediate could be produced under conditions where ion pairing is less tight, the intermediate ($C_{12}H_{10}^{2-}$ + $2K^+$) might be able to pick up two protons from the *tert*-butanol formed in the first step of the reaction. Under identical conditions to those that led to the formation of [12]annulyne,[7] THF and THF-d_8 solutions of 1,5-hexadiyne, now containing 18-crown-6, were exposed, under a high vacuum, to potassium *tert*-butoxide. Somewhat surprisingly, however, no NMR spectrum of any product from this reaction could be observed.

The lack of an NMR signal and the deep purple color of the solution led us to suspect the presence of a paramagnetic species. EPR examination of the solution revealed a strong well resolved spectrum for the anion radical of heptalene, Figure 1, superimposed on a signal for a "living polymer".[13] If crown ether

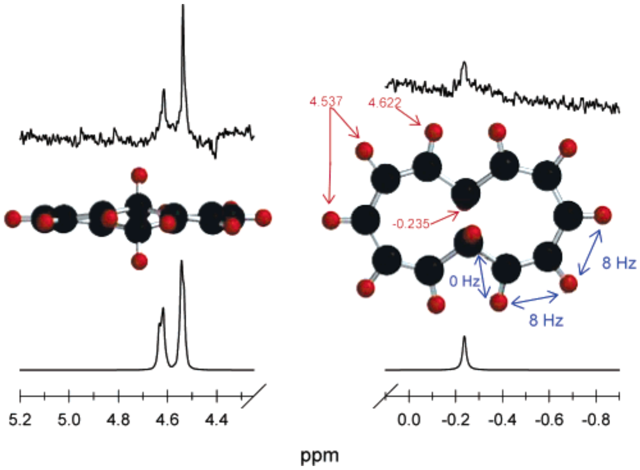


Figure 2. (Upper) 400 MHz ^1H NMR spectrum of the dianion of 1,7-di-*trans*-[12]annulene in THF-d_8 at −100 °C. The simulation (lower) was generated using the chemical shifts (red) and the *J* couplings (blue) shown. The much larger signals for the solvent, crown ether, and *tert*-butoxide exist in between these resonances and are not shown. The intensity ratio of the two peaks (referenced to TMS) is roughly 1:5.

sequestering of the cation, leaving the intermediate dianion "naked",[14] is sufficient to stimulate the heptalene formation, then the reaction should proceed in hexamethylphosphoramide (HMPA)[15] in the absence of crown ether. Exposing an HMPA solution of 1,5-hexadiyne to $KOC(CH_3)_3$ in vacuo results in a deep purple solution that exhibits a strong EPR spectrum of the heptalene anion radical. In HMPA, we found that there is no need to add the crown ether in order to produce the heptalene anion radical.

Clearly, strong coordination (solvation) of the K^+ ion (by crown or HMPA) must be present for the formation of the heptalene anion radical to take place. The $C_{12}H_{10}^{2-}$ "naked"[14] dianion (formed as shown in Scheme 4) picks up two protons from the recently formed *tert*-butanol leading to 1,7-di-*trans*-[12]annulene. The 1,7-di-*trans*-[12]annulene immediately picks up an electron from the *tert*-butoxide, to form the corresponding anion radical, or begins to polymerize. Once the 1,7-di-*trans*-[12]annulene anion radical (**3**$^{\bullet-}$) is formed, it spontaneously loses hydrogen and undergoes ring closure to form the anion radical of heptalene. As noted, commensurate with the formation of the heptalene anion radical is a considerable amount of polymerization. This is evidenced by the single broad line, due to the "living polymer"[13] under the resonances for the heptalene anion radical. Consistent with this proposed mechanism is the previously reported observation that **3**$^{\bullet-}$, synthesized by independent means, spontaneously loses H_2 and forms the anion radical of heptalene.[10]

Unavoidable disproportionation of the [12]annulene anion radical (eq 1) means that some dianion must also be present,[16]

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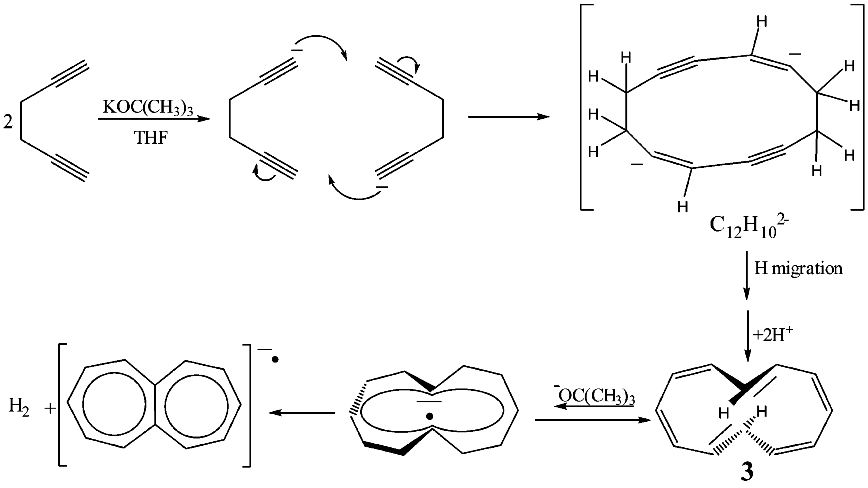
(13) (a) It is known that a single broad EPR line verifies the presence of a polymerizing radical during the anionic polymerization, the "living polymer," such as that from 9-vinylanthracene. (b) Eisenberg, A.; Rembaum, A. *Polym. Lett.* **1964**, *2*, 157. (c) Moacanin, J.; Rembaum, A. *Polym. Lett.* **1964**, *2*, 979. (d) Szwarc, M. *Carbanions, Living Polymers, and Electron-Transfer Processes*; John Wiley and Sons: New York, NY, 1968.

(14) Since the early days of crown ether chemistry, it has been known that the solubility and reactivity of a number of anions can be significantly augmented by the elimination of strong ion association via the addition of crown ethers. The resulting "naked" anions can then be much more reactive. See: Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250 and references therein.

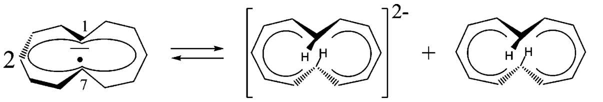
(15) Ion association is normally absent with hydrocarbon anion radicals in HMPA; see: (a) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268. (b) Stevenson, C. D.; Echegoyen, L.; Lizardi, L. R. *J. Phys. Chem.* **1972**, *76*, 1439.

(16) At 298 K in THF, the K_{eq} for the disproportionation of the [8]annulene anion radical to a dianion and neutral molecule is ca. 10^9. See: Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360.

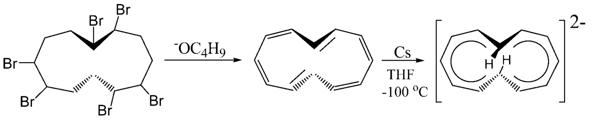
Scheme 4



leaving the possibility that it is actually the dianion that undergoes the ring closure. To exclude this possibility and obtain ^{1}H NMR data for the dianion of 1,7-di-*trans*-[12]annulene, we generated $\mathbf{3}^{2-}$ in the absence of “living polymer” via the exhaustive dehydrohalogenation of 1,2,5,6,9,10-hexabromocyclododecane ($C_{12}H_6Br_6$), followed by exhaustive reduction with cesium metal (eq 2).

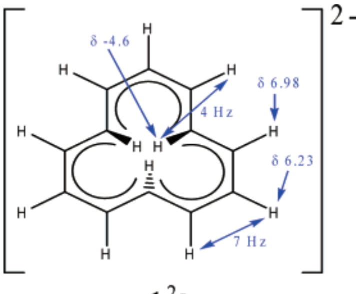


(1)



(2)

Exposure of THF-d_8 solutions, containing 18-crown-6 and NaH (to “soak up” the *tert*-butanol as it formed), of 1,2,5,6,9,-10-hexabromocyclododecane ($C_{12}H_6Br_6$) to excess potassium *tert*-butoxide at −100 °C for several minutes followed by exposure of the solution to a freshly distilled Cs mirror results in a dark purple solution yielding the EPR spectrum of $\mathbf{3}^{\bullet-}$. The unstable neutral [12]annulene was again trapped as its $4n + 1$ π-electron anion radical, which can be observed, via EPR, for hours at low temperatures. When the 1,7-di-*trans*-[12]annulene anion radical is further exposed to a cesium metal mirror at 173 K, the solution becomes EPR silent, and the resulting ^{1}H NMR spectrum sharpens and reveals a diamagnetic ring current in the 1,7-di-*trans*-[12]annulene dianion (Figure 2).

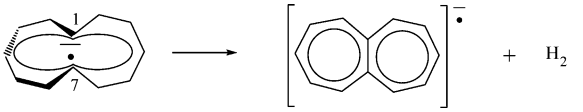


$\mathbf{1}^{2-}$

The addition of a single electron “tames” the “fugitive” neutral 1,7-di-*trans*-[12]annulene allowing low temperature observation of the anion radical. The second electron renders the system enduring at ambient temperature and in the absence of heptalene. Comparison of the chemical shift data of $\mathbf{1}^{2-}$ (from the Oth et al. report)[4] with that of $\mathbf{3}^{2-}$ suggests that the diatropicity in the dianion of 1,7-di-*trans*-[12]annulene dianion is not as pronounced as it is in the sym-tri-*trans*-[12]annulene dianion ($\mathbf{1}^{2-}$, with δ’s and J_{H-H}’s indicated).[4] This is reasonable, as the two internal protons in $\mathbf{3}^{2-}$ are closer than are the three in $\mathbf{1}^{2-}$ causing more distortion and deviation from planarity. In fact, the chemical shifts of the external protons (<4.7 ppm) coupled with the 0 Hz coupling constant are consistent with a cyclic olefin without diatropicity. In this case, the shift at ca. −0.2 ppm could be rationalized by a local anisotropic effect for a doubly charged anion. In any case, the diatropicity appears to be smaller in $\mathbf{3}^{2-}$ than in $\mathbf{1}^{2-}$.

Oth and co-workers[2] were able to obtain NMR evidence of neutral **1**. However, we have been unable to garner clear NMR signals for neutral **3**. This appears to be, at least in part, a result of broad resonances[2] and interference from all of the other materials present in the solutions. Further, **3** undergoes intramolecular rearrangement more quickly than does **1**.

The angle strain resulting from the steric conflict between the internal protons and consequent nonplanarity renders $\mathbf{3}^{\bullet-}$ thermodynamically and kinetically unstable. Warming of the solution to 298 K results in ring closure, with concomitant loss of hydrogen, to the anion radical of heptalene (eq 3).



(3)

Note that this is consistent with the mechanism proposed in Scheme 4. The proximity and orientation of the p_z orbitals on carbons 1 and 7 suggest this behavior of $\mathbf{3}^{\bullet-}$. The relative concentrations of the anion radical of heptalene and that of **3** were monitored, over time (Figure 3), revealing a rate constant of $k \approx 0.3$ min^{-1} at 298 K for reaction 3. Actually, reaction 3 is one example of many where a one-electron reduction of a neutral system with face-to-face p_z orbitals leads to the elimina-

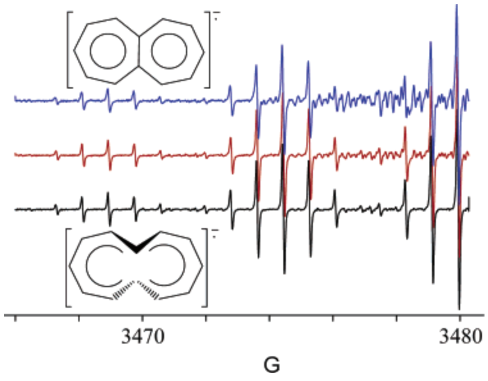
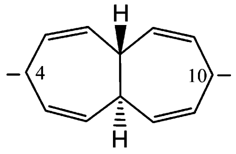


Figure 3. EPR spectra of a sample originally containing the anion radical of [12]annulene (see ref 10) that has been brought to 298 K. These spectra were recorded 2 min apart at 298 K. Computer simulations (not shown) show that the relative intensities ([heptalene$^{\bullet-}$]/[[12]annulene$^{\bullet-}$]) are 1/1.3, 1/0.5, and >1/0.1 suggesting a first-order half-life of a little under 2 min.

tion of tangential substituents, followed by the transformation of the nonclassically interacting p orbitals into a new σ-bond.[17]

We should also point out that the EPR data for $\mathbf{3}^{\bullet-}$ are not at all consistent with a closed structure, having a σ-bond joining carbons 1 and 7. Such a material would yield an electron nuclear coupling from β protons (on the sp^3 hybridized carbons) and an EPR pattern with a total spectral width that is larger than the usual 23 G, not less than 14 G as observed. Further, a B3LYP/6-31G* calculation and common symmetry considerations reveal that the EPR pattern would be much simpler than that observed, as it would be due to two pentets (each from four equivalent H's) and two triplet splittings from two pairs of protons. This is not at all consistent with observation.

Likewise, the possibility that the NMR spectrum (Figure 2) is actually that of the dianion of bicyclo[5.5.0]dodecatetraene ($\mathbf{4}^{2-}$) was considered. This could have resulted from the ring closure without the loss of hydrogen. However, we know that $\mathbf{3}^{2-}$ resulted from the further reduction of $\mathbf{3}^{\bullet-}$. Further, there is no conceivable reason that the allylic or vinyl protons of $\mathbf{4}^{2-}$ would be upfield of TMS. In fact, an HF/6-31G* calculation predicts that the protons on positions 4 and 10 of $\mathbf{4}^{2-}$ are indeed the furthest upfield, but that they should appear at 2.2 ppm.



$\mathbf{4}^{2-}$

Our success in the generation of the 1,7-di-*trans*-[12]annulene anion radical via a "one pot" synthesis prompted us to attempt an analogous synthesis of a third isomer of the [12]annulene anion radical (that of 1,5-di-*trans*-[12]annulene). The PM3 predicted geometry of 4,5,8,9,13-pentabromocyclododec-1-ene (eq 4) suggests the possibility of obtaining 1,5-di-*trans*-[12]annulene from its exhaustive dehydrohalogenation. This starting material was prepared via the single dehydrohalogenation of the hexabromocyclododecane (see Experimental Section and eq 4).

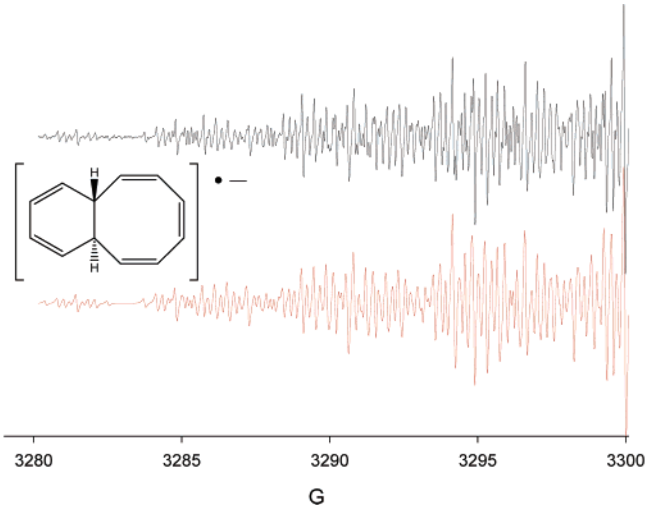
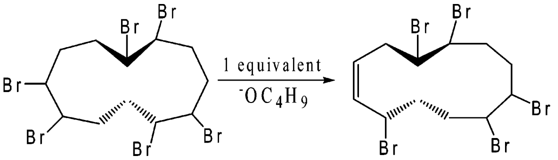


Figure 4. (Upper) Low-field half of the X-band EPR spectrum (recorded at 193 K) of the anion radical produced via the complete dehydrohalogenation of pentabromocyclododecene with an excess of potassium *tert*-butoxide followed by exposure to K metal in THF ($\mathbf{5}^{\bullet-}$). (Lower) A computer generated simulation using a_{H}'s of 5.795, 5.103, 4.277, 3.345, 0.640, and 0.415 G for 2 H's each. Δw_{pp} = 0.08 G.



(4)

The pentabromocyclododecene was dehydrohalogenated with an excess of potassium *tert*-butoxide and subsequently exposed to a freshly distilled potassium metal mirror, using the same procedure that was used for hexabromocyclododecane leading to the 1,7-tri-*trans*-[12]annulene anion radical. The resulting dark solution exhibits a strong well-resolved EPR spectrum, which degrades at elevated temperatures. This spectrum proved possible to simulate unambiguously, Figure 4, and it reveals that six pairs of protons are interacting with the odd electron. This anion radical ($\mathbf{5}^{\bullet-}$), however, does not exhibit the anticipated (and hoped for) narrow total spectral width. Indeed the total spectral width is extraordinarily large (39.14 G).

Given the large spectral width only a closed structure with at least an effective C_2 symmetry (accounting for the pairs of identical protons), such as $\mathbf{5}^{\bullet-}$, could lead to calculated spin densities in agreement with the empirical values. Also, as noted below, reoxidation of the anion radical solution leads to the isolation of **5**. The absolute values of the empirical p$_z$ spin densities (shown below) obtained using the measured coupling constants (Figure 5) and a Q of 21.5 G, suggesting a slightly nonplanar structure, are in excellent agreement with the theoretical (B3LYP/6-31G*) spin densities (shown in parentheses in Figure 5). The spin density on the four sp^2 carbons adjacent to the sp^3 ring juncture carbons leads to coupling with the β hydrogens and accounts for the "extra" spectral width. Only in positions 2 and 5 do the predicted and empirical spin densities differ significantly. This very large spectral width (39.14 G) of

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(17) Biaryl radical anions have been produced via the reduction of tetraphenylmethane, triphenylamine, triphenylboron, triphenylphosphine oxide, phenyl ethers, diphenylsilanes, trinapthyl borane, biarylureas, etc. For references, see: (a) Britt, A. D.; Urberg, M. M.; Kaiser, E. T. *J. Org. Chem.* **1966**, *31*, 1661. (b) Wan, Y.-P.; O'Brien, D. H.; Smentowski, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7680. (c) Shine, H. J.; Hughes, L. D.; Gesting, P. *J. Organomet. Chem.* **1970**, *24*, 53. (d) Lewis. F. D.; Kurth, T. L.; Hattan, C. M.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 1460. (e) Gerson, F. *Top. Curr. Chem.* **1983**, *115*, 57.

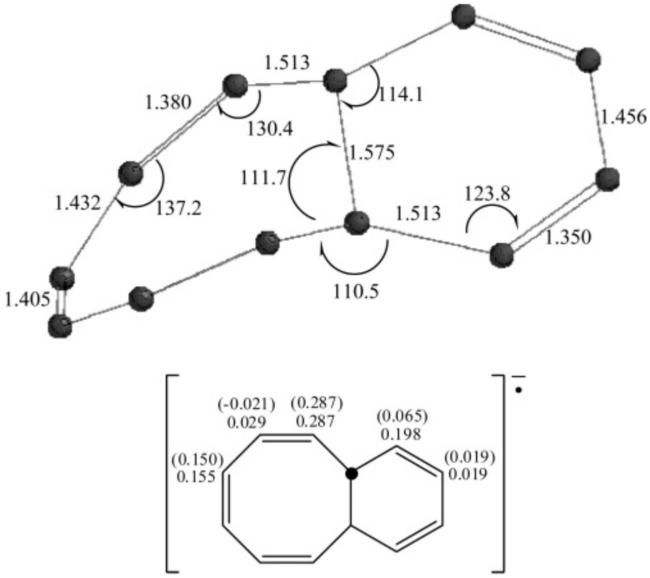

Figure 5. (Upper) B3LYP/6-31G* calculated structure, with representative bond angles and lengths, of $\mathbf{5}^{\bullet-}$. The bond angles are in degrees, and the bond lengths are in Å. (Lower) The calculated spin densities (in parentheses) and the empirical (EPR) spin densities.

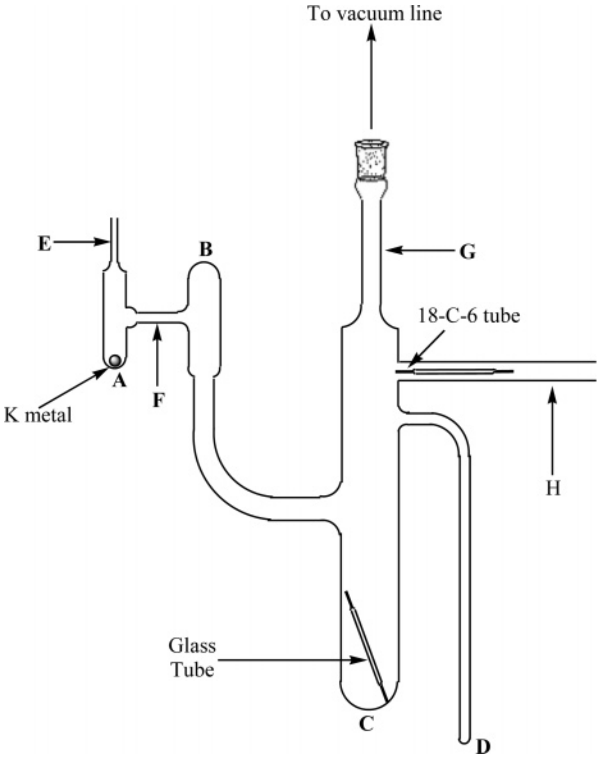

Figure 6. Apparatus used for the generation of the [12]annulyne anion radicals. Tube D can be either an EPR or NMR sample tube.

$\mathbf{5}^{\bullet-}$ is a result of having a bicyclic system with bridgehead protons. This is just one reason that an analogous bicyclic structure for $\mathbf{3}^{\bullet-}$ (spectral width = 13.5 G) is excluded.

One possible explanation is that the 1,5-di-*trans*-[12]annulene undergoes ring closure prior to electron addition, without the loss of hydrogen, as suggested by Oth and co-workers (Scheme 1).[2] To convince ourselves of the validity of our assigned structure, this anion radical solution was quenched with iodine ($2\mathbf{5}^{\bullet-} + I_2 \rightarrow 2I^- + 2\mathbf{5}$) yielding a colorless oil. The oil exhibits the previously published ^{1}H NMR of *trans*-bicyclo[6.4.0]dodeca-2.4.7.9.11-pentaene.[18] Hence, it appears that the reaction sequence, in THF, follows the path described in Scheme 5.

There are, of course, many possible configurations that can result from the dehydrohalogenation of pentabromocyclododecene, especially since the molecular morphology of the $C_{12}H_{17}Br_5$ is not known. Nevertheless, $\mathbf{5}^{\bullet-}$ was undoubtedly formed, and it was reoxidized to the known **5**. It is possible that $\mathbf{5}^{\bullet-}$ was a direct result of the complete dehydrogenation without the involvement of [12]annulene **2**. Our conjecture that the double bond in the pentabromocyclododecene is cis and that **2** is an intermediate is based upon the structure of the product ($\mathbf{5}^{\bullet-}$) and an analogy to the formation of $\mathbf{3}^{\bullet-}$ from hexabromocyclododecane. The direct conversion of **2** to **5**, shown in Scheme 5, is not thermally allowed. However, this process can take place under very basic conditions, and electron transfer may be involved.

Summary

At −100 °C, the complete dehydrohalogenation of 1,2,5,6,9,-10-hexabromocyclododecane, with *tert*-butoxide in THF, followed by alkali metal reduction leads to the anion radical of 1,7-di-*trans*-[12]annulene, which upon warming to 298 K undergoes ring closure ($t_{1/2} \approx 2$ min) with concomitant loss of H_2, to yield the anion radical of heptalene. However, if only one of the dehydrohalogenations is completed and the pentabromoalkene product is allowed to equilibrate at ambient temperature, prior to the complete dehydrohalogenation and electron transfer, the resulting 1,5-di-*trans*-[12]annulene undergoes ring closure to *trans*-bicyclo[6.4.0]dodeca-2.4.7.9.11-pentaene.

As evidenced by the formation of the heptalene anion radical, 1,7-di-*trans*-[12]annulene can also apparently be formed at room temperature via the simple addition of *tert*-butoxide to 1-5-hexadiyne in THF, containing 18-crown-6. On the other hand, this same reaction, carried out in the absence of 18-crown-6, leads to the production of two isomers of [12]annulyne.[7] The propensity of the anion radical of 1,7-di-*trans*-[12]annulene to undergo ring closure with loss of H_2 is alleviated via the addition of another electron. ^{1}H NMR observation reveals a diatropic ring current in this $4n + 2$ π-electron dianion.

Experimental Section

The synthesis of pentabromocyclododecene has been previously described, and the mass spectral isotopic distribution pattern is essentially identical to the theoretical pattern for $C_{12}H_{17}Br_5$.[7]

Formation of the Heptalene Anion Radical from 1,5-Hexadiyne: A glass tube was charged with 0.15 mmol of neat 1,5-hexadiyne and sealed (with fragile ends). This tube, in addition to 0.23 mmol of potassium *tert*-butoxide, was placed into bulb C of the Pyrex glass apparatus shown in Figure 6. A second glass tube was charged with 0.60 mmol of 18-crown-6, sealed with fragile ends, and placed in the side arm as indicated; the side arm was sealed at point H. A small amount of potassium metal was placed into bulb A, which was then sealed at point E. The entire apparatus was evacuated, and the potassium metal was sublimed into bulb B to form a potassium mirror. Bulb A was then sealed from the apparatus at point F. THF (~4 mL) was distilled from a separate flask, containing sodium potassium eutectic, directly into bulb C, and the evacuated apparatus was subsequently sealed from the vacuum line at point G. After the apparatus was cooled to 0 °C and shaken gently to suspend the *tert*-butoxide in the solvent,

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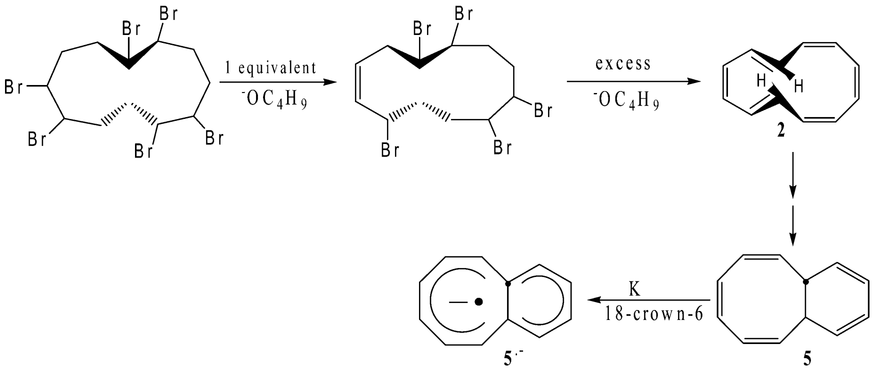
[18] Röttele, H.; Martin, W.; Oth, J. M.; Schröder. G. *Chem. Ber.* **1969**, *102*, 3985.

Scheme 5



it was vigorously agitated to break the glass tube containing the hexadiyne followed by (after a couple minutes) the tube containing the 18-crown-6. The apparatus was then quickly rotated so the solution could come into contact with the K metal mirror.

The EPR spectrum was immediately recorded by placing the 3 mm tube D into the X-band EPR cavity. The apparatus could be removed from the EPR, the solution exposed to more metal, and the spectrum recorded again.

Formation of the 1,7-Di-*trans*-[12]annulene Dianion: In a typical experiment, tube C of the apparatus, shown in Figure 6, was charged with 0.08 mmol of hexabromocyclododecane, and 0.64 mmol each of potassium *tert*-butoxide and 18-crown-6 were placed on top of this mixture. A large excess of cesium metal was then placed into bulb A, which was subsequently sealed at point E. The entire apparatus was then attached to the vacuum system and evacuated to ca. 10^{-4} torr. With bulb C maintained at 173 K, the potassium metal was distilled into bulb B to form a shiny metal mirror. Bulb A was subsequently sealed from the apparatus at point F. About 5 mL of THF were then distilled directly into bulb C (still at 173 K). The apparatus was then sealed from the vacuum system at point G and lightly shaken at 173 K for several hours. The apparatus was then tilted to bring the colorless solution into contact with the Cs metal mirror. A purple color was immediately noticed, and a sample of this solution was poured into the NMR side arm (D), which was sealed from the apparatus and placed directly into the probe of a 400 MHz NMR spectrometer.

Formation of *trans*-Bicyclo[6.4.0]dodeca-2.4.7.9.11-pentaene (5): The dark THF solution exhibiting the strong well-resolved EPR spectrum shown in Figure 4 was quenched at 195 K, by rupturing a thin walled glass tube containing I_2, while the apparatus was cooled to dry ice temperature. The apparatus was then broken open, and the THF was allowed to evaporate. Diethyl ether was added, the ether solution was washed with water and dried, and the ether was removed under reduced pressure. Silica gel chromatography produced a small amount of a colorless oil exhibiting the published NMR spectrum for *trans*-[6.4.0]-bicyclododeca-2,4,6,9,11-pentaene. Neutral [6.4.0]-bicyclododecapentaene tends to undergo polymerization, and an actual yield was not obtained. The ^{1}H NMR spectrum of *trans*-[6.4.0]-bicyclododeca-2,4,6,9,11-pentaene was previously recorded in CS_2 by Oth et al.[18] Their sample was obtained as a result of the low temperature (−70 °C) photolysis of 1,5,9-tri-*trans*-[12]annulene.[2a]

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