

Observation of Both Jahn–Teller Distorted Forms (b_{1g} and b_{2g}) of the Cyclooctatetraene Anion Radical in a 1,2-Disubstituted System

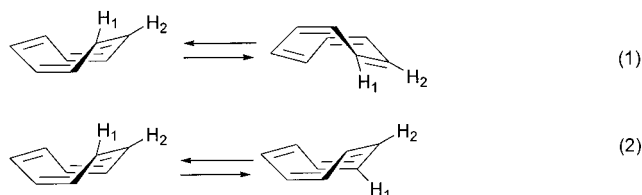
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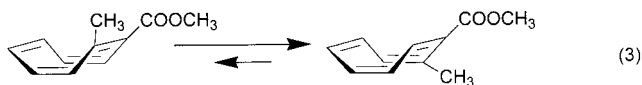
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Abstract: The anion radical of cyclooctatetraene (COT) must undergo a Jahn–Teller distortion from its ideal D_{8h} symmetry. Both B3LYP/6-31+G* calculations and EPR observation have shown that the COT moiety in the anion radical of 1,2-dicarbo-*tert*-butoxycyclooctatetraene exists in a pair of degenerate D_{4h} alternating bond angle conformations (a b_{1g} distortion). The rapid ($k = 3 \times 10^7 \text{ s}^{-1}$) interconversion between the two identical conformations leads to specifically predicted line width alternation effects in the EPR spectrum. The COT ring system in the 1,2-dicarbomethoxycyclooctatetraene anion radical $[(\text{CH}_3\text{OOC})_2\text{COT}^{\bullet-}]$, on the other hand, has a ground state with alternating bond lengths. Since this b_{2g} distorted ($\text{COT}^{\bullet-}$) system has a plane of symmetry that can be drawn through the molecule and between the two substituents, no line width alternation effects can take place. However, in this system, the B3LYP/6-31+G* calculations predict an energy difference between the b_{1g} and b_{2g} distorted $\text{COT}^{\bullet-}$ ring systems of less than 1 kcal/mol. In support of this, the EPR data are best simulated in terms of the presence of both Jahn–Teller distorted forms of the anion radical.

There was considerable disappointment following the first synthesis of cyclooctatetraene (COT) by Willstater some 89 years ago. This was a result of the realization that the properties of COT were olefinic, as opposed to those expected for an expanded benzene system.¹ In the early 60s, however, it was realized that the D_{2d} tub conformation, with alternating double bonds (1.34 Å) and single bonds (1.48 Å) of [8]annulene, endowed this system with the ability to undergo a rich collection of dynamical intramolecular processes, including ring inversion² and bond shift³ (e.g. reactions 1, and 2). The alternating single



and double bonds in neutral COT mean that two isomers (double or single bond between substituents) are possible for every 1,2-disubstituted COT system. In fact, both isomers of 1-carbomethoxy-2-methyl cyclooctatetraene have been experimentally observed (reaction 3).^{3b} The rich dynamical behavior of COT



has rendered it the subject of chapters and even entire books.^{4,5a}

(1) (a) Willstater, R.; Waser, E. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 3423. (b) Willstater, R.; Waser, E. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 517.

(2) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576.

(3) (a) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573. (b) Anet, F. A. L.; Bock, L. A. *J. Am. Chem. Soc.* **1968**, *90*, 7130.

(4) Paquette, L. A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1992; Vol. 2, pp 1–77.

Fifty two years after the first synthesis of COT,¹ experimental evidence suggesting that neutral COT could be flattened out via the addition of a single π -electron was reported.⁶ The planar nature of the anion radical of substituted COT systems would apparently eliminate the possibility of structural isomerism. Modern theory agrees regarding the planar nature of the ring system in the open shell anion of [8]annulene or substituted [8]annulene. Ab initio calculations, however, reveal that there are two possible planar structures that are of D_{4h} geometry for the planar eight-membered ring.⁷ The necessary Jahn–Teller distortion from D_{8h} symmetry⁸ comes from either a b_{2g} distortion or a b_{1g} distortion, Figure 1. Both distortions yield a pair of rapidly interconverting D_{4h} equilibrium geometries with either alternating bond lengths (ABL) or alternating bond angles (ABA).⁷ Since energy separation between the two conformers (ΔE) is some 4–5 kcal/mol, the ABL conformation is the only one to have been observed. Theory predicting an attenuation of ΔE due to the presence of electron-withdrawing substituents⁷ suggested to us the possibility of synthesizing an appropriately substituted COT anion radical with the ring system in a ground-state ABA geometry.

If, indeed, a 1,2-disubstituted COT anion radical with ABA ground state geometry for the ring system could be generated, the protons in the 3 and 8 positions would not be magnetically equivalent.⁹ This is also true for the protons in the 4 and 7, and 5 and 6 positions, see reaction 4. In fact, if reaction 4 were

(5) (a) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclo-octatetraene and its Derivatives*; Cambridge University Press: New York, 1978. (b) Stevenson C. D.; Davis, J. P.; Reiter, R. C. *J. Phys. Chem. A* **1999**, *103*, 5343.

(6) Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360.

(7) Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500.

(8) Since three electrons occupy two degenerate e_{2u} orbitals in the D_{8h} system, a Jahn–Teller distortion is necessary, see: Moss, R. E. *Mol. Phys.* **1966**, *10*, 501.

(9) In this calculation methoxy moieties represented the alkoxy groups to keep the computation time as reasonable as possible.

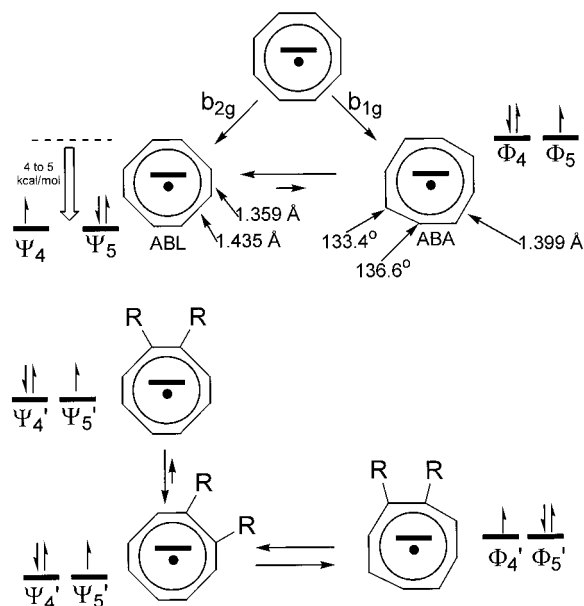
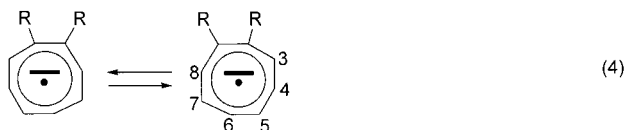


Figure 1. Pictorial representation of the Jahn–Teller distortion of the D_{8h} COT anion radical to the bond length alternating (ABL) and bond angle alternating (ABA) D_{4h} geometries. The alternating bond length geometry is the more stable form, and its wave functions are generated via the equal mixing of the two LCAOs for the alternating bond angle geometry. Below is the analogous representation for the equal mixing of Φ_4 and Φ_5 for a disubstituted system with the substituents serving as electron-withdrawing groups. The bond angles and bond lengths are those reported in ref 7. The presence of the two substituents splits the degeneracy of the ABL system due to steric interactions.

slow on the EPR time scale, six different ring protons should be observable upon EPR analysis. If, on the other hand, reaction 4 were fast on the EPR time scale, predictable line width alternation effects should be observed.¹⁰



The wave functions for the doubly degenerate orbitals containing the odd electron in the COT anion radical are fundamentally different in the ABL structure (Ψ_4 and Ψ_5 in eqs 5 and 6) than they are in the ABA structure (Φ_4 and Φ_5 in eqs 7 and 8).⁷

$$\Psi_4 = (0.5/\sqrt{2})(\psi_1 + \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6 - \psi_7 - \psi_8) \quad (5)$$

$$\Psi_5 = (0.5/\sqrt{2})(\psi_1 - \psi_2 - \psi_3 + \psi_4 + \psi_5 - \psi_6 - \psi_7 + \psi_8) \quad (6)$$

$$\Phi_4 = (1/2)(\psi_1 - \psi_3 + \psi_5 - \psi_7) \quad (7)$$

$$\Phi_5 = (1/2)(\psi_2 - \psi_4 + \psi_6 - \psi_8) \quad (8)$$

Ψ_4 and Ψ_5 simply represent 1:1 linear combinations of Φ_4 and Φ_5 [(1/√2) Φ_4 + (1/√2) Φ_5 and (1/√2) Φ_4 - (1/√2) Φ_5 , respectively]. There is no contribution from Φ_4 or Φ_5 to the EPR spectrum of the unsubstituted COT anion radical, due to their higher energy (relative to that of Ψ_4 and Ψ_5). In the case

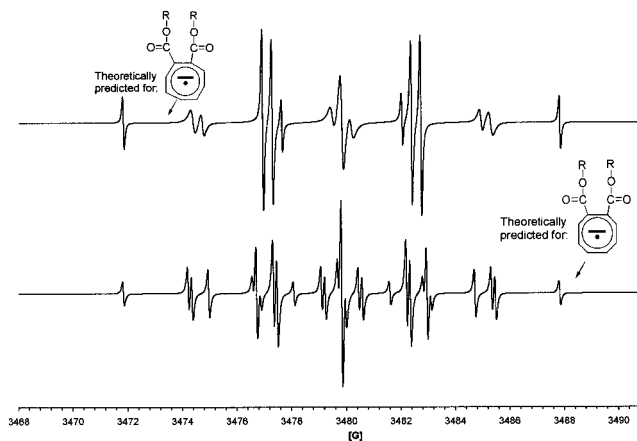


Figure 2. B3LYP/6-31+G* predicted EPR spectra for the ABA (upper) and ABL (lower) COT conformations in a hypothetical dicarboalkoxycyclooctatetraene anion radical. The rapid interchange of the protons on the opposite sides of the ring system causes dramatic line width alternation in the ABA conformation. The ABL system is symmetric (C_2 configuration) with respect to a plane drawn through the molecule and between the substituents. Hence no such line width alternation is possible in this system.

of a 1,2-disubstituted system, the degeneracies of Ψ_4 and Ψ_5 or of Φ_4 and Φ_5 are not removed. However, the presence of the substituents does result in some perturbation in the wave functions.

To a first approximation, the MOs for a 1,2-disubstituted system with the COT ring in the ABA conformation are represented by an equal mixture of Φ_4 and Φ_5 . The ABL conformer would then be represented by an equal mixture of Ψ_4 and Ψ_5 . Hence, the 3, 4, and 5 positions are all nearly equivalent in both the ABA and ABL conformations. Their degeneracy will, however, be broken due to differing proximities relative to the substituents. The two conformations differ in that positions 3 and 8, 4 and 7, and 5 and 6 will not be equivalent due to geometry considerations in the ABA structure (see structure in reaction 4).

Dicarboalkoxy groups represent ideal candidates for the choice of substituents. The functionalities allow conjugation into carbonyl moieties and thus act as electron-withdrawing substituents. To make a simple prediction as to the viability of this approach, B3LYP/6-31+G* calculations were carried out on the 1,2-dicarbomethoxycyclooctatetraene [(CH₃OOC)₂COT] anion radical.⁹ The COT ring was constrained to either the ABA (D_{4h}) or ABL (D_{4h}) configuration as described by Borden et al.⁷ The calculations were carried out allowing geometry optimization of the substituents. The p_z spin densities resulting from these calculations provided input to an EPR computer simulation program to yield rough approximations of the expected EPR patterns for the two conformers, Figure 2. A rate constant of $3 \times 10^7 \text{ s}^{-1}$ was used for reaction 4 in the computer simulation for the ABA system. Note the pronounced line width alternation predicted in the upper spectrum in Figure 2.

Symmetry considerations prohibit the ABL structure from interchanging nonequivalent hydrogens, thus the computer simulation does not predict an analogous line width alternation pattern for this conformation. The simulations of the predicted spectra are purely quantum mechanical (theoretical) in nature, but they reveal vividly different predicted EPR patterns for the ABA and ABL (COT) conformations for the two possible anion radical systems. We were motivated to generate the anion radicals of several dicarboalkoxy-COT systems and record real spectra in anticipation of unraveling their actual conformations.

(10) (a) Fraenkel, G. K. *J. Phys. Chem.* **1967**, *71*, 139. (b) Sullivan, P. D.; Bolton, J. R. *Adv. Magn. Reson.* **1970**, *4*, 39.

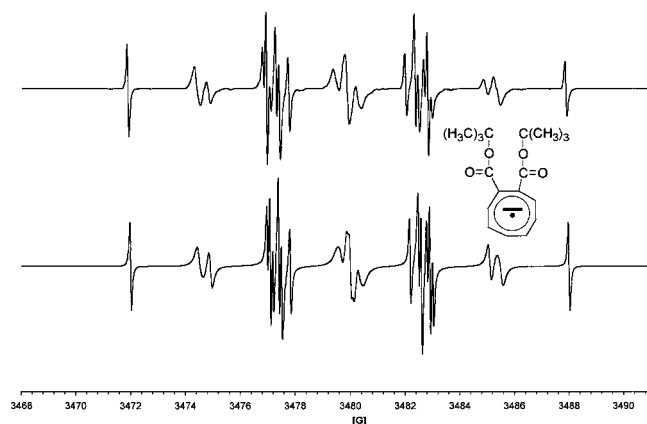
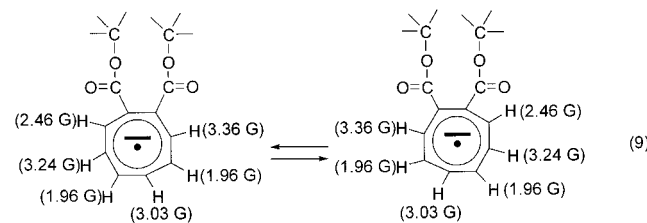


Figure 3. (Upper) EPR spectrum of the 1,2-dicarbo-*tert*-butoxycyclooctatetraene anion radical recorded in HMPA at 298 K. Note the dramatic line with alternation due to the rapid interconversion between the two degenerate ABA conformations of the COT ring system as described in reaction 4. (Lower) A computer simulation generated using the a_{HS} described in the text and a rate constant for reaction 4 of $3 \times 10^7 \text{ s}^{-1}$.

We were also hoping to observe the first example of an ABA conformation for a COT anion radical system.

Results and Discussion

The potassium metal reduction of 1,2-dicarbo-*tert*-butoxycyclooctatetraene ($[(\text{CH}_3)_3\text{OOC}]_2\text{COT}$) in hexamethylphosphoramide (HMPA)¹¹ leads to the corresponding anion radical that is free of ion association and persists for hours at room temperature (Figure 3). The EPR spectrum of $[(\text{CH}_3)_3\text{OOC}]_2\text{COT}^{\bullet-}$ appears remarkably similar to the quantum mechanically predicted spectrum for the anion radical with the COT ring undergoing rapid exchange between the two possible ABA geometric conformations as in reaction 4. A good simulation of this spectrum (Figure 3) was obtained by slightly adjusting the absolute magnitudes of the B3LYP/6-31+G* predicted a_{HS} . The computer simulation was, however, generated without altering the theoretical magnitudes of coupling constant differences for the interchanging protons ($a_{H(8)} - a_{H(3)}$, $a_{H(7)} - a_{H(4)}$, or $a_{H(6)} - a_{H(5)}$) from their quantum mechanically obtained values. The best simulation was obtained using the hyperfine splittings depicted in reaction 9 and a rate constant for reaction 9 of $3 \times 10^7 \text{ s}^{-1}$.



The analogous reduction of 1,2-dicarbomethoxycyclooctatetraene $[(\text{CH}_3\text{OOC})_2\text{COT}]$ in HMPA yields an anion radical solution that, upon EPR analysis (Figure 4), does not reveal the presence of the dynamic exchange exhibited by the di-*tert*-butyl system. In a theoretical sense this is not an unexpected result, as B3LYP/6-31+G* calculations predict that the ABL conformation for the COT ring is more stable than is the ABA

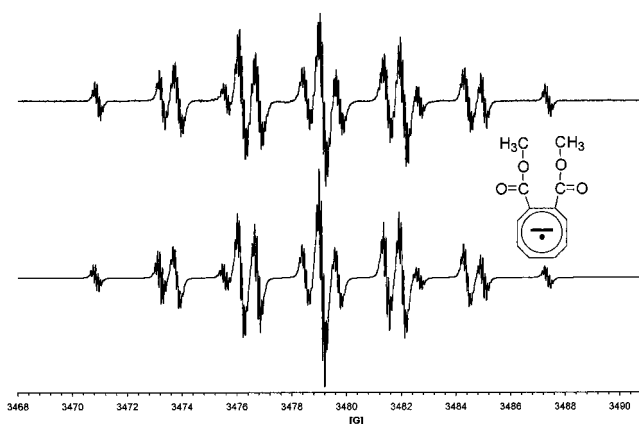
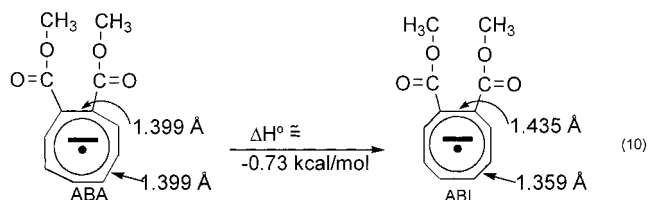


Figure 4. (Upper) EPR spectrum of the 1,2-dicarbomethoxycyclooctatetraene anion radical recorded in HMPA at 298 K. (Lower) A computer simulation generated with coupling constants of $a_{H1} = 3.054$ (2Hs), 2.884 (2Hs), 2.360 (2Hs), and 0.089 G (6Hs) for the ground-state geometry of the ABL ring conformation. A small amount (29%) of the time-averaged ABA conformation of $a_{H1} = 2.693$ (2Hs), 3.045 (2Hs), 2.325 (2Hs), and 0.071 G (6Hs) was mixed into the simulation, and its spectral center was shifted downfield by 0.22 G. The presence of the ABA conformer allows reproduction of the asymmetry observed in the line intensities.

conformation for the COT ring in $(\text{CH}_3\text{COO})_2\text{COT}^{\bullet-}$, reaction 10.^{12a} The ABL conformation cannot be involved in any process that interchanges the proton hyperfine splittings.



There are two conceivable configurations for the ABL conformer: the short bond (1.359 Å) between the substituents or the long bond (1.435 Å) between the substituents.^{12b} The B3LYP/6-31+G* calculations predict the long bond configuration is more stable by 11 kcal/mol. Hence, the EPR spectrum observed (Figure 4) is that for the ABL conformer with the long bond between the substituents. The EPR pattern for this species is accurately simulated in terms of three sets of two equivalent ring protons ($a_{H(3)} = a_{H(8)}$, $a_{H(4)} = a_{H(7)}$, and $a_{H(5)} = a_{H(6)}$) as well as a small septet ($a_{H1} = 0.084$ G) for the methyl protons. The observation of the six methyl protons results from a homohyperconjugative interaction whereby spin is transmitted to a γ proton. Such interactions in COT systems have been previously discussed.^{5b}

Close inspection of the EPR spectrum of $(\text{CH}_3\text{COO})_2\text{COT}^{\bullet-}$ reveals that the high-field hyperfine components are slightly broader than are the low-field components, Figure 4. This asymmetry in line width can only be due to the presence of two very closely related anion radicals. The two species must have coupling constants that are close but not identical, and they must have slightly different g -values. This is the very signature, indicating the simultaneous presence of both the ABA and ABL conformations that was anticipated based upon the B3LYP calculations ($K_{eq} = 0.29$ at 298 K for reaction 10). A satisfactory computer simulation was generated by assuming

(11) Anion radicals are free of ion association in HMPA, see: (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.

(12) (a) It is assumed that the change in entropy (ΔS°) for reaction 10 is 0 and $\Delta E = \Delta H^\circ$. Hence, $\Delta G^\circ = \Delta H^\circ$. (b) Borden et al. (ref 7) found that the best bond lengths for the ABL structure of $\text{COT}^{\bullet-}$ are 1.359 and 1.435 Å. In the ABA structure the bond lengths are 1.399 Å.

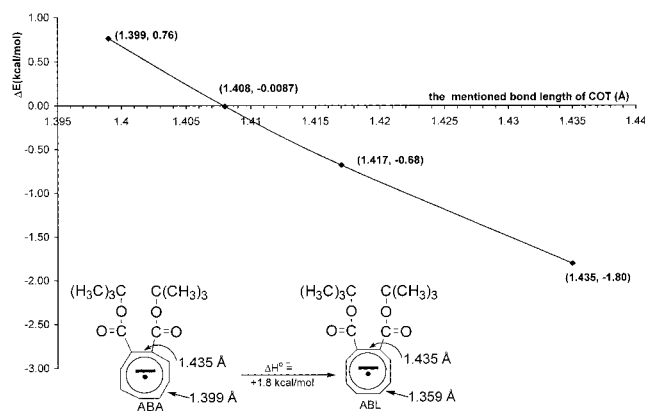


Figure 5. B3LYP/6-31+G* predicted relative energies of the ABA and ABL conformations of the COT ring in the anion radical of 1,2-dicarbo-*tert*-butoxycyclooctatetraene. The COT ring system was constrained in either the ABA or ABL conformation. Due to geometric constraints, the bond angles vary slightly with the choice of the bond length separating the substituents. Note that when the bond separating the substituents is longer than 1.408 Å, the ABA conformation is predicted to be the ground state. Steric repulsion between the substituents renders the bond length close to 1.435 Å.

the existence of both radicals with the ratio of ABA/ABL conformations of 0.29. This value corresponds to a $\Delta E = \Delta H^\circ = \Delta G^\circ$ value of 0.73 kcal/mol.

The B3LYP/6-31+G* calculations on the anion radical of $[(\text{CH}_3)_3\text{OOC}]_2\text{COT}^-$ predict that ΔE falls off rapidly as the bond length for the ring bond between the two substituents increases, Figure 5. These single-point calculations were carried out with various bond lengths between the two functional groups in the ABA conformer. It is expected that this bond length would be longer for the di-*tert*-butyl system than it is in the case of the dimethyl system, due to steric considerations. At 1.408 Å, the two conformations are calculated to be degenerate. Although our quantum mechanical protocol does not yield completely accurate predictions, it is clear that the energy of the ABA conformer is lower than that for the ABL conformer at the longer bond lengths. This would suggest that the EPR pattern for $[(\text{CH}_3)_3\text{OOC}]_2\text{COT}^-$ (Figure 3) should show the presence of the ABA conformer.

As a consequence of the steric interactions, the COT ring in the di-*tert*-butyl system exists predominantly in the two degenerate ABA conformations, while the dimethyl system resides in the ABL conformation. We were motivated to see if the mixed system (1,2-dicarbo-*tert*-butoxymethoxycyclooctatetraene anion radical) had sufficient steric interaction to render the ABA conformation the ground state. This anion radical exhibits six different ring splittings, Figure 6, but the differences in the magnitudes of these splittings ($a_{\text{H}(8)} - a_{\text{H}(3)}$, $a_{\text{H}(7)} - a_{\text{H}(4)}$, and $a_{\text{H}(6)} - a_{\text{H}(5)}$) are all less than a few hundredths of a G. These differences are much too small to indicate the presence of the ABA conformation, and there is no hint of line width alternation effects, Figure 6.

Experimental Section

Dicarboalkoxycyclooctatetraenes. Dicarboalkoxycyclooctatetraene was obtained from the photolysis of dimethylacetylenedicarboxylate in benzene as previously described.¹³ The yellow oil was distilled under reduced pressure and purified on an alumina column and eluted with an ethyl acetate (30%)/hexane (70%) mixture.

The 1,2-dicarbo-*tert*-butoxycyclooctatetraene was obtained via a transesterification of $(\text{CH}_3\text{COO})_2\text{COT}$ with *tert*-butyl alcohol. Dicarbo-

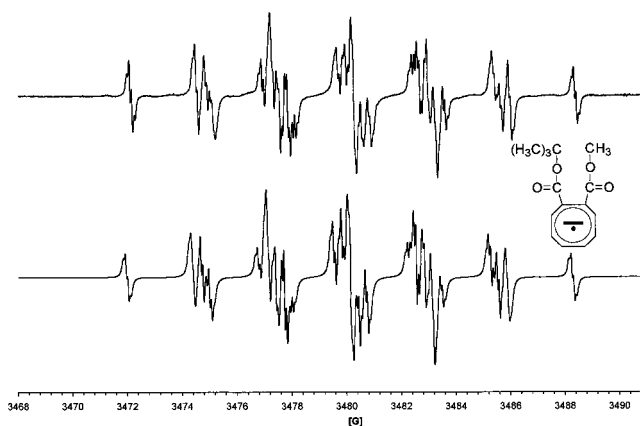


Figure 6. (Upper) EPR spectrum of the 1,2-dicarbo-*tert*-butoxymethoxycyclooctatetraene anion radical recorded in HMPA at 298 K. (Lower) A computer simulation generated with coupling constants of $a_{\text{H}} = 3.050$ (1H), 2.950 (1H), 2.740 (1H), 2.735 (1H), 2.430 (1H), 2.390 (1H), and 0.084 G (3Hs). The very small differences in the splittings for the 3 and 8, 4 and 6, and 5 and 7 positions indicate the presence of only the ABL conformation of the COT ring.

methoxycyclooctatetraene (200 mg) was dissolved in 5 mL of dry *tert*-butyl alcohol containing a small amount of the sodium *tert*-butoxide. The reaction mixture was refluxed for 2 h and left overnight at room temperature. About 20 mL of water was then added, and the product was extracted with ether. After drying of the ether layer (MgSO_4), the ether was removed under reduced pressure and the product was purified on an alumina column. The eluting solvent was a mixture of ethyl acetate (10%) and hexane (90%). The first fraction proved to be the desired product, 1,2-dicarbo-*tert*-butoxycyclooctatetraene. Only a very poor yield of this di-*tert*-butyl product could be obtained (ca. 10 mg). The second fraction proved to be 1,2-dicarbo-*tert*-butoxymethoxycyclooctatetraene (ca. 30 mg), and the third fraction consisted of starting material. NMR and mass spectral analysis are consistent with the dicarboalkoxycyclooctatetraene structures in all cases. The di-*tert*-butyl system exhibits a molecular ion peak at m/e 304, the 1,2-dicarbo-*tert*-butoxymethoxycyclooctatetraene at m/e 262, and the dimethyl system at m/e 220. The dimethyl and di-*tert*-butyl systems yield essentially the same NMR spectrum except that the methyl resonance is absent in the latter and the *tert*-butyl resonance is absent in the former. The NMR spectrum of 1,2-dicarbo-*tert*-butoxymethoxycyclooctatetraene reveals the asymmetry in the ring system (see the Supporting Information).

Computational Methodology. The ABA and ABL geometries for the COT anion radical were obtained from the UHF/3-21G results reported by Borden et al.⁷ For the $[(\text{CH}_3\text{OOC})_2\text{COT}]^-$ anion radical the two dicarbomethoxy substituents were attached to the COT systems, and a geometry optimization was carried out at the B3LYP/6-31+G* level, while keeping the COT ring system constrained in its D_{4h} (either ABA or ABL) configuration. The methyl groups were then replaced by *tert*-butyl groups to generate the $[(\text{CH}_3)_3\text{OOC}]_2\text{COT}^-$ system. While constraining the COT ring, simple molecular mechanics (MMFF) were then used to alleviate the extra steric stress between two dicarbo-*tert*-butoxy substituents. Single-point B3LYP/6-31+G* calculations were then carried out on both the ABA and ABL configurations. The theoretical EPR spectra of the ABA and ABL conformations of the "hypothetical" dicarboalkoxy-COT anion radicals were generated from the predicted ring carbon p_z spin densities. The carbon p_z spin densities were assumed to be proportional to the α proton EPR coupling constants ($a_{\text{H}} = Q\rho$).¹⁴

General. The reductions were carried out by allowing HMPA solutions of the dicarboalkoxycyclooctatetraene to come into contact with potassium metal in vacuo as previously described.¹⁵ The EPR spectra were recorded with a Bruker EMX-080 spectrometer equipped with a variable-temperature unit. NMR spectra were recorded on a

(14) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*; John Wiley and Sons: New York, 1994; p 241.

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

(13) Grovenstein, E., Jr.; Rao, D. V. *Tetrahedron Lett.* **1961**, 148.

Varian 400 MHz NMR system. All of the calculations were carried out with the Titan program on a 450 MHz Pentium II processor.¹⁶

Acknowledgment. We thank the National Science Foundation (Grant CHE-9617066) for support of this work.

(16) TITAN Version 1 program from Wavefunction, Inc. and Schrodinger, Inc.

Supporting Information Available: 400 MHz NMR spectra of 1,2-dicarbo-*tert*-butoxymethoxycyclooctatetraene and 1,2-dicarbo-*tert*-butoxycyclooctatetraene recorded at room temperature (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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