

## Spin Densities in Dialkoxy-[16]annulene Anion Radicals: Dimerization of Alkoxy-[8]annulenes

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The anion radicals of alkoxy-substituted cyclooctatetraenes in hexamethylphosphoramide spontaneously dimerize to form the dianions of dialkoxy-[16]annulenes. The dianions reveal the expected high-field NMR resonance for the internal protons. After electron transfer, the EPR spectra of the corresponding anion radicals reveal that only the 1,5-dialkoxy systems are formed. Further, the measured proton and  $^{13}\text{C}$  spin densities show that the odd electron resides in a molecular orbital with six hydrogens in "deep" nodal positions that completely hide them from EPR detection. This MO corresponds to the nonbonding (singly occupied) MO of higher energy after splitting of the degenerate nonbonding MOs by the two-electron-withdrawing substituents. The surprising electron-withdrawing nature of the alkoxy substituents is attributed to a rather strong mixing of the  $\sigma$  and  $\pi$  systems in [16]annulene.

Some 120 years passed between the discovery of the first annulene (benzene) and the synthesis of the second annulene (cyclooctatetraene) in 1911.<sup>1</sup> However, the next 4 score and 10 years witnessed a considerable maturing of the science of the annulenes, which has been nicely reviewed by Kennedy, Lloyd, and McNab.<sup>2</sup> The majority of the studies on annulene chemistry have been concerned with the aromatic (the  $4n + 2\pi$ -electron annulenes) and the antiaromatic (the  $4n\pi$ -electron annulenes) properties.<sup>2</sup> As would be predicted by the Hückel rule, the  $4n\pi$ -electron systems proved to be much more reactive than are the aromatic annulenes. Indeed, the  $4n\pi$ -electron annulenes undergo a variety of intramolecular and intermolecular reactions (including polymerization) that are not seen in aromatic systems.<sup>3</sup>

[8]Annulene (COT) undergoes a truly unique (electron catalyzed) self-condensation that results in the formation of an annulene with twice as many carbons ([16]annulene).<sup>4</sup> COT in hexamethylphosphoramide (HMPA) readily abstracts the 2s electron from lithium metal to form its

$D_{4h}$  anion radical.<sup>5</sup> The resulting anion radical, which is free of ion association,<sup>6</sup> spontaneously (over a period of several days) dimerizes at ambient temperatures, and the [2 + 2] dimer subsequently undergoes ring opening to form the dianion of [16]annulene. Simultaneously the original EPR signal for  $\text{COT}^{\cdot-}$  is gradually replaced by that of [16]annulene $^{\cdot-}$ , Figure 1, as the dianion of [16]annulene loses an electron, and the resulting anion radical disproportionates to the dianion and neutral molecule of [16]annulene, Scheme 1.<sup>4</sup> This reaction does not take place when the anion radicals are ion associated, and no other annulene system is known to undergo an analogous dimerization.

Much more information concerning the quantum chemistry of the annulenes has been garnered through the study of the anion radicals of substituted systems than from studies of the unsubstituted annulenes (or their anion radicals) themselves.<sup>5,6</sup> With the exception of substituted  $\text{COT}^{\cdot-}$ s, there are no known substituted anion radicals of  $4n\pi$ -electron annulenes. The traditional synthetic scheme for [16]annulene<sup>7,8</sup> is simply not amenable to the formation of substituted systems. Here, we report that the monosubstituted anion radicals of cyclooctatetraene can be coaxed to dimerize in a manner that is analogous to the dimerization of  $\text{COT}^{\cdot-}$  and that the anion radicals of the resulting disubstituted [16]annulenes reveal some unexpected and rather interesting quantum mechanical properties.

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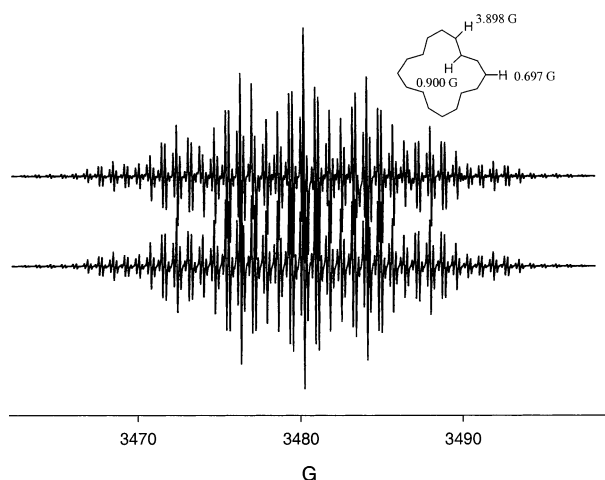
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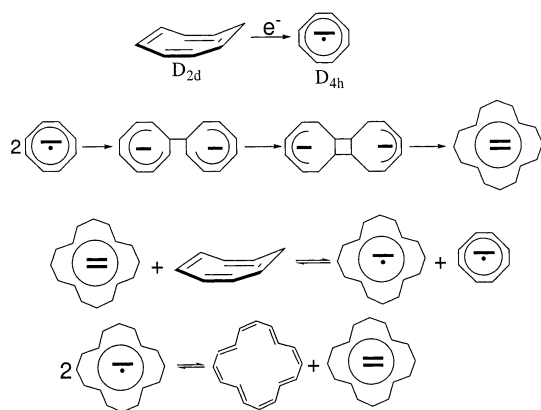
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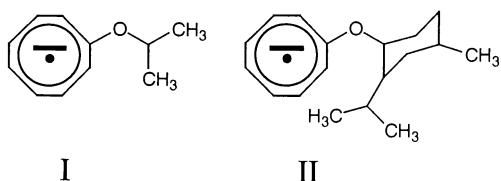
**FIGURE 1.** EPR spectrum of the anion radical of [16]annulene. Below is the computer-generated simulation using a  $\Delta W_{pp}$  of 0.05 G and coupling constants shown.

### SCHEME 1

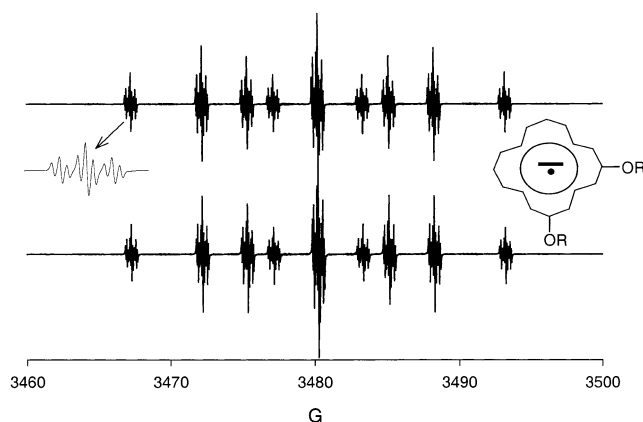


### Results and Discussion

The reduction of COTs with large or small alkoxy substituents in HMPA by lithium metal under high vacuum conditions yields solutions that upon EPR analysis result in the expected quartet of pentets.<sup>9</sup> The observed splittings are  $a_H = 5.55$  (3 Hs) and 0.76 G (4 Hs) for the isopropoxycyclooctatetraene anion radical  $\{(\text{CH}_3)_2\text{CHO}-\text{COT}^{\cdot-}\}$  and  $a_H = 5.78$  (3 Hs) and 0.68 G (4 Hs) for the menthoxycyclooctatetraene anion radical ( $\text{C}_{10}\text{H}_{19}\text{O}-\text{COT}^{\cdot-}$ ), see structures **I** and **II**.



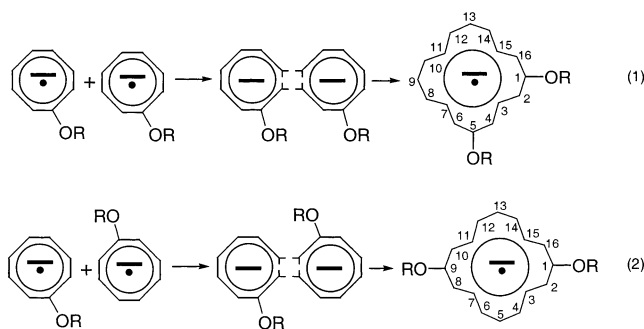
Over a period of several weeks a new EPR spectrum, due to the interaction of the odd electron with four pairs of protons ( $a_H = 8.045$ , 4.932, 0.318, and 0.092 G), appears that gradually replaces the spectra of **I** and **II**, Figure 2. This final EPR spectrum is strong and well-



**FIGURE 2.** (Upper) X-band EPR spectrum of a reduced solution of menthoxy-COT in HMPA after 2 weeks at room temperature. (Lower) A computer simulation generated using a  $\Delta W_{pp}$  of 0.035 and proton couplings of 8.045 (2H), 4.932 (2H), 0.318 (2H), and 0.092 G (2H). This is a spectrum of the anion radical of dimethoxy-[16]annulene, which resulted from the dimerization of the anion radical of menthoxy-COT. The small inset is a magnification of the first 9 lines.

resolved, and has an exceptionally narrow line width ( $\Delta W_{pp} = 0.035$  G). The gradual replacement of the 20-line EPR signals for the monomers with the 81-line patterns for the dimers follows the same time line as the replacement of the signal for  $\text{COT}^{\cdot-}$  with that for the anion radical of [16]annulene. If indeed this 81-line pattern represents  $\text{C}_{16}\text{H}_{14}(\text{OR})_2^{\cdot-}$ , only 8 of the 14 ring protons are resolved. The remaining six must be in deep quantum mechanical nodes.

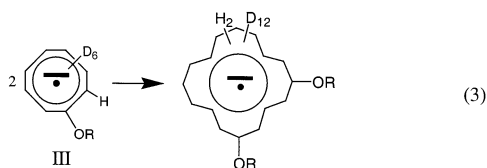
One can envision many isomers of dialkoxy-substituted [16]annulene, but the menthoxy substituent is quite large, and steric considerations eliminate the possibilities of the substituents being internal or adjacent (pseudo-ortho). Also, the 2 + 2 cycloaddition joins two double bonds to form a four-member ring. The short bonds have a bond order that better allows for the [2 + 2] cycloaddition. Considering all this, only the isomers with the substituents in the 1,5 positions (as shown in reaction 1) or in the 1,9 positions (as shown in reaction 2) represent probable products, and only the product of reaction 1 can be consistent with the observed four sets of two equivalent protons observed in the EPR spectrum. The product of reaction 2 would yield a much different EPR spectrum. Fortunately, isotope studies can be used to check the validity of reaction 1.



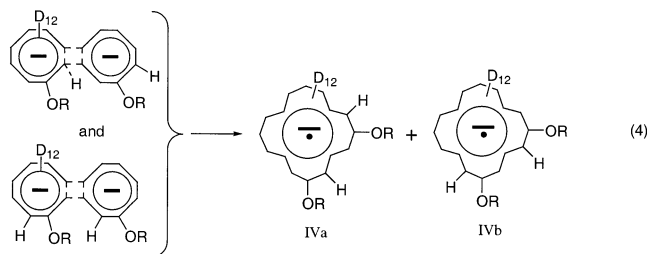
In the case of 1-menthoxy-2-protio-3,4,5,6,7,8-hexa-deuterio-COT (**III** =  $\text{C}_{10}\text{H}_{19}\text{O}-\text{C}_8\text{D}_6\text{H}$ ) all of the ring

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protons, with the exception of one of the pseudo-ortho protons, are replaced with deuteriums. The observation of ring-deuterated 1,5-dimethoxy-[16]annulene anion radicals with two ring protons found after the reaction would constitute evidence of the dimerization (reaction 3).

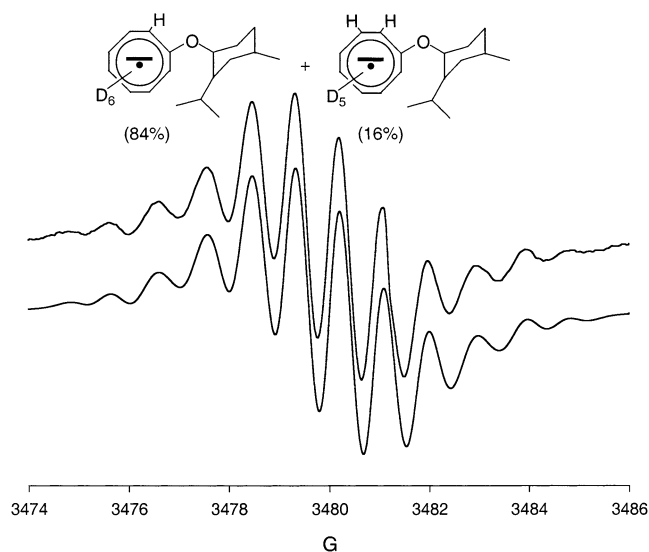


A variety of diprotio isomers can be envisioned from this dimerization, especially if the possible transannular proton shift of the hydrogen in the four-member ring of the intermediate is allowed.<sup>10</sup> Also, our sample of  $C_{10}H_{19}O-C_8D_6H$  is, of course, contaminated with diprotiated material (it contains 16%  $C_{10}H_{19}O-C_8D_5H_2$ ). Hence, a rather complicated mixture of isotopic isomers of the dialkoxy-[16]annulene anion radical is to be expected. However, the radical of highest concentration is expected to be that produced in reaction 4, since **IVa** and **IVb** are degenerate and have a double statistical chance of formation.



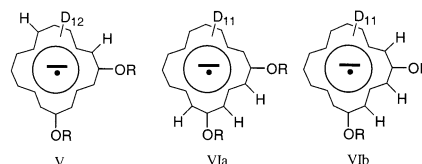
The lithium reduction of our sample of  $C_{10}H_{19}O-C_8D_6H$  yields a solution, which upon EPR analysis reveals the anion radical of  $C_{10}H_{19}O-C_8D_6H$  along with an isotopic impurity, Figure 3. One week later this EPR pattern had changed completely into a rather complex pattern resulting from a variety of anion radicals, Figure 4. One anion radical does, however, stand out as being present in a higher concentration than the others. This radical is easy to detect due to its large doublet from a single proton with  $a_H = 8.07$  G. A nice simulation of this radical is obtained by including 1 H of 8.07 G and 1 H of 0.32 G along with the deuterium splittings, Figure 4. The  $a_D$  values are simply equal to the  $a_H$  values observed in Figure 2 multiplied by the ratio of gyromagnetic ratios ( $\gamma_D/\gamma_H$ ).

By including the other isotopic isomers expected from the dimerization (structures **V** and **VI**) a computer simulation is obtained that accounts reasonably well for the experimental spectrum, Figure 4. One of the protiated impurities (triprotiated material) had to be included to account for the EPR lines at the outer edges of the spectrum. This radical is shown in structure(s) **VI** and is degenerate, accounting for its rather high relative concentration. The  $^{13}C$  splittings (explained later) make it necessary that positions 2 and 4 represent the largest



**FIGURE 3.** (Upper) EPR spectrum resulting from the Li reduction of our sample of mono-ring-protiated hexa-ring-deuterated menthoxy-COT in HMPA at room temperature. (Lower) A computer simulation generated using a line width ( $\Delta W_{pp}$ ) of 0.4 G and couplings of  $a_D = 0.87$  (3 D) and 0.105 G (3 D) and  $a_H = 0.68$  G (1H). A 16% protiated impurity with couplings of  $a_D = 0.87$  (2 D) and 0.105 G (3 D) and  $a_H = 0.68$  (1H) and 5.72 G (1H). The scan width is 20 G.

$^1H$  coupling (8.07 G) and that 6 and 16 have the 0.32 G  $^1H$  coupling.



The odd electron in the unsubstituted anion radical of [16]annulene lies in a pair of degenerate nonbonding molecular orbitals ( $\Psi_8$  and  $\Psi_9$ ) with four nodal planes going through either positions 1–9, 3–11, 5–13, and 7–15 in  $\Psi_8$  or through positions 2–10, 4–12, 6–14, and 8–16 in  $\Psi_9$ , Figure 5.<sup>11</sup> Equal mixing of these two MOs yields an MO with all of the coefficients equal to  $1/\sqrt{16}$ . This simple MO would suggest that all of the proton coupling constants for the anion radical of [16]annulene would be identical. This is, however, far from the empirical fact (the  $a_H$  values are shown in Figure 1).<sup>11</sup>

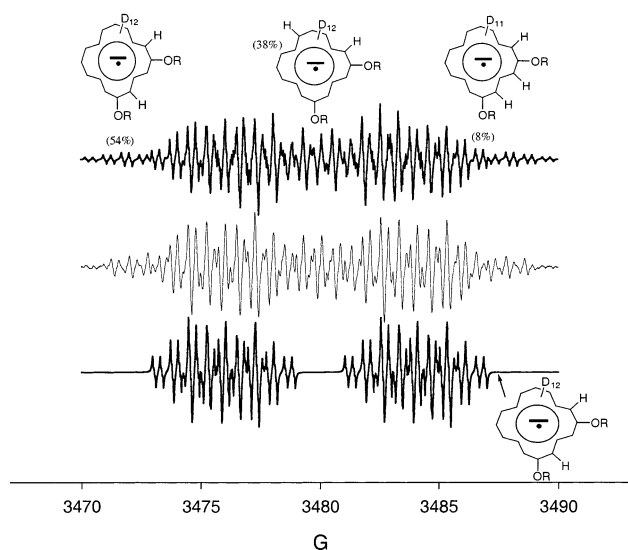
Differing intramolecular environments (e.g. internal protons) cause major perturbations in the carbon  $p_z$  spin densities ( $\rho_{p_z}$ ), which are related to the McConnell constant ( $Q$ ) and the  $a_H$  as shown in eq 5.<sup>12</sup> These perturbations are difficult to predict quantum mechanically even with high-level calculations.

$$a_H = Q\rho_{p_z} \quad (5)$$

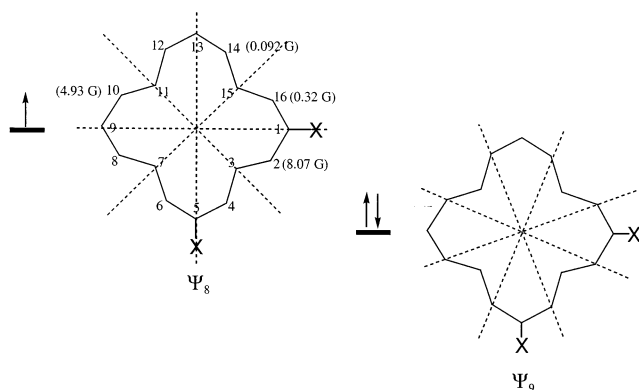
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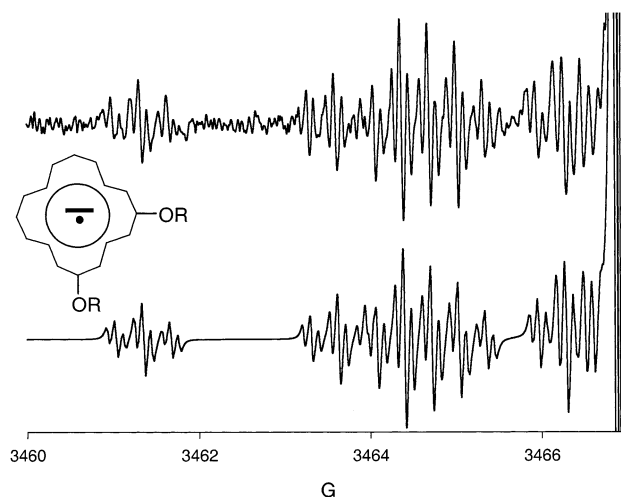
**FIGURE 4.** (Middle) Ambient temperature EPR spectrum of the same sample as shown in Figure 3 but recorded 2 weeks later. (Lower) A computer simulation generated with  $\Delta W_{pp} = 0.05$  G and couplings of  $a_D = 1.24$  (1 D), 0.049 (1 D), and 0.76 G (2 D) and  $a_H = 8.07$  G (1H) and 0.32 G (1H). (Upper) A computer simulation generated by adding three EPR signals together. One is the system mentioned above (54%) plus a radical with  $a_D = 1.24$  (2 D), 0.049 (1 D), and 0.76 G (1 D) and  $a_H = 4.93$  G (1H) and 0.32 G (1H) at 38% plus a radical with  $a_D = 0.049$  (1 D) and 0.76 G (2 D) and  $a_H = 8.07$  (2H) and 0.32 G (1H) at 8%.



**FIGURE 5.** The nonbonding molecular orbitals of the anion radical of 1,5-disubstituted-[16]annulene where the substituents act as electron-withdrawing agents stabilizing  $\Psi_9$  relative to  $\Psi_8$ . These MOs are degenerate in unsubstituted [16]annulene anion radical. The EPR couplings are given on the structure representing the singly occupied MO.

The presence of the two substituents lifts the degeneracy of  $\Psi_8$  and  $\Psi_9$ . There are three electrons in  $\Psi_8$  and  $\Psi_9$ . Hence, the odd electron resides in the MO of highest energy, and this is the MO revealed in the EPR pattern. Only  $\Psi_8$  has properties that are consistent with the observed four sets of proton pairs. Equivalent pairs of Hs are on positions 2–4, 6–16, 8–14, and 10–12. All of the remaining protons are in nodal positions and have  $a_H$  values that are less than 0.02 G.

An electron occupying  $\Psi_8$  would yield definitive proton and  $^{13}\text{C}$  EPR splitting patterns, because all of the visible protons come in pairs, but carbons #3 and #11 should be visible and unique. Even though carbons #3



**FIGURE 6.** (Upper) An enlargement of the low-field region ( $^{13}\text{C}$  portion) of the EPR spectrum of the 1,5-dimethoxy-[16]annulene anion radical in HMPA. This is the very same scan shown in Figure 2, but amplified. Only the  $^{13}\text{C}$  hyperfine lines are shown on-scale. (Lower) A computer simulation generated using  $a^{13}\text{C}$  of 11.87 (1  $^{13}\text{C}$ ), 7.31 (1  $^{13}\text{C}$ ), 5.78 (2  $^{13}\text{C}$ ), 4.51 (2  $^{13}\text{C}$ ), and 1.57 G (2  $^{13}\text{C}$ ) and the proton couplings shown in Figure 2. The lines recorded off-scale near 3467 G represent the beginning of the proton spectrum.

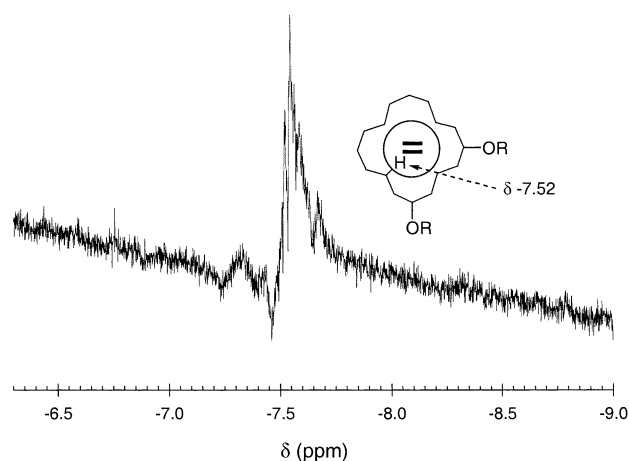
and #11 are in nodal planes and have  $p_z$  spin densities ( $\rho_p$ ) near zero, they would acquire coupling constants from the spin densities ( $\rho_j$ ) on the carbons that are adjacent to them in accord with the relationship shown in eq 6.<sup>12d</sup> It is clear from eq 6 that a large  $^{13}\text{C}$  splitting is possible even though the  $p$  orbital spin density on that particular carbon is zero ( $\rho_{p_i} = 0$ ). Such an  $a^{13}\text{C}_i$  value arises solely from the interaction between the  $^{13}\text{C}$  nucleus and the  $p_z$  spin densities ( $\rho_j$ ) on the adjacent carbons.

$$a_{^{13}\text{C}_i} = Q_i \rho_{p_i} - Q_j \sum_j \rho_j \quad (6)$$

Fortunately the EPR pattern for the dialkoxy-[16]annulene anion radical is very strong allowing easy observation of the  $^{13}\text{C}$  hyperfine pattern resulting from couplings sufficiently large to extend outside of the proton window, Figure 6. The computer simulation of the  $^{13}\text{C}$  pattern in Figure 6 does, indeed, reveal two unique carbons. The remaining carbons come in pairs, consistent with the product of reaction 1. The very large  $a^{13}\text{C}$  observed for a unique carbon is consistent with the protons on positions #2 and #4 having the largest (8.07 G) splitting, and the  $a_H$  values for position #6 and #16 being 0.32 G. All of the proton splittings can now be assigned, see Figure 5.

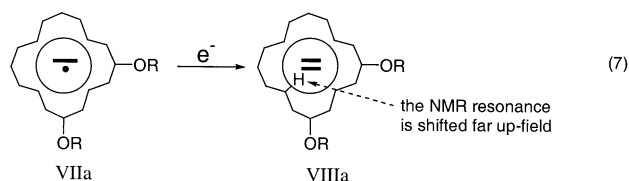
Another rather revealing feature of [16]annulene is that, due to a synergistic interaction between the shielding due to the extra electrons and the diamagnetic ring current, the NMR chemical shift<sup>7</sup> of the internal protons falls very far upfield,  $\delta -8.03$ . The presence of the very large resonances from the solvent prevents the observation of low-intensity absorptions in the region of “normal” chemical shifts, but those for the internal protons should be visible. After a sample had displayed the clear resonance for what is believed to be the anion radical of 1,5-dimethoxy-[16]annulene (**VIIa**), the solution was





**FIGURE 7.**  $^1\text{H}$  NMR spectrum of the internal protons of the 1,5-dimethoxy-[16]annulene dianion recorded in HMPA at ambient temperature. This sample was prepared by first reducing menthoxy-COT in HMPA with Li metal, leaving the sample at room temperature for two weeks, and then further reducing the anion radical to the dianion.

further exposed to the lithium metal until the solution became EPR silent. At this point, the HMPA solution was poured into an attached NMR tube, which was subsequently sealed from the remainder of the apparatus. NMR analysis of this solution (Figure 7) clearly reveals a multiplet at  $\delta -7.52$ , which must be due to the internal protons of the newly formed dianion (**VIIIa**), reaction 7.



The known dimerization of  $\text{COT}^{\cdot-}$ , the isotopic substitution experiment, the observed  $^{13}\text{C}$  splittings, and the NMR observation of protons at  $\delta -7.55$  leave little doubt that the dialkoxy- $\text{COT}^{\cdot-}$  systems analogously dimerize to form the anions of dialkoxy-[16]annulenes. The nature of the EPR spectrum, however, requires that the alkoxy groups act as electron-withdrawing substituents and stabilize  $\Psi_9$  relative to  $\Psi_8$ , Figure 5. At first this seems problematic, since alkoxy groups act in an electron-donating manner when attached to the solvated [8]-annulene anion radical. However, it is well-documented that the alkoxy group can act as either an electron-donating ( $\sigma_{\text{para}} = -0.27$  for  $-\text{OMe}$ ) or electron-withdrawing substituent ( $\sigma_{\text{meta}} = +0.12$ ).<sup>13</sup> More importantly it is an electron-withdrawing substituent in terms of its polar substituent constant, Taft's  $\sigma_1$ .<sup>13</sup> The anion radical of [16]annulene has more  $\sigma-\sigma$  interaction than does the anion radical of COT,<sup>14</sup> and the alkoxy group is strongly electron withdrawing in a  $\sigma$  framework ( $\sigma_1 = 0.27$ ).

## Conclusions

The anion radicals of alkoxy-substituted cyclooctatetraenes free of ion association in HMPA spontaneously dimerize and undergo electron transfer to yield exclu-

sively the 1,5-disubstituted isomers of the anion radical of the dialkoxy-[16]annulenes. The exclusive formation of the 1,5-isomer is a result of the inability of the substituents to be in internal or in adjacent positions. This argument, however, does not rule out the possible formation of the 1,9-disubstituted [16]annulene. However, full geometry optimization with the PM3 protocol suggests that the intermediate in reaction 1 is 3 kcal/mol lower in energy than that in reaction 2. This is sufficient to account for the exclusive formation of the 1,5 isomer.

These dialkoxy-[16]annulene anion radicals can be further reduced to their respective dianions, which demonstrate a strong diatropic ring current upon NMR analysis. Unlike when attached to an [8]annulene anion radical, the alkoxy groups act as electron-withdrawing substituents in the [16]annulene environment. This can be attributed to the greater  $\sigma-\pi$  interaction in the larger annulene anion radical, and it renders the wave function with nodal planes across the internal protons ( $\Psi_8$ ) higher in energy than the wave function with no internal nodal positions ( $\Psi_9$ ). Hence the odd electron is exclusively located in  $\Psi_8$ , and the internal protons reside in nodes. These nodal positions are so deep that no trace of an EPR splitting can be observed for the internal protons or other protons in nodal positions. This is true despite the very narrow line widths and high resolution. This represents the first study of a substituted  $4n$   $\pi$ -electron anion radical other than that of COT, and it suggests that the remaining substituted  $4n$   $\pi$ -electron annulenes also conceal a host of quantum mechanical surprises.

## Experimental Section

**Alkoxy-cyclooctatetraenes.** The syntheses of the alkoxy-COTs were based on Krieb's preparation of *tert*-butoxycyclooctatetraene.<sup>15</sup> 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 as previously described.<sup>9</sup>

The resulting alkoxy-COT was purified via vacuum distillation (1 Torr and 45 to 50 °C for isopropoxy-COT). NMR and mass spectral analysis are consistent with  $\text{C}_8\text{H}_7$ -alkoxide in all cases. In each case the parent mass spectral peak represents the molecular ion of the alkoxy-COT (e.g.  $m/e$  162 for isoprop-O-COT), and the base peak is  $m/e$  120 (from  $\text{COT-OH}^+$ ).

The synthesis of the pseudo-ortho protiated ring deuterated menthoxy-COT (**IIIa**) was also based on our synthesis of "pseudo-ortho" deuterated *tert*-butoxy-COT.<sup>16</sup>

Potassium metal (0.12 mol) was reacted with a slight excess of menthol in dry tetrahydrofuran (THF) to give a solution of the alkoxide. The mixture was subsequently refluxed for 6 h in a nitrogen atmosphere. The resulting alkoxide solution was then added dropwise to a stirred solution consisting of 0.9 equiv of perdeuterated bromocyclooctatetraene<sup>17</sup> in THF at  $-79$  °C under a nitrogen atmosphere. After the addition was complete, the solution was allowed to warm to room temperature, and the THF was removed under reduced pressure. Five equivalents of water was then added to quench the reaction.

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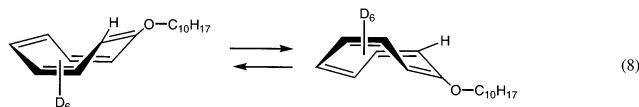
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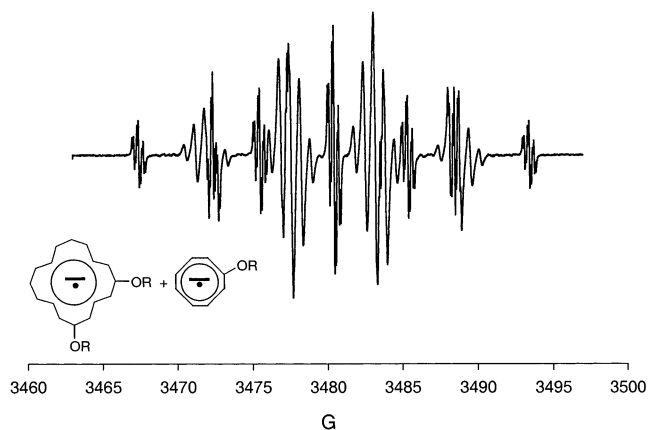
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The products were extracted with diethyl ether. The ether solution was dried and the ether removed under reduced pressure. The intermediate in the reaction between the monobromo-COT and the alkoxide is cyclooctatrieneyne.<sup>15</sup> Consequently, the excess menthol results in the formation of 1-menthoxy-2-protio-hexadeuterio-cyclooctatetraene, which exists in two dynamic conformations (reaction 8).



The resulting menthoxy-COTs were purified via vacuum distillation ( $10^{-4}$  Torr, 95 to 110 °C) and further purified on a silica gel column eluted with hexanes. NMR and mass spectral analysis are consistent with a mixture of 2-protio-hexa-ring-deuterio-menthoxy-COT and 2,3-diprotio-penta-ring-deuterio-menthoxy-COT. The parent mass spectral peaks represent the molecular ions of  $m/e$  264 and 263.

**Reductions.** The reductions were carried out by allowing HMPA solutions of the alkoxy-cyclooctatetraene to come into contact with lithium metal in vacuo as previously described.<sup>17</sup> The EPR spectra were recorded with an X-band spectrometer equipped with a variable-temperature unit. The early recordings revealed the expected spectra for the alkoxy-COT anion radicals. After a day or so, the anion radical of both the alkoxy-COT and dialkoxy-[16]annulene can be observed simultaneously, Figure 8. Eventually, only the anion radical of the [16]annulene system is observable, Figure 2. At this time, the solution was again exposed to the lithium metal and then



**FIGURE 8.** EPR spectrum of a sample of a lithium-reduced menthoxy-COT in HMPA recorded several days after the reduction. Note that the EPR spectra of the anion radicals of menthoxy-COT and of dimethoxy-[16]annulene are observed simultaneously.

poured into an attached NMR tube. An NMR of a sample obtained in this manner is shown in Figure 7.

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