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Interannular Communication in the Radical Anions of Bis-cyclooctatetraene Systems

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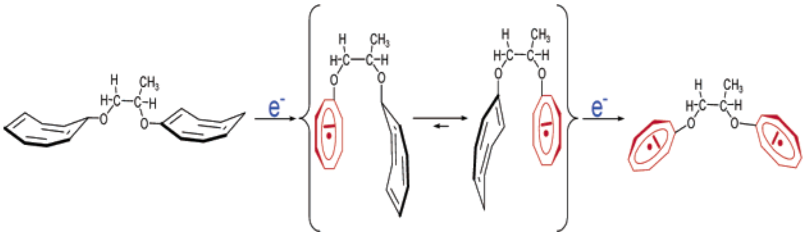
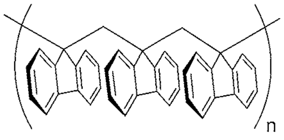
ABSTRACT

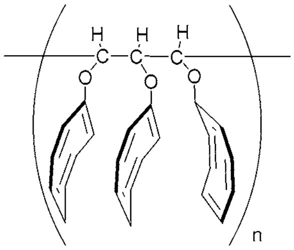


The room-temperature potassium reduction of 1,2-bis-cyclooctatetraeneoxypropane yields two different regio-spin isomer anion radicals in equilibrium (COT–O–C(Me)HCH$_2$CH$_2$–O–COT$^{\bullet-}$ = $^{\bullet-}$COT–O–C(Me)HCH$_2$CH$_2$–O–COT) that is shifted far to the right. The presence of the unreduced ring perturbs the spin density on the reduced ring. Addition of more electrons generates the diradical dianion ($^{\bullet-}$COT–O–C(Me)HCH$_2$CH$_2$–O–COT$^{\bullet-}$), and the anion radical on the secondary side splits the degeneracy of the psuedo-ortho protons of the anion radical on the primary side.

Intramolecular $\pi-\pi$ interactions can have profound effects upon molecular geometry,[1] chemical reactivity,[2] and self-assembly[3] as in the case of the dibenzofulvene dimer, trimer, and polymers (structure **1**).[4] Somewhat analogous polymers (structure **2**) involving cyclooctatetraene (COT) would not be capable of undergoing typical π-stacking due to the puckered (tub-like) nature of the COT ring system. The designers of **1** suggested that it might have unprecedented characteristics involving electron transfer.[4] The (D_{2d} to D_{4h}) conformation change that COT undergoes upon one-electron reduction should also lead to unprecedented electron-transfer characteristics in **2**.



1



2

To initiate our studies of such systems, the hydroxyl protons of 1,2- and 1,3-alkanediols were replaced with two COT units (Scheme 1)[5] and reduced to their respective anion radicals and dianions. Both of these entities reveal communication between the COT moieties that significantly alters their electronic characteristics.

The anion radical of 1,2-bis-cyclooctatetraeneoxypropane (**3**) can exist as two regio-spin (charge) isomers (Scheme 2), which can be distinguished via their EPR spectra. The

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[†] Camille and Henry Dreyfus Foundation Fellow.

[‡] Camille and Henry Dreyfus Foundation Scholar.

(1) For a recent example, see: Miller, G. P.; Mack, J.; Briggs, J. *Org. Lett.* **2000**, *2*, 3983.

(2) For a recent example, see: Prat, F.; Houk, K. N.; Foote, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 845–846.

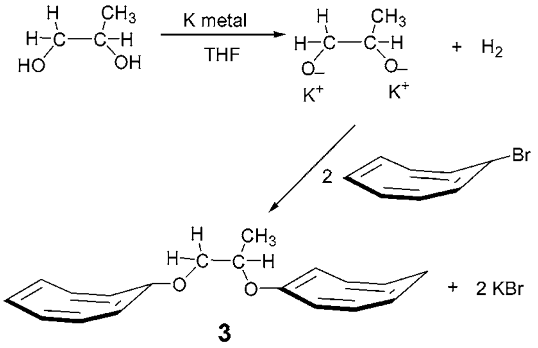
(3) For a recent example, see: Bjornholm, T.; Greve, D. R.; Reitzel, N.; Hassenkam, T.; Kjaer, K.; Howes, P. B.; Larsen, N. B.; Bogelund, J.; Jayaraman, M.; Ewbank, P. C.; McCullough, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 7643.

(4) Nakano, T.; Takewaki, K.; Yade, T.; Okamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9182.

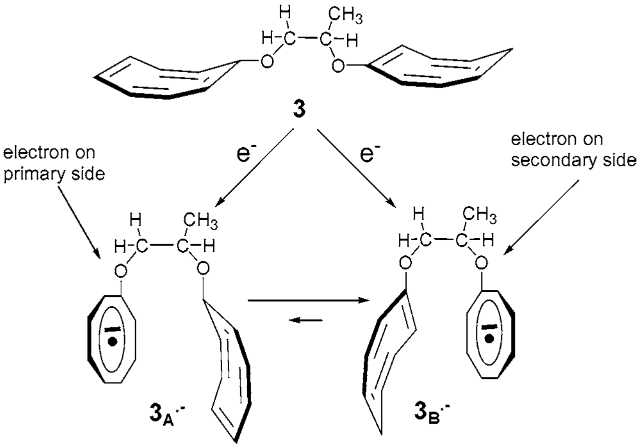
(5) The oxygens separating the COT ring from the methylene eliminate gauche interactions.

10.1021/ol034120y CCC: $25.00

Scheme 1



Scheme 2



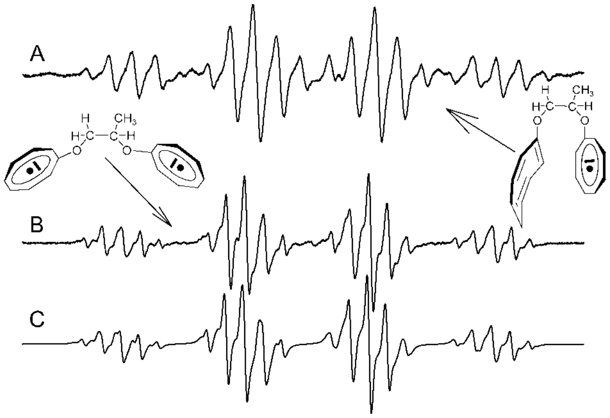
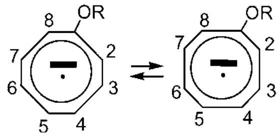


Figure 1. (A) X-band EPR spectrum (scan range = 25 G) of $\mathbf{3_B}^{\bullet-}$ in HMPA recorded at 298 K. EPR coupling constants: $a_H = 5.4$ G (3 Hs) and $a_H = 1.04$ G (4 Hs). (B) EPR spectrum of $\mathbf{3}^{2(\bullet-)}$ taken at 298 K in HMPA with a scan range of 25 G. (C) The computer simulation of B generated using a_{Hs} of 5.63 G for the three ring Hs (3, 5, and 7), 0.76 G for the two ring Hs (4 and 6), 0.81 and 0.71 G for the two pseudo ortho ring protons (2 and 8), 0.30 G for the 2 γ Hs on the primary side of $\mathbf{3}^{2(\bullet-)}$; and a_{Hs} of 5.52 G for the 3 ring Hs (3, 5, and 7), and 0.83 G for the other 4 ring Hs on the secondary side of $\mathbf{3}^{2(\bullet-)}$. The spectrum for the primary side of $\mathbf{3}^{2(\bullet-)}$ is shifted 0.04 G downfield relative to that for the secondary side, and $\Delta w_{pp} = 0.20$ G.

Scheme 3



EPR pattern for the simple isopropoxy-COT anion radical reveals coupling from only the ring protons. However, a homohyperconjugative interaction between the γ carbon and the ipso carbon results in observation of extra hyperfine lines in the case of *n*-propoxy COT$^{\bullet-}$.[6] This interaction should render the EPR pattern of $\mathbf{3_B}^{\bullet-}$ very different from that of $\mathbf{3_A}^{\bullet-}$.

The reduction of **3** in hexamethylphosphoramide (HMPA), where ion association is absent,[7] with a very molar deficient amount of potassium metal gives rise to solutions that exhibit the EPR signal for $\mathbf{3_B}^{\bullet-}$ (Figure 1). Hence, the equilibrium described in Scheme 2 lies far to the right. The solution electron affinity of the COT ring on the secondary side is larger than that on the primary side. The electron–proton couplings reveal an electronic interaction between the reduced COT moiety and the unreduced D_{2d} COT unit, which prevents the reduced COT ring system from becoming completely planar. There is spin drainage into the “neutral” ring, but $a_H < \Delta w_{pp}$.

The COT moiety in the anion radicals of primary and secondary alkoxy substituted COTs have planar D_{4h} structures (Scheme 3).[6,8] However, when the substituent is a bulky *tert*-butoxy group, perfect planarity is prohibited due to the steric interactions between the methyl and ring protons.[9] 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 due to the protons on positions 2, 4, 6, and 8.[6] The appearance of the EPR spectrum of *tert*-butoxy-COT$^{\bullet-}$ is significantly different due to the altered magnitudes of both splittings (3 Hs with $a_H = 4.89$ G and 4 Hs with $a_H = 1.30$ G).[6,9] When $[K^+] \ll [\mathbf{3}]_{total}$, the EPR pattern for $\mathbf{3_B}^{\bullet-}$ (3 Hs with $a_H = 5.4$ G and 4 Hs with $a_H = 1.04$ G) reflects a system with a degree of ring puckering between that for *tert*-butoxy-COT$^{\bullet-}$ and a planar secondary alkoxy-COT anion radical.

Further reduction of $\mathbf{3_B}^{\bullet-}$ yields solutions in which the EPR pattern of $\mathbf{3_B}^{\bullet-}$ is replaced with a pattern that is due to the

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[6] Stevenson, C. D.; Davis, J. P.; Reiter, R. C. *J. Phys. Chem. A* **1999**, *103*, 5343.

[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.

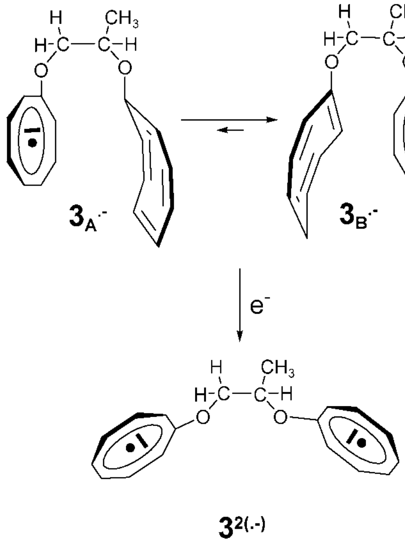
[8] (a) Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500. (b) Goldsmith, D. J.; Bowen, J. P.; Qamhiyeh, E.; Still, W. C. *J. Org. Chem.* **1987**, *52*, 951.

[9] Stevenson, C. D.; Hienle, L. J.; Davis, J. P.; Reiter, R. C. *J. Am. Chem. Soc.* **2002**, *124*, 2704.

simultaneous presence of two anion radicals with identical concentrations, Figure 1. Neither radical shows any sign of nonplanarity. One appears as a primary and the other as a secondary alkoxy-COT$^{\bullet-}$ system. The best explanation for this is the formation of the dianion diradical ($\mathbf{3}^{2(\bullet-)}$) in which there is no measurable electron−electron coupling even in the frozen solution.

The reduction of the COT moiety on the secondary side promotes an electronic interaction between the two ring systems in $\mathbf{3_B}^{\bullet-}$. Hence, the reduction (flattening) of the first ring lowers the reduction potential of the other ring, and the reactions shown in Scheme 4 prevent the observation of $\mathbf{3_A}^{\bullet-}$.[10]

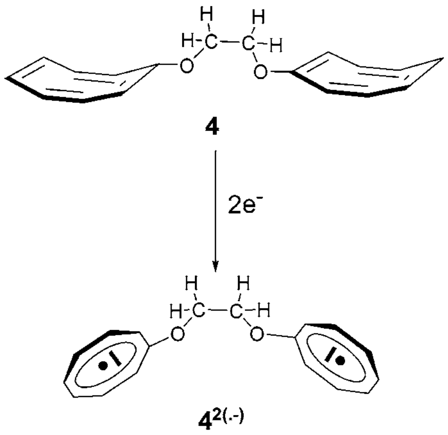
Scheme 4



The hyperfine pattern of $\mathbf{3}^{2(\bullet-)}$ reveals the nonequivalency of the psuedo-ortho protons on the primary side. The anion radicals of all previously studied monosubstituted COT systems yield identical splittings for the two psuedo-ortho protons (positions 2 and 8).[6] However one proton is actually closer to the ipso carbon. The apparent equivalency has been attributed to quantum mechanical tunneling between the two D_{4h} structures, Scheme 3.[9] Apparently, the presence of the second reduced ring renders positions 2 and 8 nonequivalent on the primary side of $\mathbf{3}^{2(\bullet-)}$.

Based upon these results, it is predicted that the reduction of 1,2-bis-cyclooctatetraeneoxyethane (**4**), where both COT moieties are primary and identical, would yield only the two electron reduction product ($\mathbf{4}^{2(\bullet-)}$) with nonequivalent psuedo-ortho protons, Scheme 5. The room temperature EPR pattern produced by the reduction of **4**, with a very deficient amount of metal, exhibits the presence of only the diradical dianion, $\mathbf{4}^{2(\bullet-)}$, which shows a clear nondegeneracy of the psuedo-ortho protons, Figure 2.[11] Further reduction results in the formation of the trianion radical and ultimately the tetraanion.[12]

Scheme 5



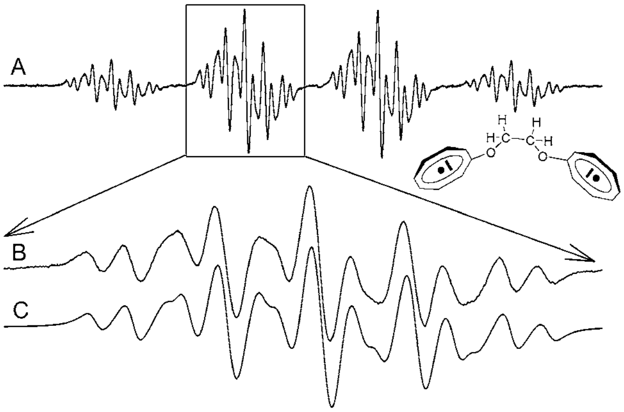


Figure 2. (A) X-band EPR spectrum (scan range = 25 G) of $\mathbf{4}^{2(\bullet-)}$ in HMPA recorded at 298 K. (B) Spectrum of the second bundle of lines (scan range = 5.0 G). (C) The computer simulation of B generated using a_{Hs} of 0.79 G for two of the ring protons (4 and 6), 0.74 and 0.84 G for each of the pseudo ortho protons (2 and 8), and 0.31 G for the 2 γ protons (note: a_{H} for the other three ring protons is 5.585 G); $\Delta w_{\mathrm{pp}} = 0.15$ G.

Complete energy minimizations using the PM3//B3LYP/3-21G* protocol carried out on the anion radical of 1,2-bis-cyclooctatetraeneoxypropane ($\mathbf{3_B}^{\bullet-}$) reveals a structure that is quite consistent with the observed electronic properties of these systems (Figure 3). Indeed, in the anion radical, there is predicted drainage of spin density from the reduced ring to the unreduced ring. This spin drainage is insufficient to produce observable splittings from the protons on the unreduced side. The predicted total p_z spin density on the unreduced COT ring system is only 0.017, spread over all eight carbons. However, the loss of spin density by the

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(10) PM3//B3LYP/3-21G* calculations suggest that when one ring is reduced to its anion radical the other ring is not as puckered as it was in the neutral system. There is some charge and spin drainage from the reduced to the unreduced ring.

(11) Studies with COT−O−CD_2−CD_2−O−COT validated our a_{H} assignments.

(12) The ^{1}H NMR spectrum of the tetraanion is consistent with the two D_{8h} fully reduced ring systems.

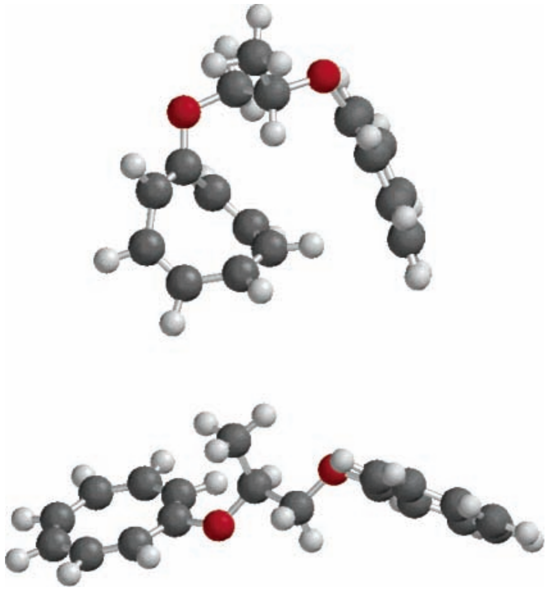

Figure 3. PM3//B3LYP/3-21G* predicted geometry of the anion radical of 1,2-bis-cyclooctatetraeneoxypropane, $\mathbf{3_B}^{\bullet-}$ (upper), and of the dianion diradical, $\mathbf{3}^{2(\bullet-)}$ (lower).

reduced ring is sufficient to cause some puckering of the COT ring on the anion radical side (Figure 3). When the unreduced $-$O$-$COT moiety is replaced with a hydrogen atom, the same PM3//B3LYP/3-21G* calculation predicts that the reduced ring remains completely planar with D_{4h} symmetry (Scheme 3).

Accordingly, the calculations predict that both anion radicals in the dianion diradical systems remain planar and with D_{4h} symmetry. The addition of the second electron causes some Coulombic repulsion between the two reduced rings resulting in the predicted geometry, shown in Figure 3. However, the presence of only the first electron causes an attraction and consequent stacking involving the two COT moieties.

The repulsion between the two negatively charged rings helps account for the lack of an observed electron$-$electron coupling in the dianion diradicals ($J \ll a_H$). This is quite consistent with the observations of Russell and Suleman while observing the tryptycene-bis-quinone dianion diradical.[13] They also were unable to observe an electron$-$electron coupling. Their system is rigid, but their semiquinones are even closer together than are the COT anion radicals in $\mathbf{3}^{2(\bullet-)}$.

The reduction of 1,3-bis-cyclooctatetraeneoxybutane (**5**), with a very deficient amount of metal ($[K^+] \ll [\mathbf{5}]_{total}$), yields only the anion radical (electron on the secondary side).[14] The addition of more metal yields (as predicted) the diradical dianion. So, the unreduced ring and the reduced ring in $\mathbf{5}^{\bullet-}$ are still (even with an extra $-CH_2-$ spacer) communicating to render the two electron reduction to the diradical dianion easier than the one electron reduction to the primary (side) anion radical.

In the case of the 1,3-bis-cyclooctatetraeneoxypropane diradical dianion, the nondegeneracy of the psuedo-ortho protons is only obvious near 0 °C. The communication between the COT rings in the anion radicals and the broken degeneracy of the pseudo-ortho protons in the diradical dianions of 1,2- and 1,3-bis-cyclooctatetraeneoxyalkanes results in unprecedented and interesting intramolecular electronic characteristics, and this trend should extend to the polymeric materials as shown in structure **2**.

Acknowledgment. We thank the National Science Foundation (CHE-9617066) and the Camille and Henry Dreyfus Foundation for support.

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(13) Russell, G. A.; Suleman, N. K. *J. Am. Chem. Soc.* **1981**, *103*, 1560.

(14) In some experiments, quantitative ratios of potassium metal to bis-cyclooctatetraene are generated by first reducing a known amount of naphthalene to exhaustion. The bis-cyclooctatetraene system is then added to the known amount of the naphthalene anion radical in solution. Electron transfer is quantitative resulting in the reduced bis-COT system and neutral naphthalene.