The Effect of Electron Releasing Groups upon the Molecular Orbitals and Anion Disproportionation Equilibria of Substituted Cyclooctatetraenes

Gerald R. Stevenson,* Jesus G. Concepción, and Luis Echegoyen

Contribution from the University of Puerto Rico, Department of Chemistry, Rio Piedras, Puerto Rico   00931.   Received February 19, 1974

Abstract: (Phenyl-d_5)cyclooctatetraene, 1,3,5,7-tetramethylcyclooctatetraene, *tert*-butoxycyclooctatetraene, and ethylcyclooctatetraene have been reduced to their respective anion radicals and dianions in hexamethylphosphoramide. The thermodynamic enthalpies controlling the disproportionation equilibrium ($\pi^{2-} + \pi \rightleftarrows 2\pi \cdot^-$) constant were studied in this solvent. A plot of ΔH° for this reaction *vs.* the σ value for the substituent on the cyclooctatetraene ring yields a ρ value of -3.8 kcal/mol. The negative value for ρ indicates that the electron-pushing effect of the substituent concentrates the charge density on the anions and this results in more ion pair formation which in turn increases the enthalpy of the reaction. The esr spectra of the anion radicals confirm that the electron-releasing substituents remove the degeneracy of the two nonbonding orbitals. The splitting of the nonbonding orbitals is about 0.4 kcal/mol for an alkyl substituent and about 0.78 kcal/mol for an alkoxy group. A plot of this splitting *vs.* the σ value of the substituent yields a positive ρ value. The disproportionation thermodynamics and the esr coupling constants for the (phenyl-d_5)cyclooctatetraene anion radical indicate that the angle between the two rings is large.

In even-membered monocyclic π-electron systems all of the HMO's except for the lowest and highest in energy are doubly degenerate. Thus the odd electron in the benzene and cyclooctatetraene (COT) anion radicals is equally distributed between the doubly degenerate orbitals which are nonbonding in the case of COT and antibonding in the case of benzene. The presence of an electron-releasing substituent in the benzene system splits the degeneracy of the antibonding orbitals and thus the odd electron in the anion radical preferentially occupies the orbital of lower energy. The spin distributions for many substituted benzene anion radicals have been observed utilizing electron spin resonance spectroscopy.[1] For the toluene system the splitting of the two antibonding orbitals due to the presence of the methyl group has been shown to be about 1.2 kcal/mol.[2]

The nonbonding orbitals in the COT system have two nodal planes. Similar to the benzene system, the presence of an electron-releasing substituent is expected to split the degeneracy of the two orbitals as shown in Figure 1.

Carrington and Todd[3] have generated the anion radicals of several monosubstituted alkyl cyclooctatetraenes and have found the coupling constants of the COT ring system to be less strongly perturbed by the alkyl groups than they are in the benzene systems. This indicates that the orbital splitting is smaller and the vibronic coupling is more important in the COT anion radicals.[3]

Useful information about the distribution of the electrons in substituted COT anion radicals and dianions can also be obtained from the relationship between the structure of the substituent and the thermodynamic parameters controlling the disproportionation reaction (eq 1). Comparing the enthalpies of reaction
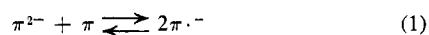
$$\pi^{2-} + \pi \rightleftarrows 2\pi \cdot^- \qquad (1)$$

1 for COT, biscyclooctatetraene (BCOT), and phenylcyclooctatetraene (PCOT) it was noticed that the enthalpy of disproportionation increases with the size of the substituent and thus with the degree of conjugation between the substituent and the COT ring.[4] This has been attributed to the lower electron–electron repulsion in the dianions with more extensive conjugation.

In a preliminary communication we reported the reduction of several substituted cyclooctatetraenes to their respective anion radicals.[5] We now wish to report the esr parameters for a series of substituted cyclooctatetraenes along with the thermodynamic parameters controlling the disproportionation equilibria with the hope of gaining new insight as to the electron distribution and its effect upon ion pairing in the COT dianions and anion radicals.

Experimental Section

X-Band esr spectra were recorded using a Varian E-3 esr spectrometer. The temperature was controlled using a Varian V-4557 variable-temperature controller calibrated with an iron–constantan thermocouple. The sample preparation was exactly as previously described.[6]

(Phenyl-d_5)cyclooctatetraene was synthesized by the method of Cope and Kinder[7a] using pentadeuteriobromobenzene in place of bromobenzene. The product was fractionally distilled at a pressure of 5 μ and collected from 59 to 60°. The nmr was identical with that for PCOT except that no proton resonance was observed for the phenyl ring. The mass spectrum yields a parent peak at m/e 185.

1,3,5,7-Tetramethylcyclooctatetraene (TMCOT), a white crystalline solid, was prepared by the method of Mayo and Yip[7b] and was purified by the method of Cotton.[8] The melting point was 68.5–69.5° (lit. 69–70°). The mass spectrum exhibited a parent peak at m/e 105.

(1) J. R. Bolton and A. Carrington, *Mol. Phys.*, 4, 497 (1961).

(2) (a) E. de Boer and J. P. Copla, *J. Phys. Chem.*, 71, 21 (1967); (b) D. Purins and M. Karplus, *J. Chem. Phys.*, 50, 214 (1969).

(3) A. Carrington and P. F. Todd, *Mol. Phys.*, 7, 531 (1964).

(4) G. R. Stevenson and J. G. Concepcion, *J. Amer. Chem. Soc.*, 95, 5692 (1973).

(5) G. R. Stevenson and J. G. Concepcion, *J. Phys. Chem.*, 78, 90 (1974).

(6) G. R. Stevenson and J. G. Concepcion, *J. Phys. Chem.*, 76, 2176 (1972).

(7) (a) A. C. Cope and M. R. Kinder, *J. Amer. Chem. Soc.*, 73, 3424 (1951); (b) P. de Mayo and R. W. Yip, *Proc. Chem. Soc., London*, 84 (1964).

(8) F. A. Cotton, J. W. Feller, and M. Musco, *J. Amer. Chem. Soc.*, 90, 1438 (1968).
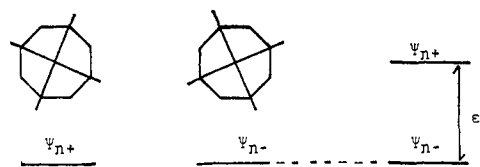
Figure 1. The two nonbonding degenerate orbitals of planar COT splitting due to the presence of an electron-releasing group.

Ethylcyclooctatetraene (ETCOT), a yellow liquid, was prepared by the method of Cope and van Orden.[9] Purification of ETCOT was accomplished by preparative gas chromatography using an 8-ft column of 30% SE-30 on Chromsorb W at a column temperature of 150°.

tert-Butoxycyclooctatetraene (TBCOT), an orange liquid, was synthesized by the method of Krebs.[10] TBCOT was purified by fractional distillation and collected from 42.0 to 42.5° at 2 μ.

The anion radical concentrations were determined using the system COT-HMPA-K as a spin standard as previously described.[6]

ETCOT   TBCOT   TMCOT   PCOT
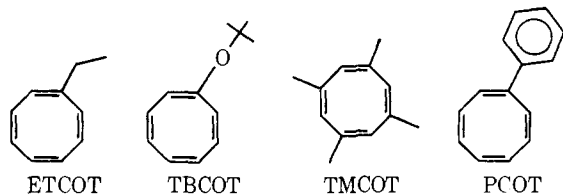
Results and Discussion

The reduction of TMCOT by potassium metal in HMPA leads to the formation of an anion radical solution yielding a well-resolved esr spectrum. This spectrum consists of 13 equally spaced pentets due to 12 equivalent protons with a coupling constant of 6.29 ± 0.01 G and four equivalent protons with a coupling constant of 0.42 ± 0.01 G. The occupancy of the Ψ_{n+} orbital by the odd electron is in accord with prediction. Ψ_{n+} is strongly destabilized by the presence of the methyl groups and thus contains the odd electron, while Ψ_{n-} is left essentially unaffected by the presence of the methyl groups and contains the two electrons. The fact that the protons in the nonnodal positions possess a finite coupling constant indicates that the odd electron is not in a pure Ψ_{n+} orbital but in a combination of the two orbitals. Describing the wave function for the odd electron as a linear combination of the two orbitals we obtain $\psi = C_{n-}\Psi_{n-} + C_{n+}\Psi_{n+}$. From the esr coupling constants $C_{n-}{}^2 = 6.29/(6.29 + 0.42)$ and $C_{n+}{}^2 = 0.42/6.71$ ($\psi = 0.25\Psi_{n-} + 0.97\Psi_{n+}$). The difference in energy between Ψ_{n+} and Ψ_{n-} can now be obtained by the use of eq 2.[11] Solving this expression

$$C_{n-}{}^2 = e^{-\epsilon/kT}/(1 + e^{-\epsilon/kT}) \tag{2}$$

for ϵ yields a value of 1.60 kcal/mol. Since each alkyl group contributes one-fourth of this total splitting, a single alkyl group should result in a splitting of 0.4 kcal/mol.

The reduction of ethyl COT in the same manner yields a well-resolved esr pattern consisting of a quartet of 4.33 G due to three equivalent ring protons, a pentet of 1.99 G due to four equivalent ring protons, a triplet of 2.69 G due to the methylene protons, and a small

(9) A. C. Cope and H. O. van Orden, *J. Amer. Chem. Soc.*, **74**, 175 (1952).

(10) A. Krebs, *Angew. Chem.*, **77**, 966 (1965).

(11) Dividing both numerator and denominator by $\exp(-E_{n-}/kT)$ in the equation $C_{n-} = \exp(-E_{n-}/kT)/[\exp(-E_{n-}/kT) \exp(-E_{n+}/kT)]$ yields eq 2, if E_{n-} and E_{n+} represent the energies of the lower and upper energy levels, respectively. $\epsilon = E_{n+} - E_{n-}$.
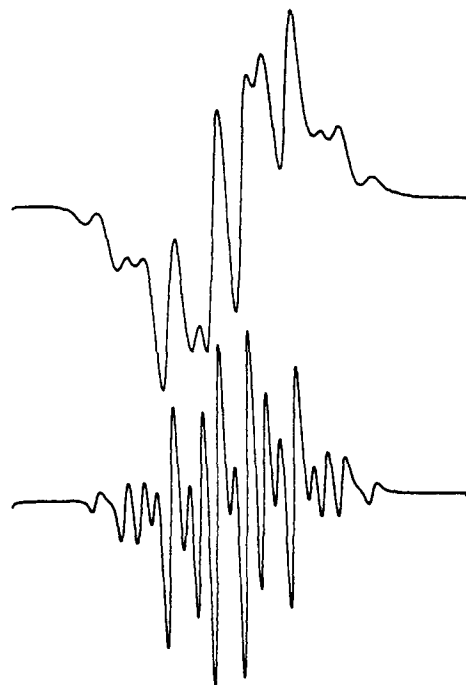
Figure 2. Esr spectra of the phenylcyclooctatetraene (upper) and the (phenyl-d_5)cyclooctatetraene (lower) anion radicals. The spectra were recorded at room temperature.

quartet of 0.26 G due to the methyl protons. These results are in complete agreement with those of Carrington and Todd.[3] For this system, the nonnodal ring proton splitting of 4.33 G and the nodal ring proton splitting of 1.99 G yield values for $C_{n-}{}^2$ and $C_{n+}{}^2$ of 0.31 and 0.69, respectively. From eq 1 the splitting of the nonbonding orbitals is found to be 0.45 kcal/mol. This is in good agreement with the value predicted from the tetrasubstituted system.

Previous reductions of PCOT in either THF at $-100°$[12] or in HMPA[4] have resulted in an esr spectrum consisting of 12 broad lines. These lines have been assigned to be due to a pentet of 3.8 G and a quartet of 2.2 G. However, no further hyperfine splitting could be observed and no information as to the extent of the splitting due to the phenyl protons was available.

The reduction of (phenyl-d_5)-COT by potassium metal in HMPA results in the formation of a solution that yields a strong well-resolved esr signal, Figure 2. This pattern consists of a pentet of 3.68 G and a quartet of 2.38 G due to four and three equivalent protons, respectively. These results indicate that all of the hyperfine lines observed for the PCOT anion radical were due to the protons on the eight-member ring, and the broad lines are due to unresolved hyperfine splitting from the phenyl protons. The substitution of the phenyl ring protons with deuteriums resulted in a decrease in the line width from 1.0 to 0.35 G.

Using 1.415 Å for all of the carbon–carbon bonds within the phenyl and COT ring systems and 1.54 Å for the carbon–carbon bond between the two rings, a Hückel and Pariser–Parr–Pople SCF calculation was carried out for the PCOT anion radical. The p_z spin densities calculated in this manner are compared with the experimental spin densities in Table I. The ex-

(12) A. Carrington, R. E. Moss, and P. F. Todd, *Mol. Phys.*, **12**, 95 (1967).
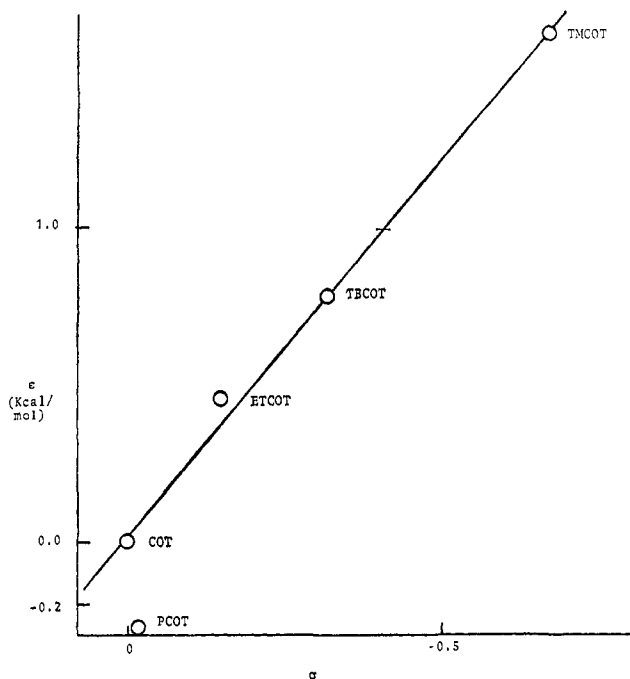
Figure 3. A plot of ϵ vs. σ of the substituent on the COT ring.

Table I. π Electron Spin Densities for the PCOT-d_5 Anion Radical

Position	Hückel	PPP-SCF	Exptl
1	0.1053	0.0868	
2	0.0	0.0135	
3, 7	0.0263	0.0214	ca. 0.01
4, 6	0.0	0.0015	0.0
5	0.0263	0.0256	ca. 0.01
8, 14	0.1250	0.1463	0.144
9, 13	0.1053	0.0708	0.093
10, 12	0.1250	0.1621	0.144
11	0.1053	0.0656	0.093

perimental spin densities were calculated from the McConnell relationship using 25.6 G for Q and 25.6 G is the experimental Q value for the COT anion radical.[13]

From Table II it is noticed that almost all of the spin

Table II. Values for $C_{n-}{}^2$, $C_{n+}{}^2$, ϵ, and σ for the Following Substituent on the COT Ring

Substituent	$C_{n-}{}^2$	$C_{n+}{}^2$	ϵ, kcal/ mol	σ
Tetramethyl	0.06	0.94	1.60	−0.68
Ethyl	0.31	0.69	0.45	−0.151
tert-Butoxy	0.21	0.79	0.78	−0.320
Phenyl-d_5	0.61	0.39	−0.26	−0.01

density on carbons to which protons are attached in the phenyl ring comes from positions 3, 7, and 5 (ortho and para positions). Further, since these three protons are essentially equivalent, it is reasonable to assume that given higher resolution for the PCOT anion radical a further splitting due to three approximately equivalent protons would be observed. Since the line

(13) F. J. Smentowski and G. R. Stevenson, *J. Amer. Chem. Soc.*, **89**, 5120 (1967).

width was reduced by 0.65 G upon substitution of the phenyl protons by deuteriums, this unresolved phenyl proton triplet must be *ca.* 0.3 G. This splitting would result from a π-electron density at the 3, 7, and 5 positions of about 0.012. From Table I it is clear that this experimentally estimated value is about half of that expected from the calculations, while the spin densities on the COT ring are in good agreement with the calculated values. This is most probably due to the fact that the dihedral angle between the two rings is quite large.

Since the pentet splitting is larger than that for the quartet, it is clear that Ψ_{n+} is of lower energy than Ψ_{n-} and ϵ is less than zero. This means that the phenyl group is acting as an electron-withdrawing group on the COT ring system. The values for $C_{n+}{}^2$, $C_{n-}{}^2$, and ϵ are given in Table II.

The reduction of TBCOT also yields a strong well-resolved esr pattern. This spectrum consists of a quartet of 4.89 ± 0.02 G due to three equivalent protons and a pentet of 1.30 ± 0.02 G due to four equivalent protons. $C_{n-}{}^2$, $C_{n+}{}^2$, and ϵ are given in Table II. These results indicate that the splitting of the non-bonding orbitals due to the presence of the alkoxy group is about double that for an alkyl group. A plot of ϵ vs. the σ value for the substituent (Figure 3) gives a good correlation except for the case of the phenyl substituent. The reason for the departure of the phenyl group from the Hammett plot is due to its direct conjugation with the eight-member ring.

It is interesting to note here that the substitution of a single deuterium for a proton in the benzene anion radical resulted in a splitting of the degeneracy of the antibonding orbitals by about 0.05 kcal/mol.[14] However, no splitting of the degeneracy of the nonbonding orbitals of the COT ring was observed upon mono-deuteration.[15] These experimental observations can be explained by taking into account the fact that an alkyl group on the COT system causes a splitting of only about one-fourth of that on the benzene ring. Thus a deuterium would probably result in a splitting of the nonbonding orbitals of COT by 0.05/4 kcal/mol. Such a splitting would be too small for experimental observation by esr.

The enthalpy for the disproportionation reaction (eq 1) was determined for the systems TMCOT–HMPA-K, ETCOT–HMPA-K, and TBCOT–HMPA-K using the previously described technique.[6] The anion radical concentration is proportional to the area under the integrated esr over-modulated line. The equilibrium constant for eq 1 is then given by

$$K_{eq} = BA^2/(\pi^{2-})(\pi)$$

where B is a proportionality constant and A represents the area under the over-modulated esr line. Once it is verified by the use of a spin standard that the anion radical concentration is much smaller that the dianion and neutral molecule concentration, a modified van't Hoff plot of ln A vs. $1/RT$ should yield a straight line with a slope of $-\Delta H^\circ/2$. For all of the systems studied this plot was linear (Figure 4). The corresponding enthalpies are shown in Table III. The error in the

(14) R. G. Lawler, J. R. Bolton, G. K. Fraenkel, and T. H. Brown, *J. Amer. Chem. Soc.*, **86**, 520 (1964).
(15) A. Carrington, H. C. Longuet-Higgins, R. E. Moss, and P. F. Todd, *Mol. Phys.*, **9**, 187 (1965).
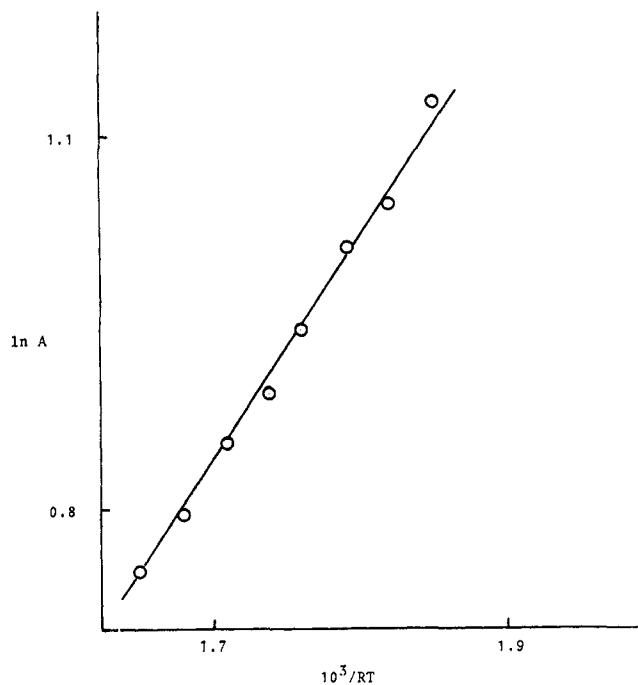
Figure 4. A plot of the ln of the area under the overmodulated esr curve vs. $1/RT$ for the system ETCOT-HMPA-K.

Table III. Enthalpies of the Disproportionation Equilibria for the Following Substituted COT's Reduced by Potassium Metal in HMPA

Compound	ΔH°, kcal/mol	σ (substituent)	Ref
COT	-4.6 ± 0.7	0.0	6
PCOT	-3.7 ± 0.5	-0.01	4
ETCOT	-3.4 ± 0.3	-0.151	This work
TBCOT	-3.2 ± 0.3	-0.32	This work
TMCOT	0.36	-0.68	This work
BCOT[a]	-2.4 ± 0.5	0[b]	4

[a] BCOT stands for biscyclooctatetraene. [b] This is an estimated value.

slope of a single plot is smaller than the error obtained by comparing the individual plots, each from a sample made independently, to each other. Therefore the errors in Table III represent the standard deviation in the enthalpy from the different plots.

From Table III it is clear that the enthalpy of disproportionation is a function of the substituent. The order of increasing enthalpies is COT < PCOT < ETCOT < TBCOT < BCOT < TMCOT. Disregarding the cases of BCOT and PCOT, which can have considerable conjugation between the two rings, this is the same order as the electron-releasing character of the substituents based upon the σ values. A Hammett
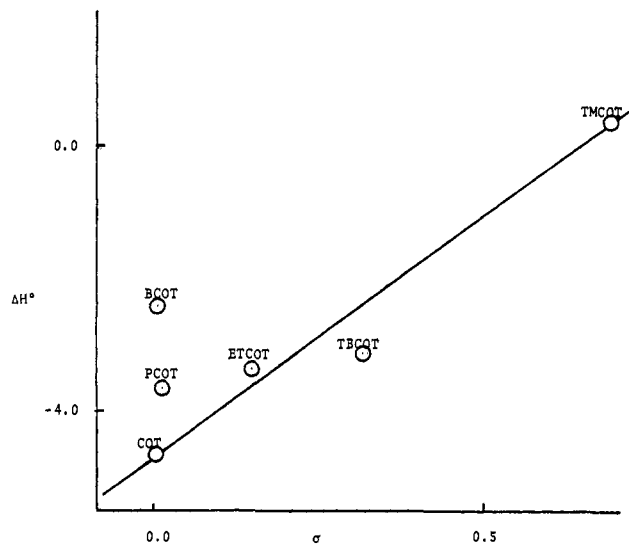

Figure 5. A plot of the σ value for the substituent vs. the enthalpy of disproportionation.

plot of the enthalpy of disproportionation vs. the σ value for the substituent is reasonably linear for the four monocyclic systems (Figure 5) and yields a ρ value of -7.2 kcal/mol. The slope of the plot was taken to be $-\rho RT$.[16]

To explain these results we must consider two effects of the substituent upon the disproportionation enthalpy: one is ion pairing and the other is the electron-electron repulsion in the dianion. For a series of nitrobenzene anion radicals it was found that concentrating the charge and spin density in the NO_2 group resulted in the formation of more ion pairing.[16] In a similar manner concentration of the charge density in the COT ring system by the presence of electron-pushing groups should result in more ion pairing. Increased ion pairing in the COT anion-dianion systems always results in shifting the disproportionation equilibrium to the left. This accounts for the observed negative value for ρ. The fact that the PCOT and BCOT systems do not fit on the Hammett plot is probably due to the fact that these systems allow the electrons to be delocalized in the two rings thus decreasing the electron-electron repulsion in the dianion. The electron-electron repulsion factor in the dianion has previously been described as an important one in the disproportionation of COT dianions,[4] and for the cases of PCOT and BCOT this effect becomes more important than the ion pairing effect.