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Anion Radicals of Di-*trans*-[12]annulene and Heptalene in a One-Pot Synthesis from a Common Fire Retardant

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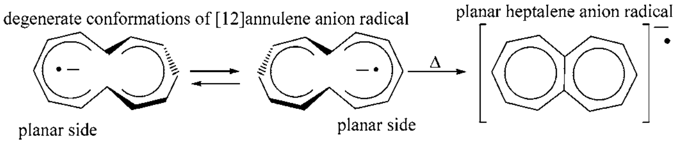
ABSTRACT



Low temperature (–100 °C) dehydrohalogenation of 1,2,5,6,9,10-hexabromocyclododecane (a common fire retardant) with potassium *tert*-butoxide in THF followed by one-electron reduction yields the anion radical of the di-*trans* form of [12]annulene. This system yields a well-resolved EPR signal that reveals that most of the spin density resides on one side (the planar side) of the anion radical. Five of the carbons in this [12]annulene system are twisted from the plane of the remaining seven carbons, and the rate of rearrangement between the degenerate conformations is on the EPR time scale ($k = 10^6$–10^7 s^{-1}). Warming of the solution results in the formation of a σ-bond between the two internal carbons, loss of molecular hydrogen, and consequent generation of the anion radical of heptalene. Tractable quantities of neutral heptalene can be obtained via the reoxidation of this anion radical with iodine.

Investigations into the nature of the annulenes have resulted in a greater contribution to our understanding of conjugation and the Hückel $4n + 2$ rule than has the study of any other series of compounds. We now have a working knowledge of all but one of the small ($n < 20$) annulene systems.[1] Only the [12]annulene system remains controversial. In fact, there is some doubt as to whether it has ever been formed. To quote a leading worker in this area, “The $4n$ π-electron [12]-annulene has received little study and does not appear to have been prepared.”[1] The origin of the controversy and lack of study lies in the electron count ($4n$ π-electrons), which acts synergistically with the bond angle strain and internal protons to render [12]annulene thermodynamically unstable.[1] Here we report that the addition of an extra electron, creating a $4n + 1$ π-electron system, can sufficiently stabilize two of the isomers of [12]annulene to render them spectroscopically observable.[2] The isomer with two *trans* double bonds spontaneously loses hydrogen and rearranges to the anion radical of heptalene.

Nearly 20 years ago, we reproduced Oth’s original[3] (and controversial)[1] synthesis of [12]annulene.[4] Immediately following the final synthetic step (the photolysis shown in Scheme 1), the newly formed compound was exposed to potassium metal, and the EPR spectrum was recorded. The resulting EPR pattern is characteristic of a highly strained nonplanar system,[5] probably the tri-*trans* form of $C_{12}H_{12}^{\bullet -}$ (tri-*trans*-$C_{12}H_{12}^{\bullet -}$) with three internal protons, Scheme 1.[4] Using a Q value of 9.84 G (the total spectral width),[5] along the with the McConnell relationship ($a_H = Q\rho$)[6] the p_z spin densities (ρs) were obtained from the observed proton coupling constants (a_H’s). They proved to be in reasonable agreement with those predicted from a B3LYP/6-31G* calculation shown in parentheses, Scheme 1.

The astounding aspect of the EPR spectrum of tri-*trans*-$C_{12}H_{12}^{\bullet -}$ is the narrow total spectral width of 9.84 G. This

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[1] Wiberg, K. B. *Chem. Rev.* **2001**, *101*, 1317.

[2] (a) Peters, S. J.; Turk, M. R.; Kiesewetter, M. K.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 11212. (b) Broadus, K. M.; Kass, S. R. *J. Am. Chem. Soc.* **2000**, *122*, 10697. (c) Broadus, K. M.; Kass, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 4189.

[3] Oth, J. F. M.; Rottele, H.; Schroder, G. *Tetrahedron Lett.* **1970**, *1*, 61.

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

[5] Nonplanarity in an anion radical leads to poor spin transfer from the π-system to the σ-bond to which the hydrogen is attached. Hence, Q and the total spectral width are smaller in nonplanar systems than those found in planar anion radicals.[2a]

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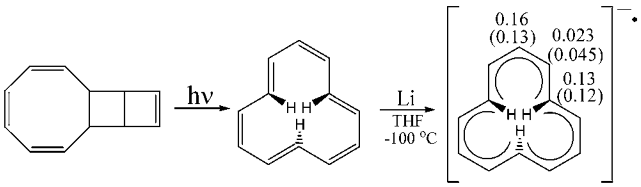
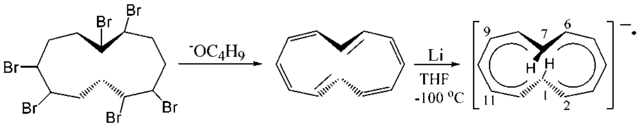
Scheme 1



means that the system is very strained and nonplanar, and our calculations indicate that two internal protons lie above the plane of the ring and one below. Since there are no negative spin densities, the total spectral width is identical to the Q value.

Boosted by our recent success with a one-pot potassium *tert*-butoxide dehydrohalogenation of bromo-[8]annulene followed by electron transfer from potassium metal to give the anion radical of [8]annulyne,[7] we envisioned an analogous dehydrohalogenation of hexabromocyclododecane ($C_{12}H_6Br_6$) followed by electron capture of the resulting transient [12]annulene, Scheme 2. The DFT calculated structure of $C_{12}H_6Br_6$ reveals that the complete dehydrohalogenation may not yield the [12]annulene system with three *trans* double bonds and three internal protons (as described above) but could produce the isomer with two *trans* double bonds and two internal protons, di-*trans*-$C_{12}H_{12}^{\bullet-}$ (Scheme 2).

Scheme 2



Exposure of THF solutions (containing 18-crown-6) of $C_{12}H_6Br_6$ to potassium *tert*-butoxide at −100 °C for several minutes followed by exposure of the solution to a freshly distilled potassium mirror results in a dark purple solution that yields a well-resolved EPR spectrum with an exceptionally small total spectral width (13.5 G as compared to the 25.6 G observed for the [8]annulene anion radical). This spectral width is consistent with that expected for a [12]-annulene anion radical, but it does not represent tri-*trans*-$C_{12}H_{12}^{\bullet-}$, Figure 1.

If di-*trans*-$C_{12}H_{12}^{\bullet-}$ indeed represents the system observed, the proximity and orientation of the p_z orbitals on carbons 1 and 7 suggest some very predictable behavior of this anion radical. The literature is replete with examples of one-electron reductions of neutral systems with face-to-face p_z orbitals, which lead to elimination of tangential substituents, followed by the transformation of the nonclassically interacting p orbitals into a new σ-bond.[8] The most analogous comparison is the case of the alkenyl *m*-cyclophane anion radical. The rigidly enforced interaction of the p_z orbitals in the opposite aryl moieties allows this anion radical to lose molecular hydrogen leading to the formation of a σ-bond between the opposing aryl groups (Scheme 3).[8e]

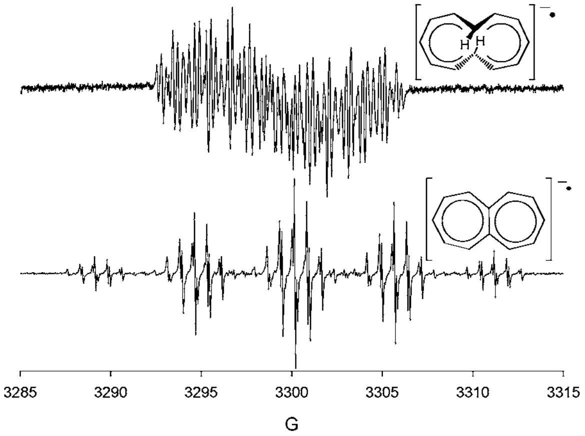
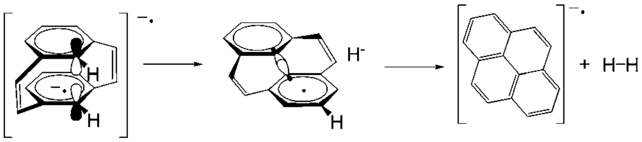


Figure 1. (Upper) X-band EPR spectrum of di-*trans*-$C_{12}H_{12}^{\bullet-}$, recorded at 170 K, immediately after the potassium metal reduction of the potassium *tert*-butoxide dehydrohalogenation product of 1,2,5,6,9,10-hexabromocylododecane in THF containing 18-crown-6. (Lower) EPR of the same solution after warming to ambient temperature and recooling to 170 K. This spectrum is due to the anion radical of heptalene and is nicely simulated with a_H's of 5.52 G (4 Hs), 0.69 G (4 Hs), and 0.810 G (2 Hs). The peak-to-peak line width (Δw_{pp}) is 0.080 G.

Scheme 3



The unique orientation of the p_z orbitals on carbons 1 and 7 of di-*trans*-$C_{12}H_{12}$, likewise, may result in the loss of molecular hydrogen upon the one-electron reduction. This in turn should lead to the formation of the anion radical of heptalene ($C_{12}H_{10}^{\bullet-}$). Such behavior was, in fact, observed. Warming of the tentatively assigned di-*trans*-$C_{12}H_{12}^{\bullet-}$ solutions to ambient temperatures results in an immediate replacement of the narrow spectrum for the [12]annulene anion radical by a strong well-resolved spectrum with a

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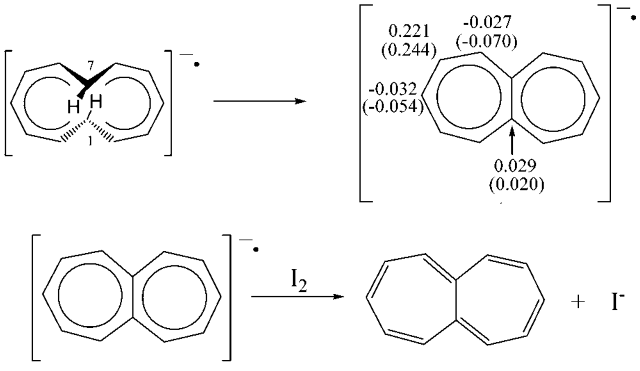
(6) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*; Wiley: New York, 1994.

(7) Peters, S. J.; Turk, M. R.; Kiesewetter, M. K.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 11264.

(8) Biaryl radical anions have been produced via the reduction of tetraphenylmethane, triphenylamine, triphenylboron, triphenylphosphine oxide, phenyl ethers, diphenylsilanes, trinaphthyl 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.

Scheme 4

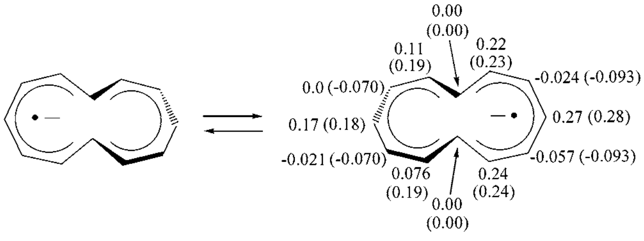


normal total spectral width (26.5 G) representing a planar hydrocarbon anion radical, Figure 1. This EPR pattern is identical to that previously observed for the anion radical of heptalene,[9] Scheme 4. The anion radical of heptalene can be reoxidized with molecular iodine to the corresponding neutral molecule (base peak $m/e = 153$ AU and parent peak $m/e = 154$ AU).

The B3LYP/6-31G* protocol coupled with the McConnell relationship has proven to be exceptionally viable in predicting the coupling constants for planar anion radicals.[2a,7,10] The anion radical of heptalene is clearly planar, whereas di-*trans*-$C_{12}H_{12}^{\bullet-}$ is not. The di-*trans*-$C_{12}H_{12}^{\bullet-}$ of lowest energy has a structure wherein the seven carbons on one side lie close to being in the same plane. The remaining five carbons, on the other side of the nodal carbons, are twisted from planarity. Hence, the di-*trans*-$C_{12}H_{12}$ anion radical undergoes pseudorotation around a "Mexican hat" in a manner that is analogous to that found in the benzene and [18]annulene systems.[11]

As in the case of the [18]annulene anion radical,[11b] the pseudorotation is not fast on the EPR time scale, and the structure and spin densities oscillate as shown in Scheme 5.

Scheme 5



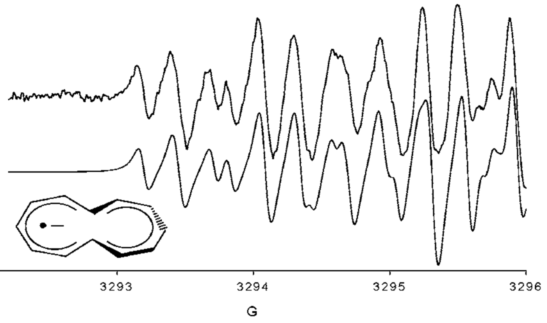


Figure 2. (Upper) The first few G of the EPR spectrum of di-*trans*-$C_{12}H_{12}^{\bullet-}$ shown in Figure 1. (Lower) A Comlputer simulation generated using nine single proton spins with a_H's of 0.240, 0.275, 0.884, 0.639, 1.229, 1.854, 2.578, 2.716, and 3.105 G. This expanded portion includes the effects of all nine observable coupling constants, and $\Delta w_{pp} = 0.080$ G.

The relatively slow kinetics, coupled with the unequal bond lengths and the out-of-plane protons, render all of the non-nodal carbon spin densities (shown with calculated ρs in parentheses) unequal.[12] This is in agreement with experiment, Figure 2. The carbon in position 10 remains coplanar with the planar seven-member moiety on the opposite end of the molecule and retains a relatively high spin density. The spin densities on the planar side of the ring are higher (as expected) than those on the twisted side. The agreement is reasonably good between the DFT predicted and empirical spin densities; see the structure in Scheme 5. The largest disagreements are in the positions with negative spin densities, which are small in magnitude.

The predicted spin densities come from small differences between relatively large numbers in the α and β spin density matrices. When this difference is very small, the percent disagreement is augmented. The total spectral width of 13.6 G along with the negative spin densities mean that Q is only 11.5 G for this very unusual anion radical, which can be synthesized from a common fire retardant and which rearranges to the anion radical of heptalene upon warming.

Careful inspection of Figure 1 reveals clear line width modulation effects at the spectral center. The line width modulation is due to the transitions between the degenerate structures shown in Scheme 5. These transitions occur at an appropriate rate with respect to the EPR time scale to yield line width modulation effects.

The B3LYP/6-31G* predicted structure for di-*trans*-$C_{12}H_{12}^{\bullet-}$ is shown in Figure 3, and the predicted bond lengths are shown in Table 1. The C−C bond lengths and bond angles undergo rapid exchange as described in Scheme 5. The observation of the line width modulation in the EPR

Table 1. DFT Predicted C_n−C_m Bond Lengths in Å for Di-*trans*-$C_{12}H_{12}^{\bullet-}$

	$n-m$					
	1−2 6−7	2−3 5−6	3−4 4−5	7−8 12−1	8−9 11−12	9−10 10−11
bond length	1.505	1.371	1.414	1.514	1.375	1.418

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(9) Mullen, K. *Helv. Chim. Acta* **1974**, *57*, 2399.

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

(11) (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.

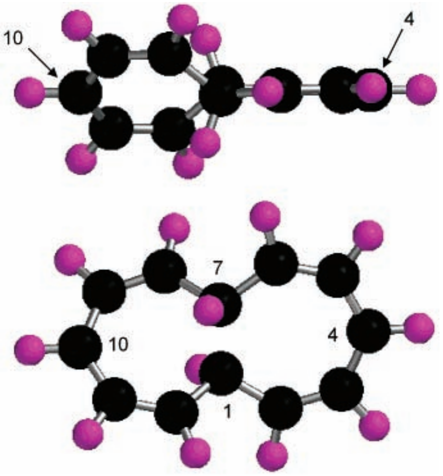

Figure 3. B3LYP/6-31G* predicted geometry of di-*trans*-$C_{12}H_{12}^{\bullet-}$ with the planar portion shown perpendicular to page (upper) and in the plane of the page (lower).

spectrum reveals that the rate constant for this exchange is ca. 10^6-10^7 s^{-1}.[13]

The DFT model shown in Figure 3 suggests that the distance between carbons 1 and 7 is only 1.589 Å. Hence, these two carbons are sufficiently close to allow p_z orbital overlap (shown in Figure 4) and consequent ring closure resulting in the formation of the heptalene anion radical.

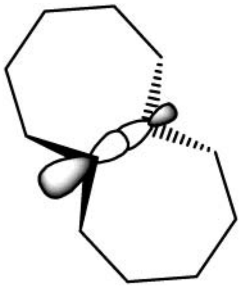

Figure 4. A view of the anion radical of di-*trans*-[12]annulene revealing the overlap of the p_z orbitals on carbons 1 and 7. This orbital overlap irreversibly evolves into a σ-bond at elevated temperatures.

The quote (above) from Wiberg's article (an interesting review of the annulenes)[1] refers to neutral [12]annulene, and our observations of the anion radicals of the tri-*trans*- and di-*trans*-[12]annulenes do not contradict his statement. We are currently exploring the possibility of isolating the neutral di-*trans*-[12]annulene via the cryogenic oxidation of di-*trans*-$C_{12}H_{12}^{\bullet-}$. We also anticipate the generation of the dianion via the transfer of one more electron to di-*trans*-$C_{12}H_{12}^{\bullet-}$. This would be analogous to our generation and NMR observation of the dianion of a disubstituted [16]annulene from the corresponding neutral molecule.[14]

Acknowledgment. We thank the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society for support of this work.

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(12) Rounding off to two significant figures (corresponding to the experimental error) makes some of the calculated spin densities appear degenerate.

(13) The interchange of spins in this time frame causes line width modulation in EPR spectra; see ref 10 and Franekel, G. K. *J. Phys. Chem.* **1967**, *71*, 139.

(14) Stevenson, C. D.; Gard, M. N.; Reiter, R. C. *J. Org. Chem.* **2003**, *68*, 1464.