J|A|C|S
ARTICLES

Polycyclooctatetraeneoxy Alkane Polyanionic Polyradicals

Cheryl D. Stevenson,*,‡ Richard C. Reiter,‡ Lisa F. Szczepura,‡ and
Steven J. Peters*,†

*Contribution from the Department of Chemistry, Illinois State University,
Normal, Illinois 61790-4160, and Department of Chemistry, California State University,
Sacramento, California 95819-6057*

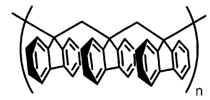
Received June 22, 2004; E-mail: cdsteve@ilstu.edu

Abstract: The room temperature potassium reduction of 1,2,3-triscyclooctatetraeneoxypropane, in hexamethylphosphoramide (HMPA), yields an anion radical, which disproportionates so strongly to the dianion diradical that the anion radical cannot be observed via EPR. The dianion diradical has one unpaired electron in a primary and one in a secondary ring system, and it can be readily reduced to the corresponding trianion triradical. An analogous reduction of 1,2,3,4-tetrakiscyclooctatetraeneoxybutane does produce an observable anion radical, but it also is readily reduced to the system corresponding to one electron per eight-membered ring (the tetraanion tetraradical). These results and those obtained from systems containing two cyclooctatetraene (COT) moieties are explained in terms of the geometry changes COT undergoes upon one-electron reduction, the interactions between reduced and adjacent unreduced ring systems, and the electron− electron repulsion present in the polyanion polyradicals.

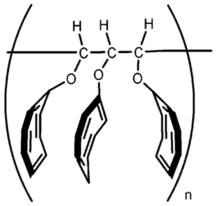
Introduction

There are a variety of systems containing isolated aryl moieties folded into structures in which the π-systems of the aryl groups interact.[1] Their secondary analogues form extended structures with $\pi-\pi$ interactions as do dibenzofulvene polymers (**1**) and related molecules.[1c] In these and similar diaryl systems, $\pi-\pi$ interactions are often weak,[2] but may be augmented by oxidation[3] or reduction.[4] If the oxidation or reduction is concomitant with the evolution of unpaired electrons, a variety of interesting spin multiplicities modulated by the $\pi-\pi$ interactions is possible.

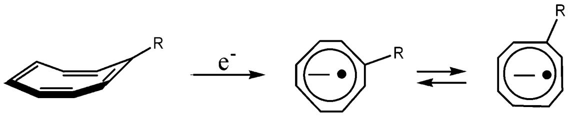
Polymers involving cyclooctatetraene (e.g., structure **2**) would not be capable of undergoing typical π-stacking, as in **1**, because of the puckered (tub-like) nature of the cyclooctatetraene (COT) ring system. However, because of the D_{2d} to D_{4h} conformation change that COTs undergo upon one-electron reduction (reaction 1), more typical π-stacking can be envisioned after the multi-electron reductions of **2**. Since the COT anion radical, formed via one-electron reduction of COT (reaction 1, R= H), can readily disproportionate (reaction 2),[5] the three-electron reduction of **2**, with $n = 1$ (structure **3**), can result in three possible spin distribution isomers, two doublets, and a triradical (Scheme 1).



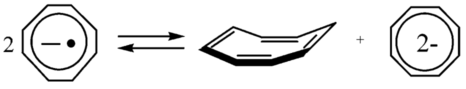
1



2



(1)



(2)

It was anticipated that π-stacking in such polymers might provide through-space delocalized solution analogues of the doped biaryl systems[6] that would consequently lead to some electron−electron coupling. On the other hand, Coulombic repulsion might lead to such splayed out structures as those shown in Scheme 1, but since one COT unit can accommodate two electrons, the possibility of multicharged $\pi-\pi$ interactions remained. However, the EPR spectrum of the solution resulting from the two-electron reduction of 1,2-bis-cyclooctatetraeneoxyethane (**4**) in hexamethylphosphoramide (HMPA), where ion

---

‡ Illinois State University.

† California State University.

[1] (a) Lepore, G.; Migdal, S.; Blagdon, D. E.; Goodman, M. *J. Org. Chem.* **1973**, *38*, 2590. (b) Tanatani, A.; Kagechika, H.; Azumaya, I.; Fukutomi, R.; Ito, Y.; Yamaguchi, K.; Shudo, K. *Tetrahedron Lett.* **1997**, *38*, 4425. (c) Rathore, R.; Abdelwahed, S. H.; Guzel, I. A. *J. Am. Chem. Soc.* **2003**, *125*, 8712.

[2] Bushey, M. L.; Hwang, A.; Stephens, P. W.; Nuckolls, C. *J. Am. Chem. Soc.* **2001**, *123*, 8157.

[3] Salhi, F.; Lee, B.; Metz, C.; Bottomley, L. A.; Collard, D. M. *Org. Lett.* **2002**, *4*, 3195.

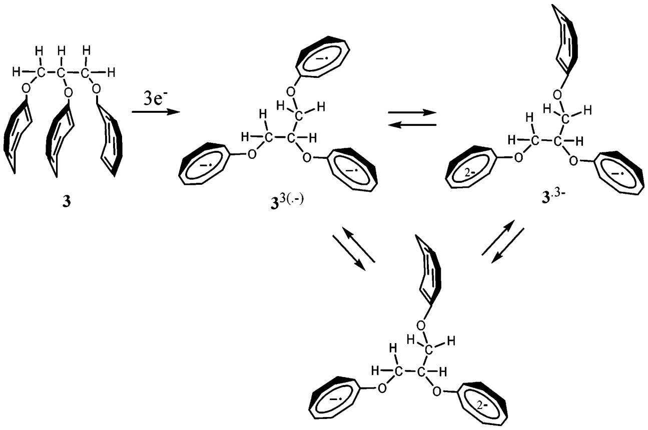
[4] Baumgarten, M.; Gherghel, L.; Friedrich, J.; Jurczok, M.; Rettig, W. *J. Phys. Chem. A* **2000**, *104*, 1130.

[5] (a) Katz, T. J.; Reinmuth, W. H.; Smith, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 802. (b) Stevenson, C. D.; Concepcion, J. G.; Echegoyen, L. *J. Am. Chem. Soc.* **1974**, *96*, 5452.

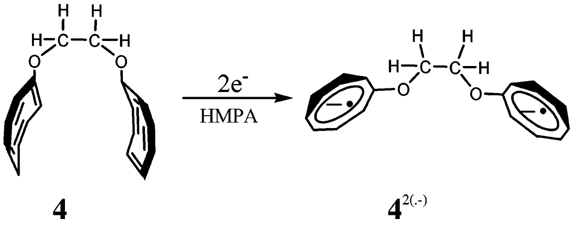
[6] Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.

10.1021/ja046312+ CCC: $30.25 © 2005 American Chemical Society

Scheme 1



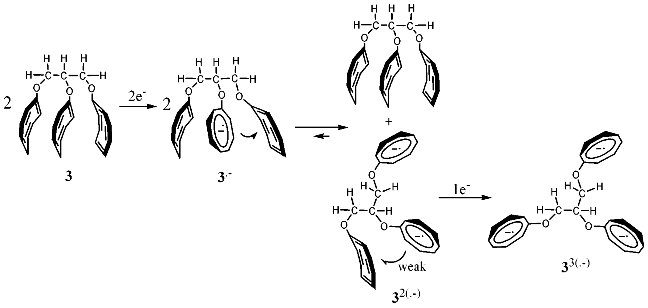
association involving hydrocarbon anion radicals is absent,[7] indicates the predominant presence of the dianion diradical ($\mathbf{4}^{2(\bullet-)}$).[8] This dianion diradical is a true di-doublet with no apparent electron−electron coupling (communication).



(3)

The EPR pattern for the simple isopropoxy-COT anion radical reveals coupling from only the ring protons and exhibits a characteristic EPR spectrum for an [8]annulene (C_8H_8) anion radical with an electron-releasing substituent, having four small proton couplings from the even numbered carbons and three large a_H's from H's on the odd numbered carbons.[9] This is consistent with the odd electron residing in the molecular orbitals of an alkoxy-[8]annulene, wherein the COT moiety has a D_{4h} geometry with alternating long and short bond lengths.[9] This quartet of pentets pattern is observed for all alkoxy-COT anion radicals. However, a homohyperconjugative interaction between the γ-carbon and the ipso carbon results in observation of extra hyperfine lines in the cases of *n*-propoxy-COT$^{\bullet-}$ and the other primary alkoxy-COT$^{\bullet-}$ systems.[9] Very rapid interchange, involving quantum mechanical tunneling,[10] between the D_{4h} alternating bond length geometries hides the nonequivalency of the pseudo-ortho protons, which are not exactly equivalent because of proximity effects (the 1−2 C−C bond is not the same length as is the 1−8 C−C bond). The reported EPR spectrum of $\mathbf{4}^{2(\bullet-)}$ exhibits a small splitting (0.31 G) for the two γ-protons.[8] One surprising feature, however, is that the two D_{4h} forms of the COT anion radicals moieties in $\mathbf{4}^{2(\bullet-)}$ do not undergo tunneling, as there is a clear nonequivalency of the two pseudo-ortho protons (a_H's = 0.74 and 0.84 G). It would appear that an interannular communication (interaction) terminates the quantum mechanical tunneling between the two D_{4h} structures.

Scheme 2



We anticipated unprecedented multicharged $\pi-\pi$ interactions to be present in the larger polyalkoxy-COT systems, which may even have some relevance to supramolecular assemblies and devices,[11] semiconductors, and light emitting diodes, for which polyphenyls have attracted great interest.[12] The formation of polarons (anion radicals) of oligomeric materials with alkali metals is known to produce dramatic perturbations in their conductivity.[6]

Results and Discussion

The potassium metal reduction of 1,2,3-triscyclooctatetraeneoxypropane (**3**) using just a trace of potassium metal, (moles K/moles **3**) < 0.1 in HMPA, results in a solution exhibiting an EPR spectrum that is consistent with a 1/1 mixture of two alkoxy-COT anion radicals. One anion radical appears to be that of a primary alkoxy-COT, which exhibits a splitting from the two γ-protons, and the other is that of a secondary alkoxy-COT (on the same molecule). As long as the mole ratio of metal to **3** is in the range of ca. 0.01 to 0.1, this signal is invariant, suggesting that the only EPR active species in solution is the dianion diradical $\mathbf{3}^{2(\bullet-)}$ with no electron−electron coupling (Scheme 2), where the curved arrows indicate an electronic interaction. Perdeuteriation of the alkane backbone followed by potassium reduction leads to a simpler EPR pattern that is perfectly simulated in terms of $\mathbf{3}^{2(\bullet-)}$-d_5 (Figure 1).

Even though the solution electron affinity of the COT ring on the secondary side is larger than that on the primary side,[8,9] the anion radical of **3** is never observed. The reduction of the COT moiety on the secondary side promotes an electronic interaction between two of the ring systems in $\mathbf{3}^{\bullet-}$, resulting in some flattening of one of the unreduced rings. Hence, the reduction (flattening) of the center ring lowers the reduction potential of the outer (primary) ring, rendering $\mathbf{3}^{\bullet-}$ easier to reduce than **3**. In other words, the isolated COT moieties in $\mathbf{3}^{\bullet-}$ fold into a structure in which different COT π-systems interact, and the disproportionation described in Scheme 2 lies far to the right.

Increasing the amount of K used in the reduction leads to a new EPR spectrum due to the same two species but in a 2/1 ratio of primary/secondary alkoxy-COT anion radicals with no evidence of a spin multiplicity greater than 2, indicating the presence of $\mathbf{3}^{3(\bullet-)}$ (Figure 1C and Scheme 2). Again, this ratio is invariant with the K/[**3**] ratio, as long as the ratio is greater than about 0.3/1.

---

(7) (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.

(8) Peters, S. J.; Reiter, R. C.; Stevenson, C. D. *Org. Lett.* **2003**, *5*, 937.

(9) Stevenson C. D.; Davis, J. P.; Reiter, R. C. *J. Phys. Chem. A* **1999**, *103*, 5343.

(10) Stevenson, C. D.; Hienle, L. J.; Davis, J. P.; Reiter, R. C. *J. Am. Chem. Soc.* **2002**, *124*, 2704.

(11) (a) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863. (b) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.

(12) (a) Braun, D.; Heeger, A. *J. Appl. Phys. Lett.* **1991**, *58*, 1982. (b) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

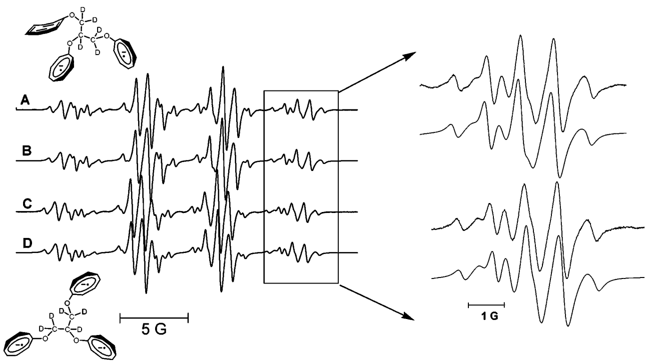
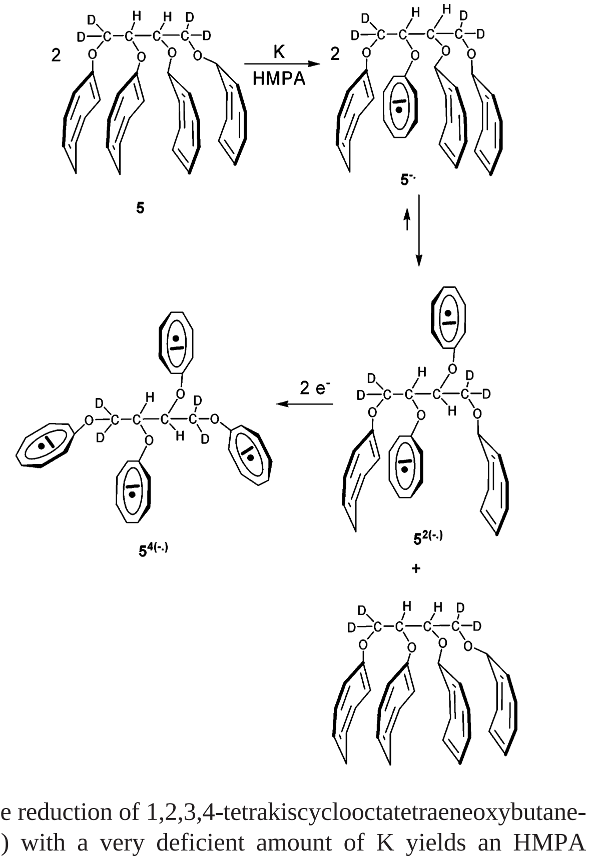


Figure 1. **A** and **C** are the x-band EPR spectra of $\mathbf{3}^{2(-\bullet)}$-d_5 and $\mathbf{3}^{3(-\bullet)}$-d_5, respectively, in HMPA recorded at 298 K. **B** and **D** are computer-generated simulations of **A** and **C**, respectively, using an a_H value of 5.438 G for the three ring protons (3, 5, and 7), and an a_H value of 0.919 G for the four ring protons (2, 4, 6, and 8) attached to the secondary COT ring ($\Delta w_{pp} =$ 0.22), and 5.60 G (3 H's) and 0.739 G (4 H's) for those on the primary ring ($\Delta w_{pp} = 0.27$), whose spectrum is shifted 0.03 G downfield from that of the secondary ring. Simulation **B** includes equal portions of primary and secondary species, while simulation **D** requires a double portion of the primary component.

Scheme 3



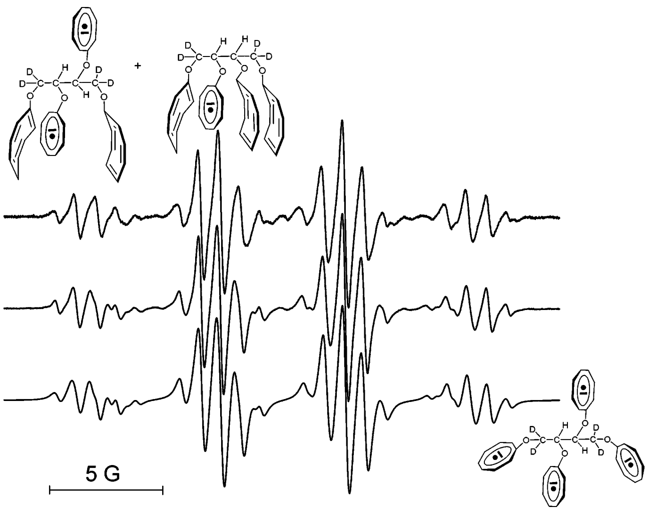


Figure 2. (Upper) EPR spectrum of a mixture (2.5:1) of the dianion diradical and anion radical of **5** (simulation not shown). (Middle) Spectrum of the corresponding tetraanion tetraradical $\mathbf{5}^{4(-\bullet)}$ produced by the addition of more metal to the solution represented by the upper spectrum. (Lower) Computer simulation of the middle spectrum generated using a_H's of 5.61G (3H's) and 0.77 G (4H's) for the primary radicals, and 5.46 G (3H's) and 0.875 G (4H's) for the secondary radicals ($\Delta w_{pp} = 0.31$ G for both species). The primary radical is shifted downfield 0.04 G relative to the secondary radical, and both radicals are found in identical concentrations.

The reduction of 1,2,3,4-tetrakiscyclooctatetraeneoxybutane-d_4 (**5**) with a very deficient amount of K yields an HMPA solution that reveals a mixture of two different paramagnetic species. One is the anion radical with the odd electron located solely on a secondary COT ring system. The other is the dianion diradical with both unpaired electrons located on secondary ring systems (Scheme 3). The deuteriation of the terminal carbons in the alkane backbone allows simpler simulation of the spectrum (Figure 2, upper).

The COT moiety in the anion radicals of primary and secondary alkoxy substituted COTs have planar D_{4h} structures (reaction 1).[9,13] However, when the substituent is a bulky *tert*-butoxy group, perfect planarity is prohibited because of the steric interactions between the methyl and ring protons.[10] Reduction of a wide variety of primary or secondary alkoxy-COT systems in HMPA with alkali metal results in solutions exhibiting a quartet of pentets upon EPR analysis with a_H's of about 5.6 G for protons on positions 3, 5, and 7 and around 0.7 G because of the protons on positions 2, 4, 6, and 8.[9]

The appearance of the EPR spectrum of *tert*-butoxy-COT$^{\bullet-}$ is significantly different than that of $\mathbf{5}^{\bullet-}$, because of altered magnitudes of both splittings (3 H's with $a_H = 4.89$ G and 4 H's with $a_H = 1.30$ G).[9,10] When $[K^+] \ll [\mathbf{5}]_{total}$, the EPR pattern for $\mathbf{5}^{\bullet-}$ (3 H's with $a_H = 5.41$ G and 4 H's with $a_H = 1.04$ G) reflects a system with a degree of ring puckering between that for *tert*-butoxy-COT$^{\bullet-}$ and that for a planar secondary alkoxy-COT anion radical. The dianion diradical ($\mathbf{5}^{2(\bullet-)}$) couplings (5.47 G, 0.88 G) reflect a somewhat higher degree of planarity. The lack of total planarity in the reduced eight-membered rings is due to spin and charge “drainage” into adjacent (formally neutral) rings. This causes some flattening of the formally neutral ring systems.

The addition of even more K metal leads to an EPR spectrum that now reveals a 1/1 ratio of primary to secondary COT-oxyalkane anion radicals. These data are consistent with the presence of the tetraanion tetraradical, with no electron−electron communication, as the only EPR active species (Figure 2, middle). Reduction of these poly-COT-oxyalkane systems tends to favor the polyanion polyradical state (one unpaired electron on each COT moiety). Further, these unpaired electrons do not interact with each other and represent isolated doublets. As more and more electrons are added to this system, the EPR signal grows weaker and weaker, ostensibly because of the pairing of the added electrons and the ultimate formation of the octaanion.

---

(13) (a) Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500. (b) Goldsmith, D. J.; Bowen, J. P.; Qamhiyeh, E.; Still, W. C. *J. Org. Chem.* **1987**, *52*, 951.

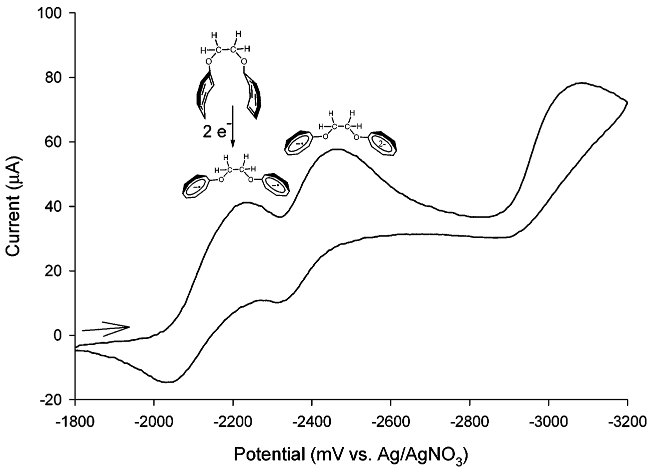
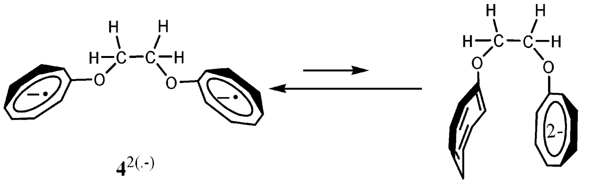


Figure 3. Cyclic voltammogram of 1,2-biscyclooctatetraeneoxyethane (**4**) in HMPA (0.2 M Bu_4NBF_4, 5 mV/s).

Further, there appears to be some C−O bond cleavage in the more highly reduced states.

Cyclic voltammetry represents the best way to empirically observe the transfer of electrons to these systems. Unfortunately, the complexity of the **3** and **5** systems is sufficient to lead to considerable overlap of the relatively broad reduction waves and consequent difficulty in the data interpretation. However, the 1,2-bis-cyclooctatetraeneoxyethane system (**4**) follows the analogous reduction sequence,[8] with the possibility of the addition of only four electrons. The EPR pattern produced by the reduction of **4**, with a very deficient amount of metal, exhibits the presence of only the diradical dianion (reaction 3), which shows a clear nondegeneracy of the psuedo-ortho protons.[8] Further reduction results in the formation of the trianion radical, and ultimately the tetraanion.[8]

Starting at −1.80 V and scanning in a negative direction, three reductive waves are observed for **4** in HMPA. If the scan is reversed at −2.80 V, the first two waves are quasi-reversible and occur at $E_{1/2} = -2.14$ and −2.39 V vs Ag/$AgNO_3$ (Figure 3). If the scan is reversed at a more negative potential, −3.20 V, a third irreversible wave appears at $E_{p,c} = -3.08$ V. On the basis of the EPR data, we know the first two reductions occur almost simultaneously. Therefore, in the cyclic voltammogram the first wave is due to a two-electron reduction, i.e., the generation of the dianion diradical (the EPR of an identical solution reveals the dianion diradical). The second and third reductive waves at $E_{1/2} = -2.39$ and $E_{p,c} = -3.08$ V would then be assigned to the generation of the trianion and the tetraanion, respectively. The irreversibility of the third wave verifies that addition of four electrons to **4** leads to decomposition. The observation of just the single two-electron reduction wave supports the EPR data, which is consistent with the equilibrium between the dianion diradical and the diamagnetic dianion being shifted far to the left (reaction 4).[8]



(4)

$\mathbf{4}^{2(\cdot-)}$

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

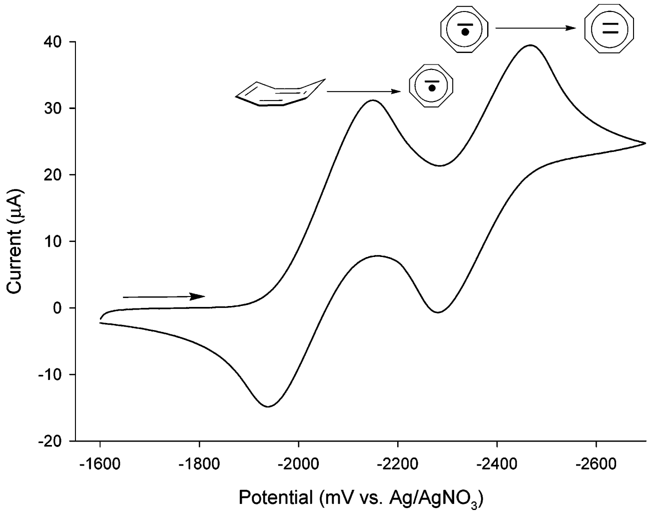


Figure 4. Cyclic voltammogram of cyclooctatetraene in HMPA (0.2 M Bu_4NBF_4, 2 mV/s). The conditions are the same as for the reduction represented in Figure 3.

A CV experiment with COT was carried out under identical conditions, and starting at −1.60 V and scanning in a negative direction, two cathodic waves are observed at $E_{1/2} = -2.04$ and −2.38 V vs Ag/$AgNO_3$ (Figure 4). This cyclic voltammogram is similar to that reported by Allendoerfer.[14] However, the potentials are shifted; this is not surprising since different reference electrodes were employed and no corrections have been made. It has been shown that the first couple corresponds to the reduction of COT to its anion radical, and the second to the addition of another electron to generate COT^{2-}. The dianion diradical of **4** appears at a slightly more negative potential than does the anion radical of COT due to the electron-releasing nature of the alkoxy backbone rather than to electron−electron repulsion in $\mathbf{4}^{2(\bullet-)}$. Electron−electron repulsion does, however, restrict the formation of $\mathbf{4}^{2-}$ (reaction 4), because this repulsion energy can be relieved via the formation of the dianion diradical. The formation of the dianion diradical is thermodynamically preferred over the formation of two separate anion radicals. This, in part, results from spin drainage from the reduced ring to the unreduced ring in $\mathbf{4}^{\bullet-}$. The reduction of the first COT moiety promotes an electronic interaction between the two ring systems. Hence, the reduction (flattening) of the first ring lowers the reduction potential of the other ring, and interactions analogous to those shown in Scheme 2 prevent the observation of $\mathbf{4}^{\bullet-}$. Analogous arguments hinder the formation of paired electron systems in the reductions of **3** and **5**.

The relatively higher electron affinity of the secondary rings accounts for the observation of the 1,2,3,4-tetrakiscyclooctatetraeneoxybutane anion radical. Steric crowding due to the presence of two secondary COT ring systems in 1,2,3,4-tetrakiscyclooctatetraeneoxybutane (**5**) and presumably in 2,3-biscyclooctatetraeneoxybutane (**6**) amplifies the spin and charge drainage from the reduced ring to the unreduced ring in the anion radicals. Steric crowding also augments the interannular electron−electron repulsion in the dianion diradicals. An analogous augmentation of the $\pi-\pi$ interactions in diaryl urea systems via methyl group substitution on the secondary nitrogens has been reported.[15] Consequently, we were motivated to investigate the possibility of a nonclassical conjugative interac-

---

(14) Allendoerfer, R. D. *J. Am. Chem. Soc.* **1975**, *97*, 218.

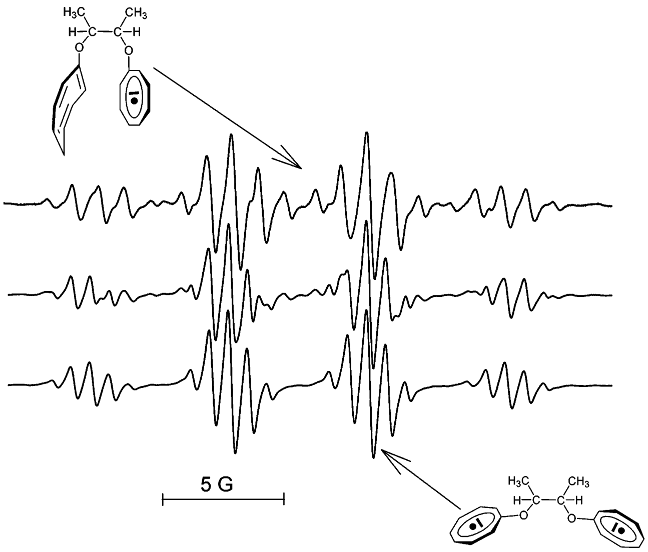
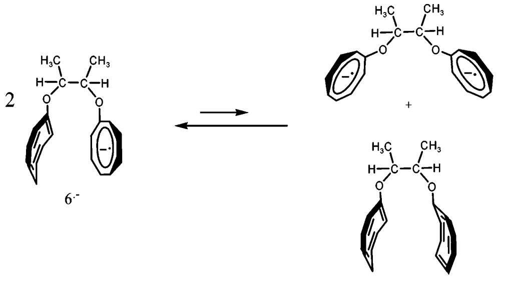


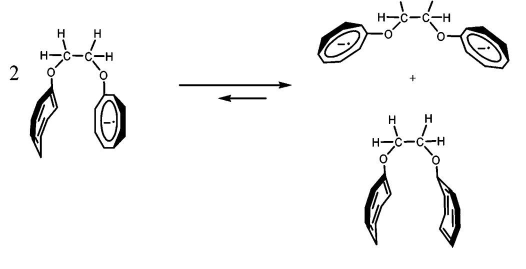
Figure 5. (Upper) EPR spectrum (25 G sweep width) of the earliest reduction stage of **6** at 298 K in HMPA. (Middle) EPR spectrum of the same solution after further reduction. (Lower) EPR spectrum of obtained after the addition of two electrons per molecule of **6**. It can be simulated using a_H's of 5.57 G for 3H's and 0.75 G for 4H's. This spectrum is that of $\mathbf{6}^{2(\bullet-)}$. The other two spectra represent mixtures of $\mathbf{6}^{\bullet-}$ [5.40 G (3H's), 1.035 G (4H's)] and $\mathbf{6}^{2(\bullet-)}$. Simulations (not shown) reveal that $[\mathbf{6}^{\bullet-}]/[\mathbf{6}^{2(\bullet-)}] = 5/1$ and 1/3 in the upper and middle spectra, respectively ($\Delta w_{pp} = 0.27$ G). The dianion diradical spectrum is shifted 0.065 G downfield with respect to that of $\mathbf{6}^{\bullet-}$.

tion between the two COT moieties in the anion radical of **6**. This would lead to an EPR spectrum reflecting six equivalent large and eight equivalent small proton couplings.

The reduction of **6** with a very deficient amount of K in the same manner as described above led to the observation of the parent monoanion radical. Further addition of metal leads first to a mixture of the anion radical and the dianion diradical, then to the exclusive observation of $\mathbf{6}^{2(\bullet-)}$ (Figure 5). From Figure 5, it is clear that the hoped-for nonclassical interannular conjugation was not realized. However, the clear observation of the anion radical means that the disproportionation described in reaction 5 is shifted to the left (relative to that in reaction 6), presumably due to augmented interannular electron−electron repulsion in $\mathbf{6}^{2(\bullet-)}$.



(5)



(6)

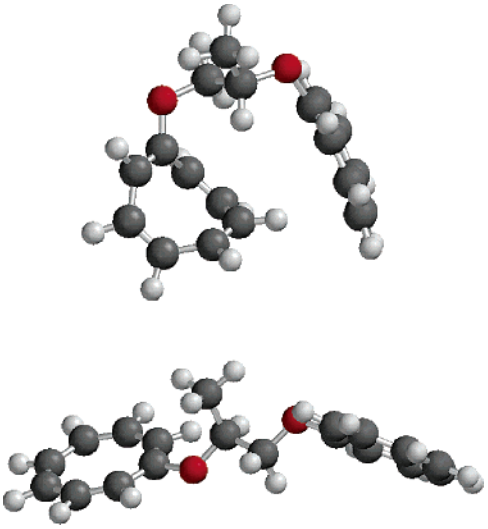


Figure 6. (Upper) B3LYP/3-21G* predicted geometry of the anion radical of 1,2-bis-cyclooctatetraeneoxypropane, $\mathbf{4}^{\bullet-}$. Note that the reduced ring is not quite planar and that the unreduced ring is less puckered than is neutral COT. (Lower) B3LYP/3-21G* predicted geometry of the dianion diradical, $\mathbf{4}^{2(\bullet-)}$. Note the splayed out noninteracting COT moieties.

Conclusions

Under conditions preventing ion association, the initial reduction of 1,2,..*n*-polykiscyclooctatetraene-oxyalkanes (with all *n* COT moieties having a D_{2h} configuration) leads to the formation of anion radicals, where the unpaired electron is predominantly located in a secondary ring system. The reduced eight-membered ring is nearly planar, and it interacts with an adjacent unreduced ring to render the latter more planar than a noninteracting D_{2h} COT system. This flattening of adjacent rings (supported by B3LYP/3-21G* calculations on a simple system, Figure 6) amplifies the solution electron affinity of the interacting unreduced ring, making disporportionation to the dianion diradical and further reduction to the polyanion polyradical systems very favorable. Electron−electron repulsion prevents interaction of the reduced rings, even in highly reduced systems. These true polyanion polyradicals exist with each COT moiety having one unpaired electron with no electron−electron coupling. This protocol represents a convenient method for generating true poly-doublet multiplicities as opposed to high spin (ferromagnetic) or low spin (anti-ferromagnetic) materials. Further, these systems are free of ion association in HMPA. Any "sandwiching" (solvation) of the metal cation between neighboring COT π-clouds (p-orbital-cation overlap) would necessarily lead to hyperfine from the metal cation.[16] This metal hyperfine is not observed.

Experimental Section

Materials. Synthesis of 1,1,4,4-Tetradeutero-threitol. 2,3-Butanediol, ethylene glycol, and glycerol-d_5 were purchased from Aldrich and used without further purification. The 1,1,4,4-tetradeutero-threitol was synthesized based upon the procedure outlined by Willer.[17] A solution of cyclohexanone (110 mmol), diethyl tartrate (70 mmol), and *p*-

---

(15) (a) Lewis, F. D.; Kurth, T. L.; Liu, W. *Photochem. Photobiol.* **2002**, *1*, 30−37. (b) Kurth, T. L.; Lewis, F. D.; Hattan, C. M.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 1460.

(16) Peters, S. J.; Turk, M. R.; Kiesewetter, M. K.; Reiter, R. C.; Stevenson, C. D.; *J. Am. Chem. Soc.* **2003**, *114*, 11212.

(17) Willer, R. L. *J. Org. Chem.* **1984**, *49*, 5150.

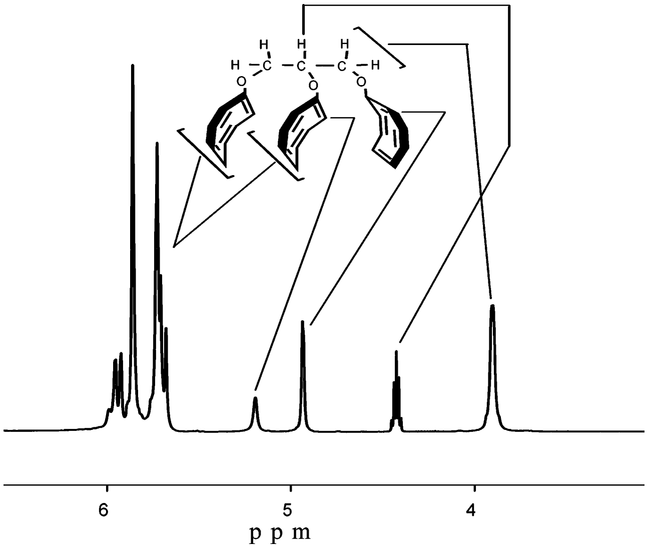


Figure 7. 400 MHz ^{1}H NMR spectrum of 1,2,3-triscyclooctatetraeneoxypropane. Note that the "pseudo-ortho" protons separated from the ipso carbon by a double bond are upfield (more so for the outside rings) from the rest of the COT ring protons.

toluenesulfonic acid monohydrate (2.9 mmol) dissolved in 300 mL of benzene was prepared. This solution was refluxed for 20 h, and the water produced was collected via a Dean−Stark trap. The solution was subsequently cooled, washed with 20 mL of an aqueous 12% NaOH solution, and dried with $MgSO_4$. The solution was filtered and then concentrated by removing the solvent at reduced pressure. The crude liquid was purified by vacuum distillation, and mass spectral analysis revealed it to be diethyl-2,3-cyclohexylene-tartrate, the precursor to threitol. This precursor (43 mmol) was dissolved in 100 mL of dry THF and added dropwise, over a 1 h period, to a slurry of lithium aluminum deuteride (73 mmol) in 200 mL of dry THF. The entire system was purged with Ar. Once the tartrate derivative was added, the solution was stirred for an additional 3 h. The resulting solution was worked up by the addition of 5 mL of water (added slowly), 10 mL of 12% NaOH, and an additional 30 mL of water. This slurry was filtered, and the solid material was washed with 200 mL of hot THF. The two THF solutions were combined, and the THF was removed at reduced pressure to yield the crude 2,3-*O*-cyclohexylene-tetradeuterothreitol. Without further purification, this crude product was dissolved in 50 mL of water and 1 mL of concentrated HCl. This mixture was heated, and the water/cyclohexanone azeotrope was distilled off under atmospheric pressure for approximately 2 h. The aqueous solution remaining in the distillation flask was cooled and washed twice with 50 mL of diethyl ether. The water layer was concentrated at reduced pressure, leaving a thick oil. This oil was dissolved in 95% ethanol and cooled to −10 °C, during which time white crystals precipitated out of solution. This precipitate was further purified by vacuum sublimation. ^{1}H NMR, proton coupled ^{13}C NMR, and mass spectroscopy revealed this product to be 1,1,4,4-tetradeutero-threitol.

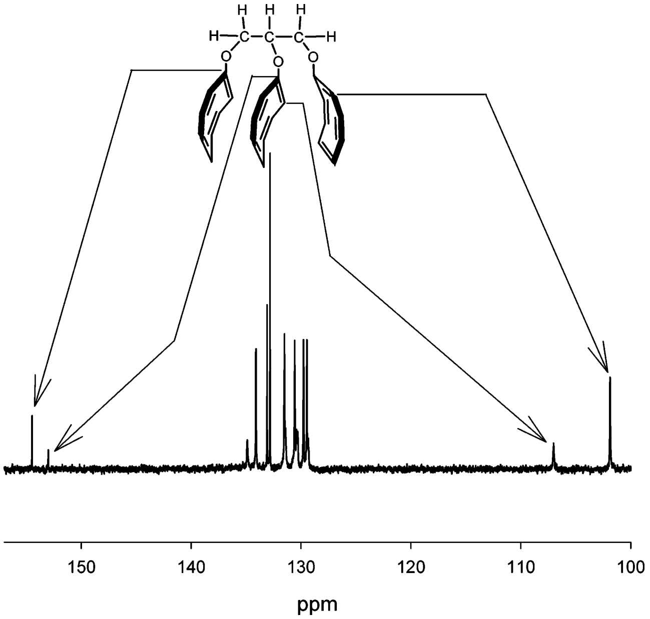


Figure 8. 100 MHz ^{13}C NMR spectrum of 1,2,3-tri-cyclooctatetraeneoxypropane. Note that the "pseudo-ortho" carbons separated from the ipso carbon by a double bond are upfield (more so for the outside rings) from the rest of the COT ring carbons. The peak assigned to the "pseudo-ortho" carbons for the inside rings is significantly broader than that for the outer rings "pseudo-ortho" carbons. This is due to the various conformational structures of these two inner rings (i.e., two COT tub geometries are facing right and one left; the reverse of this is possible, etc.). Not shown are the peaks assigned to the two types of carbons in the propane chain, at 74.4 ppm (C2) and 66.1 ppm (C1 and C3). A magnified view and assignments of the ring carbons (all are observed) appears in the Supporting Information.

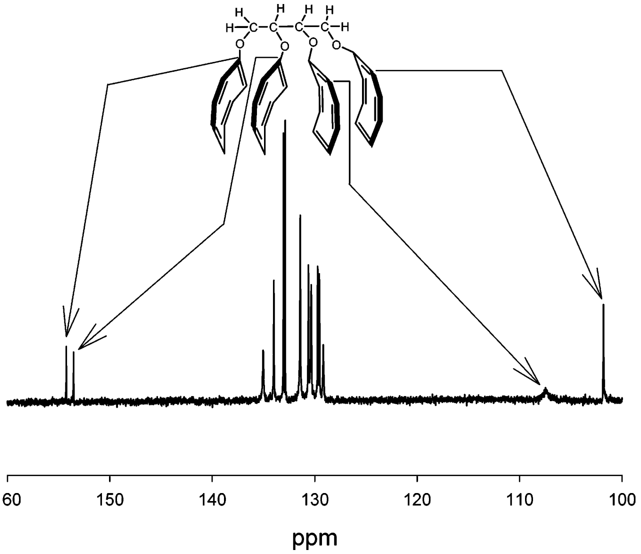


Figure 9. 100 MHz ^{13}C NMR spectrum of 1,2,3,4-tetrakiscyclooctatetraeneoxybutane. Note that the "pseudo-ortho" carbons separated from the ipso carbon by a double bond are upfield (more so for the outside rings) from the rest of the COT ring carbons. The peak assigned to the "pseudo-ortho" carbons for the inside rings is significantly broader than that for the outer rings' "pseudo-ortho" carbons. This is due to the various conformational structures of these two inner rings (i.e., both COT tub geometries are facing inward, one tub faces inward the other outward, both tubs face outward, position of both inner rings relative to the outer rings, etc.). Not shown are the peaks assigned to the two types of carbons in the butane chain: 74.4 ppm (C2 and C3) and 66.1 ppm (C1 and C4).

Cyclooctatetraeneoxyalkanes Synthesis. The syntheses of all the cyclooctatetraeneoxyalkanes were carried out based on Kreb's preparation of *tert*-butoxycyclooctatetraene.[18] COT was brominated to yield [4,2,0]-bicyclo-5,6-dibromo-1,3-octadiene, which was then dehydrohalogenated with potassium *tert*-butoxide to yield monobromocyclooctatetraene (BrCOT). The cyclooctatetraeneoxyalkanes were all prepared by adding monobromocyclooctatetraene to the appropriate potassium di-, tri-, or tetra-alkoxide. The potassium alkoxides were prepared by refluxing a dry THF solution containing the appropriate alcohol with excess potassium metal for 12 h under an argon atmosphere. The THF and excess metal were removed, leaving the potassium alkoxide salt behind. This salt was subsequently dissolved in dry DMSO. A stoichiometric excess of BrCOT was dissolved in dry DMSO, and this solution was added dropwise to the alkoxide solution at 20 °C. The

---

(18) Krebs, A. *Angew. Chem.* **1965**, *77*, 1966.

solution turned a dark opaque burgundy color. After the addition was complete, the solution was stirred for 12 h. Then the solution was added to an aqueous acetic acid solution; three ether extractions followed. The ether solution was dried with $MgSO_4$ and filtered, and the ether was removed under reduced pressure. The crude cyclooctatetraeneoxy-alkanes were purified by column chromatography (silica gel with a 15% ethyl acetate/pentane mobile phase) and further purified by vacuum sublimation. ^{1}H NMR spectra are consistent for all cyclooctatetraeneoxy-alkane compounds. Figure 7 shows the ^{1}H NMR spectrum of 1,2,3-triscyclooctatetraeneoxy propane, and Figure 8 shows the ^{13}C NMR.

The ^{1}H and ^{13}C of spectra of the 1,2,3,4-tetrakis-cyclooctatetraeneoxybutane system is very analogous (Figure 9). The vinylic "pseusdo-ortho" carbon resonance for the internal rings is very broad. These two carbons appear only as equivalent time-averaged resonances.

Reductions. The reductions where carried out by allowing HMPA solutions of the cyclooctatetraeneoxy−alkanes to come into contact with a potassium metal mirror in vacuo as previously described.[19] The EPR spectra were recorded with a Bruker EMX-080 spectrometer equipped with a variable temperature unit.

Cyclic Voltammetry. The electrochemical studies were carried out in HMPA distilled from potassium metal under high vacuum. A conventional three-electrode cell consisting of a platinum disk working electrode, a platinum wire auxiliary electrode, and a $Ag/AgNO_3$ (0.01 M) reference electrode was used. The cyclic voltammograms were run in a 0.2 M Bu_4NBF_4 solution in an inert atmosphere glovebox at a scan rate of 2−5 mV/s. The scanning limits were +0.40 to −3.2 V vs $Ag/AgNO_3$, and the ferrocene/ferrocenium couple appeared at +0.11 V vs the $Ag/AgNO_3$ reference. All potentials are reported vs the $Ag/AgNO_3$ reference electrode, and scans are compensated for IR drop.

Acknowledgment. L.F.S. (an NSF Career Awardee) and C.D.S. thank the National Science Foundation and the donors of the American Chemical Society Petroleum Research Fund. S.J.P. thanks the Camille and Henry Dreyfus Foundation for a Supplemental Award through the Scholar/Fellow program.

Supporting Information Available: Two figures showing expanded views of the ^{13}C NMR spectrum from the non-ipso and non-vinyl pseudo-ortho ring carbons of the 1,2,3-tricyclooctatetraeneoxybutane and 1,2,3,4-tetrakiscyclooctatetraeneoxybutane in $CDCl_3$ along with tentative assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

JA046312+

---

(19) Stevenson, C. D.; Burton, R. D.; Reiter, R. C. *J. Am. Chem. Soc*. **1992**, *114*, 399.