ORGANIC
LETTERS

2005
Vol. 7, No. 13
2623−2626

The Capture of *sym*-[8]Annuldiyne: The Cyclooctadienyne-η^2-ynyl Potassium Zwitterionic Radical

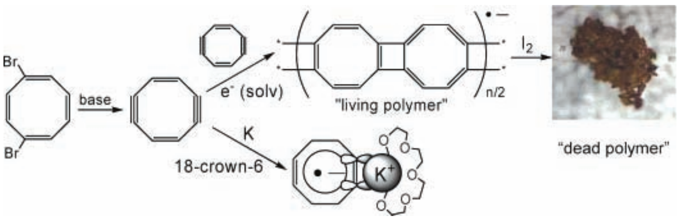
Matthew K. Kiesewetter, Richard C. Reiter, and Cheryl D. Stevenson*

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160

cdsteve@ilstu.edu

Received April 12, 2005

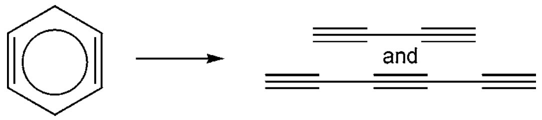
ABSTRACT



Reaction of 1,4-dibromo-[8]annulene ($C_8H_6Br_2$) with potassium *tert*-butoxide in THF followed by exposure to potassium metal leads to the formation of the anion radical of *sym*-[8]annuldiyne. The rapid interchange of Jahn–Teller-induced alternating bond angle conformers of *sym*-[8]annuldiyne is halted by ion association with a metal–crown ether complex forming the cyclooctadienyne-η^2-ynyl potassium zwitterionic radical, rendering all four protons nonequivalent. Neutral *sym*-[8]annuldiyne can form the [2 + 2] polymer, which is not soluble in the THF solution.

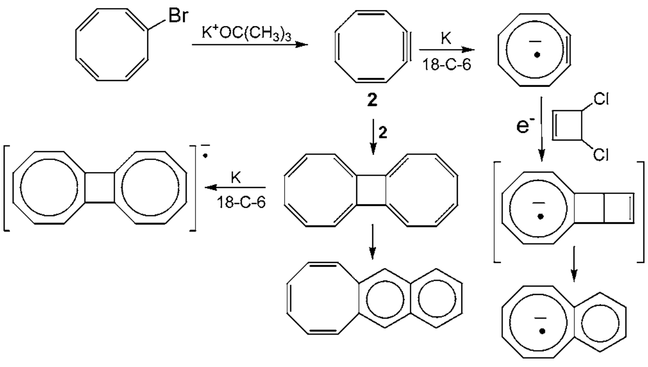
In contrast to *sym*-[6]annuldiyne, which spontaneously breaks apart to form acetylenes even below 12 K (Scheme 1),[1] it is predicted that *sym*-[8]annuldiyne (**1**) would be thermodynamically stable.[2] To quote Fritch and Vollhardt (over 20 years ago):[2] "The anticipated strain in such a system, although appreciable, should not be prohibitive, on the basis of literature analogies, particularly the remarkable stability of cycloocta-1,5-diyne." However, the rapid dimerization of [8]annulyne (**2** in Scheme 2) to form bi-[8]annulenylene, which rearranges to form naphtho-[8]annulene,[3] coupled with the two reactive sites of [8]annuldiyne (and of its dimer), suggests that the latter may undergo rapid polymerization via analogous [2 + 2] dimerizations.

Scheme 1



The one-electron entrapment of both [8]annulyne and of bi-[8]annulenylene as their corresponding anion radicals (Scheme 2) allowed for their spectroscopic (EPR) observa-

Scheme 2



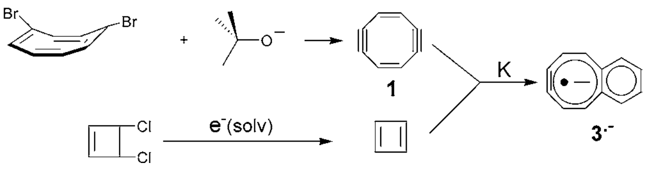
---

(1) Moriyama, M.; Ohana, T.; Yab, A. *J. Am. Chem. Soc.* **1997**, *119*, 10229.

(2) Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590.

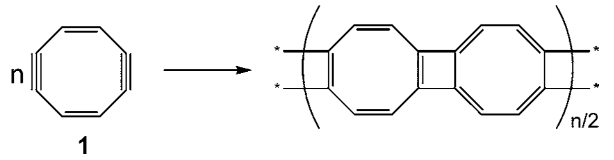
10.1021/ol050795k CCC: $30.25

Scheme 3



tions.[3] Further, [8]annulyne could be trapped with cyclobutadiene to provide benzo-[8]annulene.[3] Analogously, we were motivated to investigate (with some success) the possibility of finding reactions with in situ cyclobutadiene followed by one-electron transfer that would indicate the presence of the anion radical of **1**. However, the high propensity of **1** toward polymerization via extended [2 + 2] cycloaddition (Scheme 4) could render such a regime tenuous. Indeed, a cross-linked polymer that has some interesting properties was found.

Scheme 4



To verify the formation of **1**, we hoped to trap it, prior to polymerization, with cyclobutadiene leading to *sym*-benzo-[8]annulyne (**3**) and subsequently catch **3** as its anion radical (Scheme 3).[4] Optimistically, a weak EPR signal could be observed for **3**$^{\bullet-}$. Unfortunately, **3** and its anion radical are unknown. However, the anion radical of 3,4-benzo-[8]annulyne at ambient temperature was reported.[5]

Since the B3LYP/6-31G* protocol predicts the ρs (p_z spin densities) for the anion radical of benzo-[8]annulene and for **2**$^{\bullet-}$ very accurately (Figure 1),[3] we anticipated an accurate prediction for **3**$^{\bullet-}$. Further, Gerson's[5] work suggests that **3**$^{\bullet-}$ will endure at room temperature. Hence, **3**$^{\bullet-}$ should be stable, and the observation of even a weak signal on top of that for the "living polymer" will be unmistakable. Use of the calculated ρs and the known Q (in $a_H = Q\rho$)[6] of 25.6 G allowed a quantum mechanically predicted EPR spectrum for **3**$^{\bullet-}$ to be generated (Figure 2).

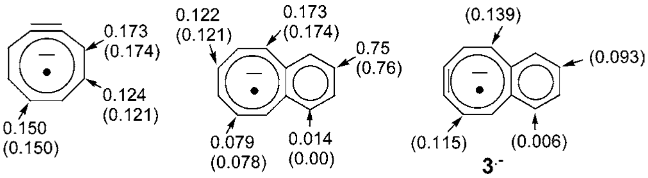


Figure 1. For the anion radials of [8]annulyne and benzo-[8]annulene, the B3LYP/6-31G*-predicted carbon p_z spin densities (shown in parentheses) are in extraordinary agreement with the experimental spin densities obtained from the a_H values and the McConnell relationship ($a_H = Q\rho$ with $Q = 25.6$ G). The Q of 25.6 G is that observed for the planar anion radical of [8]annulene.[3] This calculation protocol may not be the theoretician's preferred choice, but pragmatically (for predictive value) it is ideal. Values predicted for benzo-[8]annulyne are shown on the right.

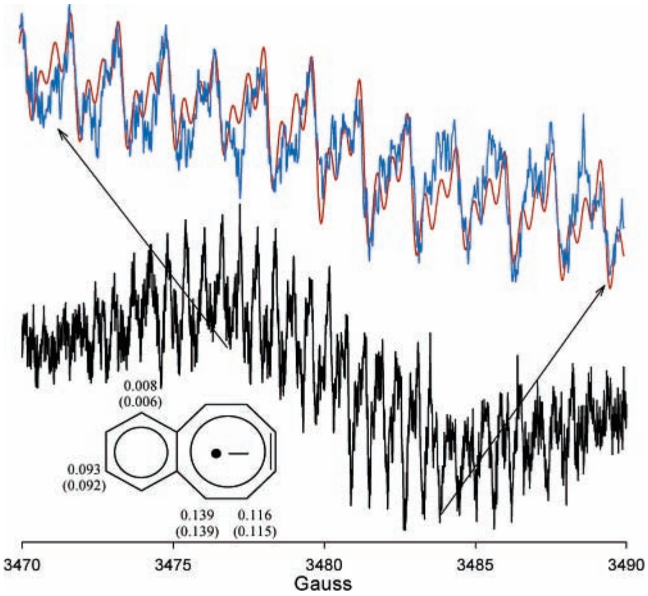


Figure 2. X-band EPR spectrum of the anion radical produced by trapping **1** with cyclobutadiene followed by one-electron reduction. (Upper inset) an expanded view of this spectrum (blue) superimposed upon the predicted spectrum for **3**$^{\bullet-}$ (red). The simulation was generated using a_H values of 3.55, 2.95, 2.36, and 0.20 G each for 2Hs, which come from the DFT-predicted spin densities shown in parentheses. The K splitting is 0.58 G. The living polymer represents the majority of the signal at a ratio of 250:1. This ratio makes the signal for **3**$^{\bullet-}$ appear weak.

When a mixture of 1,4-dibromo-[8]annulene ($C_8H_6Br_2$),[4] dichlorocyclobutene, 18-crown-6, and potassium *tert*-butoxide in tetrahydrofuran (THF) at 173 K is exposed to a potassium metal mirror, a dark green solution results that exhibits a well resolved EPR spectrum at ambient temperature. The spectrum resulting from the reduction of **1** also contains the broad, single-line signal expected from a "living polymer" (Figure 2). Since **1** is undergoing a rapid polymerization (Scheme 4) and free electrons are present, the living polymer[7] is necessarily formed.

Having observed the capture of **1** with cyclobutadiene and the solvated electron, we hoped to stabilize **1** via direct

---

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

(4) (a) $C_8H_6Br_2$ is contaminated to the extent of 8% with the 1,5-isomer. However, this isomer also dehydrohalogenates to form **1**. (b) Konz, W. E.; Hechtl, W.; Huisgen, R. *J. Am. Chem. Soc.* **1970**, *92*, 4104.

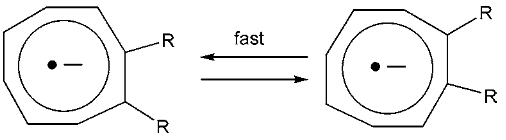
(5) Gerson, F.; Heckendorn, R.; Wong, H. N. C. *Helv. Chim. Acta* **1983**, *66*, 1409.

(6) (a) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*; John Wiley and Sons: New York, 1994; p 241. (b) Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360. (c) Successful theoretical interpretation appears in ref 10.

electron transfer and view it in the presence of its living polymer. The treatment of $C_8H_6Br_2$ with excess potassium *tert*-butoxide (KOC_4H_9) in THF containing 18-crown-6 at 198 K followed by exposure of the solution to a fresh potassium metal mirror[8] yields a green mixture, which, under low-resolution conditions (modulation amplitude of 0.2 G), reveals an EPR spectrum resulting from the odd electron interacting with four equivalent protons. Further, this spectrum sits on top of the much larger single broad resonance from the living polymer.

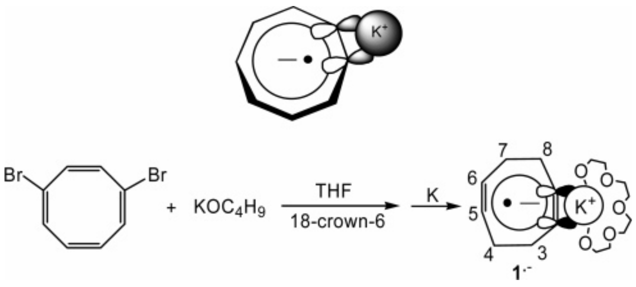
The observation of a 1:4:6:4:1 pentet is not entirely consistent with the expected spectrum for the anion radical of [8]annuldiyne. Since $\mathbf{1}^{\bullet-}$ is a degenerate system, it would necessarily undergo a Jahn–Teller distortion to break the degeneracy. The anion radical of a 1,2-disubstituted [8]annulene (also a degenerate system) is distorted into two degenerate alternating bond angle (ABA) conformers that are in rapid (on the EPR time scale) equilibrium with each other (Scheme 5).[9,10] In analogy to this situation, the Jahn–Teller distortion of $\mathbf{1}^{\bullet-}$ should result in an anion radical with alternating bond angles. This, in turn, would render the two protons over wide C–C–C angles different from the two over narrow angles.

Scheme 5



Also, the p_y orbitals of the anion radical of [8]annulyne interact strongly with the 4s orbital of the potassium cation, even when the K^+ is encapsulated in the 18-crown-6.[11] A similar situation is anticipated in the case of $\mathbf{1}^{\bullet-}$ (Scheme 6). This association with the potassium ion, coupled with the ABA distortion, should render all four protons nonequivalent. Under high-resolution conditions (modulation amplitude = 0.05 G), a weaker signal is obtained. However, it does, indeed, clearly reveal that all four protons are nonequivalent (Figure 3).

Scheme 6



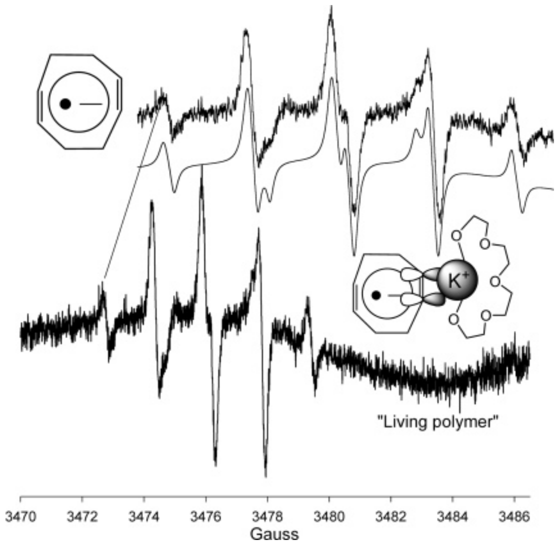
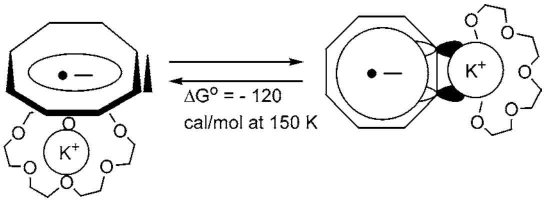


Figure 3. (Lower) X-band EPR spectrum resulting from the K reduction of [8]annuldiyne in THF recorded at 298 K. The broad single line is due to a living polymer. (Above) an expanded view of the signal and a computer-generated simulation using coupling constants of 1.58, 1.62, 1.66, and 1.99 G each for 1 H and an a_K of 0.08 G. The simulation also contains 40% of a species which is not involved in p_y-4s association and which exhibits an a_H of 1.56 for 4 Hs. [Living polymer]/[**5**] = 25/1.

The ABA ground-state geometry results in the protons in the 3 and 7 positions (lying over wide C–C–C angles) being magnetically nonequivalent to those in the 4 and 8 positions, which lie over narrow angles. Further symmetry breaking results from the K^+ association with one alkyne moiety.[11] Hence, all four protons are unique in the cyclooctadienyne-η^2-ynyl potassium zwitterionic radical.

The cyclooctatriene-η^2-ynyl potassium zwitterionic radical was found to be in thermodynamic equilibrium with another association isomer (Scheme 7), and the K_{eq} for isomerization is 1.6.[11] At −120 °C, the encapsulating power of the crown is insufficient to prevent spin delocalization into the K^+ ion in the cyclooctatriene-η^2-ynyl potassium zwitterionic radical system, but it does attenuate the a_K to only 0.072 G.

Scheme 7



---

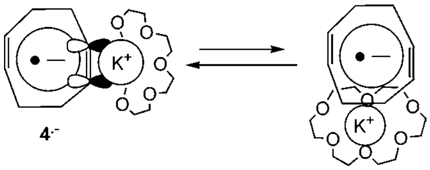
(7) (a) It is known that a single broad EPR line verifies the presence of a polymerizing radical during the anionic polymerization, a "living polymer", such as that from 9-vinylanthracene. (b) Eisenberg, A.; Rembaum, A. *Polym. Lett.* **1964**, *2*, 157. (c) Moacanin, J.; Rembaum, A. *Polym. Lett.* **1964**,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

(8) K was freshly distilled under vacuum to form the K mirror, and the entire reaction was carried out under high vacuum as described in ref 3.

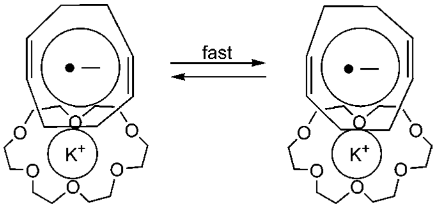
(9) Stevenson, C. D.; Kim, Y. S. *J. Am. Chem. Soc.* **2000**, *122*, 3211.

Likewise, even in the presence of excess 18-crown-6, $\mathbf{1}^{\bullet-}$ exists predominantly as an associated species, wherein an overlap of the 4s orbital of the K^+ with the π-orbitals of the alkyne moiety is present (Scheme 8).[11] This association locks the system into one of the degenerate ABA conformations ($\mathbf{4}^{\bullet-}$). When the ion association does not involve the alkynyl group,[9] the two degenerate ABA conformations are involved in rapid (on the EPR time scale) interchange (Scheme 9).

Scheme 8



Scheme 9



Careful examination and computer simulation of the EPR signal for $\mathbf{1}^{\bullet-}$ (Figure 3) reveal the simultaneous presence of this rapidly oscillating structure and of the "locked" cyclooctadienyne-η^2-ynyl potassium zwitterionic radical (K_{eq} $\sim$ 0.4 in Scheme 8).

B3LYP/6-31+G* geometry optimization calculations produced the D_{2h} anion radical, $\mathbf{1}^{\bullet-}$. The bond angles were then distorted to 118° for the wide sp^2 carbon angles and 115° for the narrow angles (as in [8]annulene).[10] The results show that the charge densities on adjacent sp carbons are not equivalent. By simply placing the K^+ closer (by 0.04 Å) to the carbon with the larger charge density followed by a single-point calculation, we were able to find a structure exhibiting the empirical spin densities. However, we could only do this using the McConnell relationship ($a_H = Q\rho$),[6] where $Q = 10.4$ G. This small Q indicates poor spin transfer from the π-system to the C−H σ-bond. For example, Q and the total spectral width are smaller in nonplanar systems than those found in planar anion radicals.[12] However, molecular modeling and chemical intuition indicate the improbability of nonplanarity in $\mathbf{1}^{\bullet-}$. Perhaps, ABA distortion of $\mathbf{1}^{\bullet-}$ enforces a σ-interaction with the alkynyl p_y orbitals that attenuates the spin transfer.

Characterization of the insoluble polymer resulting from the reaction depicted in Scheme 4, after oxidation with I_2 in pentane and washing with water, indicated extensive cross linking. Microscopic examination of the "dry" solid polymer as it is exposed to solvent (pentane), suggests that it is a rigid, unswellable solid, which indicates a high degree of cross-linking.[13] MALDI mass spectral analysis reveals a periodic series of peaks separated by 100 mass units up through 10^4 m/e. The cross linking results from suprafacial−suprafacial [2 + 2] cycloadditions involving the cyclobutadiene units in stacked polymer chains.

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

Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

OL050795K

---

[10] Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500.

[11] Peters, S. J.; Turk, M. R.; Kiesewetter, M. K.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 11212.

[12] Broadus, K. M.; Kass, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 4189.

[13] Allcock, H. R.; Lampe, F. W.; Mark, J. E. *Contemporary Polymer Chemistry*, 3rd. ed.; Pearson Education: Upper Saddle River, New Jersey, 2003; p 5.