Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1007; (d) P. Warner, to be published. We thank Professor Warner for a reprint of his paper.

(3) (a) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4729 (1966); (b) M. Ogliaruso and S. Winstein, *ibid.*, **89**, 5290 (1967); (c) M. Ogliaruso, *ibid.*, **92**, 7490 (1970); (d) S. Winstein, G. Moshuk, R. Rieke, and M. Ogliaruso, *ibid.*, **95**, 2624 (1973). There now exists some question regarding the authenticity of the dianion generated under the conditions employed by these workers.[4-6]

(4) (a) W. H. Okamura, T. I. Ito, and P. M. Kellett, *Chem. Commun.*, 1317 (1971); (b) T. I. Ito, F. C. Baldwin, and W. H. Okamura, *ibid.*, 1440 (1971).

(5) S. V. Ley and L. A. Paquette, *J. Am. Chem. Soc.*, **96**, 6670 (1974).

(6) M. Barfield, R. B. Bates, W. A. Beavers, I. R. Blacksburg, S. Brenner, B. I. Mayall, and C. S. McCulloch, *J. Am. Chem. Soc.*, **97**, 900 (1975).

(7) S. W. Staley and N. J. Pearl, *J. Am. Chem. Soc.*, **95**, 3437 (1973).

(8) A. T. Blomquist, E. S. Wheeler, and Y. Chu, *J. Am. Chem. Soc.*, 77, 6307 (1955).

(9) L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *J. Am. Chem. Soc.*, **97**, 1101 (1975).

(10) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).

(11) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, Chapter 3.

(12) C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960); I. T. Jacobson, *Acta Chem. Scand.*, **21**, 2235 (1967); L. A. Paquette, G. V. Meehan, and S. J. Marshall, *J. Am. Chem. Soc.*, **91**, 6779 (1969).

(13) Review: C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions", Academic Press, New York, N.Y., 1968, pp 81–98.

(14) See, for example, W. S. Johnson, M. Neeman, S. P. Birkeland, and N. A. Fedoruk, *J. Am. Chem. Soc.*, **84**, 989 (1962); E. Zbiral, J. Jaz, and F. Wessely, *Monatsh. Chem.*, **92**, 1155 (1962); E. Zbiral, F. Takonacs, and F. Wessely, *ibid.*, **95**, 402 (1964); W. T. Tai and E. W. Warnhoff, *Can. J. Chem.*, **42**, 1333 (1964).

(15) J. B. Press and H. Shechter, *Tetrahedron Lett.*, 2677 (1972).

(16) J. T. Lumb and G. H. Whitham, *Tetrahedron*, **21**, 499 (1965).

(17) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

(18) M. A. McKinney and P. P. Patel, *J. Org. Chem.*, **38**, 4059 (1973).

(19) R. Shapiro and M. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967); G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

(20) E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *J. Am. Chem. Soc.*, **92**, 5224 (1970); *J. Org. Chem.*, **38**, 26 (1973).

(21) H. Gerlach, T. T. Huang, and W. Muller, *J. Chem. Soc., Chem. Commun.*, 1215 (1972).

(22) See, for example, L. A. Paquette and M. J. Kukla, *Tetrahedron Lett.*, 1241 (1973).

(23) R. D. Sands, *J. Org. Chem.*, **29**, 2488 (1964); **34**, 2794 (1969).

(24) J. B. Hendrickson, *J. Am. Chem. Soc.*, **86**, 4854 (1964); **89**, 7036, 7043, 7047 (1967).

(25) (a) M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967); (b) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Am. Chem. Soc.*, **93**, 1637 (1971); see also footnote 7 or ref 27a.

(26) (a) R. F. Bryan and J. D. Dunitz, *Helv. Chim. Acta*, **43**, 3 (1960); (b) S. G. Dahl and P. Groth, *Acta Chem. Scand.*, **25**, 1114 (1971); (c) P. Groth, *ibid.*, **23**, 1311 (1969).

(27) (a) F. A. L. Anet and J. J. Wagner, *J. Am. Chem. Soc.*, **93**, 5266 (1971); (b) G. Borgen and J. Dale, *J. Chem. Soc., Chem. Commun.*, 1105 (1970).

(28) R. B. Turner, B. J. Mallon, M. Tichy, W. von E. Doering, W. R. Roth, and G. Schroder, *J. Am. Chem. Soc.*, **95**, 8605 (1973).

(29) W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yu, *J. Am. Chem. Soc.*, **86**, 3178 (1964).

(30) W. R. Roth, *Justus Liebigs Ann. Chem.*, **671**, 10 (1964); K. G. Untch and R. J. Kurland, *J. Am. Chem. Soc.*, **85**, 346 (1963).

(31) G. Binsch, *J. Am. Chem. Soc.*, **91**, 1304 (1969).

(32) Reviews: F. A. L. Anet and R. Anet, "Determination of Organic Structures by Physical Methods", Vol. 3, Academic Press New York, N.Y., 1971, p 343 ff, "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press New York, N.Y., 1975, Chapter 14.

(33) R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *J. Am. Chem. Soc.*, **95**, 926 (1973).

(34) S. W. Staley and G. M. Cramer, *J. Am. Chem. Soc.*, **95**, 5051 (1973).

(35) S. W. Staley and A. W. Orvedal, *J. Am. Chem. Soc.*, **95**, 3384 (1973).

(36) S. W. Staley and N. J. Pearl, *J. Am. Chem. Soc.*, **95**, 2731 (1973).

(37) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(38) We view the pioneering work in this area to be the protonation [A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950)] and methylation [D. A. Bak and K. Conrow, *J. Org. Chem.*, **31**, 3958 (1966)] of the cyclooctatetraene dianion. Unfortunately, only regioselectivity was evaluated in these studies.

(39) A. F. McKay, D. L. Garmaise, G. Y. Paris, S. Gelblum, and R. J. Ranz, *Can. J. Chem.*, **38**, 2042 (1960).

An Electron Spin Resonance Study of the Radical Anions of Two Dimethylcyclooctatetraenes

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Abstract: The radical anions of 1,4- and 1,5-dimethylcyclooctatetraene have been generated by electrolysis in DMF at −55 °C, and their ESR spectra have been recorded. These are the first examples of ESR spectra of 1,4- and 1,5-disubstituted :COT radical ions. In 1,5-Me$_2$COT$\cdot^-$ virtually all of the π spin density is localized on the four odd-numbered ring carbons. In complete contrast, the π spin density in 1,4-Me$_2$COT$\cdot^-$ is spread almost equally over all eight ring carbons. These results are shown to provide strong support for symmetry-orbital models of substituted COT radical anions.

Introduction

Reports of ESR spectra of radical ions of benzene and its mono- and polysubstituted derivatives abound in the literature.[2] These studies have provided elegant confirmation of a symmetry-orbital model for the π system of benzene. In contrast, while there have been a number of ESR studies of monosubstituted cyclooctatetraene (COT) radical anions,[3] particularly in the last 2 years, investigations of polysubstituted COT radicals have been limited to two 1,3,5,7-tetrasubstituted derivatives[3d,4a,b] and a single 1,2-disubstituted one.[5] This difference presumably has its origins in the far greater synthetic difficulties inherent in COT chemistry.

Recently the syntheses of 1,4- and 1,5-Me$_2$COT have been accomplished.[6] The availability of these compounds offered us the opportunity to obtain ESR spectra of the corresponding radical anions, with a view toward exploring further the predictions of symmetry-orbital models of COT$\cdot^-$.

Experimental Section

The radical anions of COT and its two dimethyl derivatives were generated by electrolytic reduction of the neutral hydrocarbons in *N*,*N*-dimethylformamide (DMF) at −55 °C with tetra-*n*-propylammonium perchlorate as electrolyte. The electrolysis was done in a flat quartz cell (Wilmad Glass Co., No. WG-808) small enough to fit inside the Dewar system of the spectrometer. The cathode was a platinum wire passed into the bottom of the cell through a Teflon plug. The platinum anode was brought in through a rubber septum on one arm of a Y-tube at the top of the cell. Outgassed solutions of compound and electrolyte were drawn from a storage flask into a syringe equipped with a Teflon valve and a 10-in. long 26-gauge needle. The solutions were injected into the flat part of the cell through a septum on the other arm of the Y-tube. The spectra were recorded on a standard Varian X-band spectrometer,[7] and the magnetic field strength was calibrated at 5-G intervals with a precision Gaussmeter. Analyses of the spectra were confirmed by computer simulation; the reported coupling constants are the values obtained by least-squares fitting.[8]

Results and Discussion

A. COT·⁻. The ESR spectrum of COT·⁻ is that of a radical anion with eight equivalent protons. The proton coupling constant a_H for COT·⁻ in tetrahydrofuran (THF) is −3.21 G,[9] while in NH_3 the radical shows a slightly larger splitting, −3.278 G.[10] We find that a_H for COT·⁻ in DMF at −55 °C is −3.27 G. This radical anion in solvents of low polarity, such as THF, and in the presence of alkali metal cations exists as ion pairs. There appears to be no evidence that COT·⁻ forms ion pairs with tetraalkylammonium cations, however, and we accordingly consider our ESR spectra to be those of the free anions, uncomplicated by effects of ion pairing.

For planar π radicals, one commonly calculates the unpaired π-electron spin density ρ_μ on carbon μ from the experimental coupling constant $a_{H,\mu}$ by the McConnell equation:

$$a_{H,\mu} = Q\rho_\mu \qquad (1)$$

where Q is a proportionality constant having a value of −22 to −28 G. As a_H is the same for all eight protons of COT·⁻, the spin density ρ must be ⅛ at each carbon. Therefore, in the following discussion we take $Q = -3.27/0.125 = -26.16$ G for substituted COT radical anions in DMF at −55 °C.

There are several different molecular structures for COT·⁻ which are consistent with the observation of equal spin densities at all eight carbons. Of these, a tub-shaped (D_{2d}) geometry like that of the neutral compound has been ruled out on the basis of the normal Q value, as well as other evidence.[10,11] A planar structure with a fourfold symmetry axis and alternating short and long C–C bonds (D_{4h}) has received more serious consideration. The two occupied orbitals of highest energy for a COT·⁻ with D_{4h} symmetry would be π MO's ψ_4 and ψ_5, belonging to B_{1u} and B_{2u} representations. These MO's would have the forms:[12]

$$\psi_4 = 0.354(\phi_1 + \phi_2 - \phi_3 - \phi_4 + \phi_5 + \phi_6 - \phi_7 - \phi_8) \qquad (2)$$

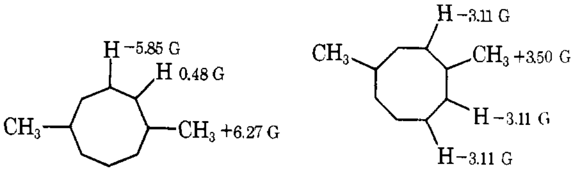
$$\psi_5 = 0.354(\phi_1 - \phi_2 - \phi_3 + \phi_4 + \phi_5 - \phi_6 - \phi_7 + \phi_8) \qquad (3)$$

If the short bonds are taken to be C-1:C-2, C-3:C-4, C-5:C-6, and C-7:C-8, ψ_4 is lower in energy than ψ_5. In the ground state ψ_4 is filled, and the unpaired electron occupies ψ_5. It is clear from the form of this MO that the unpaired spin density should be equally distributed over all eight carbons, as is observed experimentally.

Also possible is a regular octagonal structure (D_{8h}) like that generally accepted for the diamagnetic COT dianion.[13] The MO's ψ_4 and ψ_5 are a valid pair of symmetry orbitals for COT·⁻ in the D_{8h} point group, just as in D_{4h}. However, in the more symmetrical structure they are energetically degenerate, belonging to an E_{2u} representation. Consequently, there are two equienergetic electronic states, one with the unpaired electron in ψ_4 and the other with ψ_5 as the half-filled MO.

It might be expected that a D_{8h} COT·⁻ would undergo a Jahn-Teller distortion to a structure of lower symmetry, such as D_{4h}, to remove the energetic degeneracy.[14] It has been argued on the basis of the electronic spectrum of COT·⁻, though, that it does have a D_{8h} structure.[10] In any case, ESR evidence including the anomalously large line width and the power-saturation behavior indicates that the ground state is in fact degenerate.[4b]

B. 1,5-Me₂COT·⁻. The ESR spectrum of 1,5-Me_2COT·⁻ in DMF at −55 °C results from a six-proton splitting of 6.27 G, which we assign to the six methyl hydrogens; a four-proton splitting of 0.48 G, assigned to the hydrogens at C-2, C-4, C-6, and C-8; and a two-proton splitting of 5.85 G, assigned to the hydrogens at C-3 and C-7 (Figure 1a). With $Q = -26.16$ G, an a_H of 0.48 G corresponds to a very low spin density at the four even-numbered carbons: $\rho_{2,4,6,8} = 0.018$. The large splitting of 5.85 G for $a_{3,7}$ shows that the spin density at these two odd positions is high: $\rho_{3,7} = 0.224$. Using Vincow's value of $Q_{CCH_3} = +25$ G,[4b] one can calculate from $a_H(CH_3) = 6.27$ G that $\rho_{1,5} = 0.25$. As the total π spin density must be 1.00, the large ρ values for the four odd positions clearly are positive. Accordingly, $a_{3,7}$ must be negative and $a_H(CH_3)$ positive. Because of the very small absolute magnitude of $\rho_{2,4,6,8}$ and the uncertainty in the value of Q_{CCH_3}, the sign of $a_{2,4,6,8}$ cannot be established from considerations of unit total π spin density.



1a **1b**

Figure 1

The ρ values we find for 1,5-Me_2COT·⁻ can be accounted for in terms of the same symmetry–orbital model previously used to explain the coupling constants found for other substituted COT radical ions.[3] The MO's required are not ψ_4 and ψ_5, but are instead linear combinations of these two MO's, which we designate as ψ_A and ψ_S to indicate that ψ_A is antisymmetric and ψ_S symmetric with respect to a plane perpendicular to the ring plane and passing through C-1 and C-5. The forms of ψ_A and ψ_S are:

$$\psi_A = 0.50(\phi_2 - \phi_4 + \phi_6 - \phi_8) \qquad (4)$$

$$\psi_S = 0.50(\phi_1 - \phi_3 + \phi_5 - \phi_7) \qquad (5)$$

Electron-releasing groups like methyl, when located at odd positions, raise the energy of ψ_S more than that of ψ_A. Consequently, in the ground state the unpaired electron occupies ψ_S, in which it is localized on the odd carbons only. The values of $\rho_{1,3,5,7}$ and $\rho_{2,4,6,8}$ from Hückel MO theory for an electron in ψ_S are 0.25 and 0.00, respectively. Plainly the distribution of spin density predicted by this simple model is in remarkably good agreement with our experimental ρ values.

If the unpaired electron did in fact occupy a "pure" ψ_S MO, however, electron correlation should result in substantial induced negative spin density at the even carbons and correspondingly enhanced positive spin density at the odd positions. To the extent that comparison with a nondegenerate radical-like allyl[15] is valid, $\rho_{1,3,5,7}$ might well be as large as 0.35, with a negative $\rho_{2,4,6,8}$ of −0.10. This estimate is supported by our INDO calculation on MeCOT·⁻ (D_{8h} geometry for the ring carbons), which gives $\rho_{1,3,5,7} = 0.337 \pm 0.004$ and $\rho_{2,4,6,8} = -0.095$.

It has been pointed out, though, that in degenerate systems like COT·⁻ the electronic and vibrational wave functions are coupled. From the form of the D_{4h} MO ψ_5 it can be seen that a vibration which distorts the ring from D_{8h} to D_{4h} geometry (the b_{2u} mode) will tend to distribute the unpaired electron more evenly over the eight ring carbons on the average. Our INDO calculation on MeCOT·⁻ with alternating C–C lengths of 1.34 and 1.46 Å gives almost uniform distribution of the π spin density, with ρ values ranging from a minimum of 0.111 to a maximum of 0.135. Concepcion and Vincow[4b] state that in alkyl COT radical anions the contributions of electron correlation and vibronic coupling tend to cancel, and consequently "the Hückel model yields a fairly good approximation for the spin-density distribution".

The distribution of π spin density in substituted COT radical anions is strongly dependent on the nature of the substituent. This dependence has generally been accounted for in terms of thermal (Boltzmann) mixing of the ground state, in which the unpaired electron occupies ψ_S, with a low-lying excited state in which ψ_A is the half-filled MO. The electronic effects of the substituent determine the energy difference ΔE between the two states and consequently the extent to which the upper state contributes. The value of πE can be calculated from the equation:

$$\rho(\mathrm{T}) = \frac{\rho^G + \rho^E \exp(-\Delta E/kT)}{1 + \exp(-\Delta E/kt)} \qquad (6)$$

where $\rho(\mathrm{T})$ is the spin density at a given position at temperature T, and ρ^G and ρ^E are the spin densities at that position in the ground and excited states, respectively. Assuming $\rho^G = 0.25$ for odd carbons and 0.00 for even ones, with $\rho^E = 0.00$ for odd positions and 0.25 for even ones, Stevenson[3c,d] found ΔE to be 0.45 kcal/mol for $CH_3CH_2COT\cdot^-$. The splitting produced by the four methyl groups of 1,3,5,7-$Me_4COT\cdot^-$ is reported to be approximately four times larger.[3d,4b] Taking ΔE for 1,5-$Me_2COT\cdot^-$, with two alkyl groups, to be 0.9 kcal/mol, and assuming the same values of ρ^G and ρ^E, we calculate that at −55 °C $\rho_{1,3,5,7} = 0.222$ and $\rho_{2,4,6,8} = 0.028$. These values are in quite satisfactory agreement with our experimental values of 0.224 and 0.018.

The existence of a low-lying excited state with ψ_A half-filled implies that spin density should shift from the odd to the even carbons with increasing temperature, and that the coupling constants should be temperature dependent. Vincow has found that the coupling constants of 1,3,5,7-$Me_4COT\cdot^-$ are indeed temperature dependent.[4b] The signs of the temperature coefficients for both splittings, as well as the magnitude of that of the methyl splitting, are entirely consistent with the expected redistribution of spin density.

We find a very similar temperature dependence for $a_H(CH_3)$ and $a_{3,7}$ in 1,5-$Me_2COT\cdot^-$. The absolute values of these coupling constants over the range −55 to +21 °C change from +6.27 to +6.10 and −5.85 to −5.60 G, respectively, corresponding to da_H/dT values of −2.2 and +3.3 mG per degree. These values are somewhat smaller than the ones predicted for $E = 0.9$ kcal/mol. Using Vincow's equation:[4b]

$$\frac{da_H}{dT} = \frac{Q(\rho^E - \rho^G)(\Delta E/kT)\exp(-\Delta E/kT)}{T[1 + \exp(-\Delta E/kT)]^2} \qquad (7)$$

one calculates $da_H(CH_3)/dT = -5.1$ and $da_{3,7}/dT = +5.3$ mG per degree for $T = 273$ K.

As for $a_{2,4,6,8}$, it appears to remain constant from −55 to +21 °C within our limits of accuracy. Any change in its value must be an order of magnitude or more smaller than the change predicted from eq 7. Vincow[4b] also found an anomalously small temperature dependence for $a_{2,4,6,8}$ in his study of 1,3,5,7-$Me_4COT\cdot^-$. The source of these discrepancies between theory and experiment is not clear. It would seem that at the present time our understanding of the temperature dependence of spin densities in substituted COT radical anions and similar radicals is incomplete.

C. 1,4-$Me_2COT\cdot^-$. To date the only $COT\cdot^-$ derivative with substituents at both odd and even carbons to be studied by ESR is the radical anion of bicyclo[6.2.0]deca-1,3,5,7-tetraene. Bauld et al. reported that the six olefinic protons in this radical ion all have the same coupling constant, −3.25 G.[5] This result is also consistent with the symmetry-orbital argument. Inspection of eq 4 and 5 reveals that the combined effect of the perturbations produced by the two methylene groups at C-1 and C-2 would be to raise the energies of the MO's ψ_S and ψ_A equally. Thus, a 1,2-disubstituted $COT\cdot^-$ with two identical substituents should, like $COT\cdot^-$ itself, have a doubly degenerate ground state, and the unpaired electron should be uniformly distributed over all eight positions, just as in $COT\cdot^-$.

The argument applies in exactly the same way to 1,4-$Me_2COT\cdot^-$, which is also predicted to have uniform distribution of spin density around the ring. The ESR spectrum of this radical anion in DMF at −55 °C results from two six-proton coupling constants (Figure 1b). One of them, $a_H = 3.11$ G, which we assign to the six ring protons, corresponds to a π spin density at these six carbons of 0.119. The other, $a_H = 3.50$ G, is assigned to the methyl protons; with $Q_{CHH_3} = +25$ G, one calculates $\rho_{1,4}$ to be 0.140. As the total π spin density must be 1.00, both ρ values are positive. Therefore, $a_{1,4}$ is positive and $a_{2,3,5,6,7,8}$ negative.

The nearly even distribution of π spin density we find for 1,4-$Me_2COT\cdot^-$ is in excellent agreement with the prediction based on symmetry arguments.

Summary

This appears to be the first ESR study of 1,4- and 1,5-disubstituted COT radical anions. The dramatic contrast between the uniform distribution of π spin density in 1,4-$Me_2COT\cdot^-$ and the pronounced odd–even alternation in the 1,5 isomer provides a striking demonstration of the power of symmetry-orbital models for $COT\cdot^-$ and its derivatives.

References and Notes

(1) (a) Swarthmore College; (b) Ohio State University.

(2) See, for example, G. Vincow, Chapter 4, and K. W. Bowers, Chapter 5 in "Radical Ions", E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N.Y., 1968.

(3) (a) A. Carrington and P. F. Todd, *Mol. Phys.*, 7, 533 (1963–1964), and **8,** 299 (1964); (b) G. R. Stevenson and I. Ocasio, *J. Am. Chem. Soc.*, **98,** 890 (1976); (c) G. R. Stevenson and J. G. Concepcion, *J. Phys. Chem.*, **78,** 90 (1974); (d) G. R. Stevenson, J. G. Concepcion, and L. Eschegoyen, *J. Am. Chem. Soc.*, **96,** 5452 (1974).

(4) (a) R. D. Rieke and R. A. Copenhafer, *Tetrahedron Lett.*, 4097 (1971); (b) J. G. Concepcion and G. Vincow, *J. Phys. Chem.*, **79,** 2042 (1975).

(5) N. L. Bauld, F. R. Farr, and C. E. Hudson, *J. Am. Chem., Soc.*, **96,** 5634 (1974).

(6) (a) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **94,** 9224 (1972); (b) L. A. Paquette, R. K. Russell, and R. E. Wingard, Jr., *Tetrahedron Lett.*, 1713 (1973); (c) L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, and M. Oku, *J. Am. Chem. Soc.*, **96,** 5806 (1974).

(7) We thank Professor David Dalton and Mr. George Kemmerer of Temple University for their generosity in making their ESR spectrometer available to us.

(8) The fitting program used was ESRCON by Dr. J. Heinzer. It is available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University. Satisfactory least-square fits were obtained for the spectra of all three radical ions.

(9) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32,** 1873 (1960).

(10) P. I. Kimmel and H. L. Strauss, *J. Phys. Chem.*, **72,** 2813 (1968).

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

(12) The coefficients given for these symmetry orbitals are those obtained when one assumes that $S_{ij} = 0$. These coefficients are changed only very slightly when nonzero S_{ij}'s are included.

(13) S. Z. Goldberg, K. N. Raymond, C. A. Harmon, and D. H. Templeton *J. Am. Chem. Soc.*, **96,** 1348 (1974).

(14) See, for example, ref 10. However, theoretical arguments have been made that $COT\cdot^-$ should have a doubly degenerate vibronic ground state with a very low-lying D_{8h} energy barrier between two D_{4h} minima; see H. M. McConnell and A. D. McLachlan, *J. Chem. Phys.*, **34,** 1 (1961).

(15) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39,** 2147 (1963).

(16) These calculations were done with the CNDO–INDO program of Pople and Dobosh, which is available from the Quantum Chemistry Program Exchange (see ref 8). For the D_{8h} calculation the C–C length for the ring bonds was taken as 1.40 A.