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ELECTRON SPIN RESONANCE STUDY OF THE RADICAL ANIONS OF SUBSTITUTED
CYCLOOCTATETRAENES. THE EFFECTS OF JAHN-TELLER
DISTORTIONS AND VIBRONIC MIXING

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ABSTRACT:

The radical anions of methyl-, methoxy-, fluoro-, cyclopropyl-, and cyanocyclooctatetraene were generated by electrolytic reduction of the neutral compounds in liquid ammonia. The electron spin resonance spectrum of each radical anion is assigned, and a clean even-odd alternation of the spin densities is observed in each. This alternation can be correlated with the electronic properties of the substituent. For the radical anions of methyl-, methoxy-, and cyclopropylcyclooctatetraene, the temperature dependence of the coupling constants is reported. The results are accounted for in terms of vibronic mixing and Jahn-Teller distortions, and are discussed in relation to INDO calculations.

INTRODUCTION

The redistribution of the unpaired electron density which results from a substitution on a highly symmetrical radical is a very interesting problem. The first study of the electron spin resonance spectrum of the cyclooctatetraene anion radical, $COT^{\cdot-}$, was made by Katz and Strauss in 1960.¹ They found that the unpaired electron was uniformly distributed

over the eight carbons and that the ring seemed to be planar. The introduction of a single alkyl group² or other substituent,^{3,4} gives a sharp even-odd alternation of pi-spin densities. In the cases of 1,5-dimethyl-COT⁻⁵ and 1,3,5,7-tetramethyl-COT⁻⁶ an unusual dependence of the proton coupling constants on temperature has been reported; this dependence has been interpreted in terms of a redistribution of spin density from the odd to the even positions.

Although an early theoretical study of alkyl-substituted COT⁻'s considered vibronic mixing explicitly,⁷ recent work on COT⁻ derivatives has not treated the interplay of inductive perturbations and Jahn-Teller distortions.³⁻⁶ In this paper, we report the esr spectra of methyl-, methoxy-, fluoro-, cyclopropyl-, and cyano-substituted cyclooctatetraene anion radicals, and show how they can be interpreted in terms of the opposing consequences of distortion of the eight-membered ring and the tendency of substituents to accept or repel electrons. In addition, we present a theoretical model for the estimation of vibronic and thermal mixing in derivatives of COT⁻.

EXPERIMENTAL SECTION

The substituted cyclooctatetraenes were kindly supplied to us by Professor A. Streitwieser, Jr., and Dr. Claude Harmon, both from the Department of Chemistry, University of California, Berkeley. We purified each sample immediately before use by preparative gas chromatography on carbowax or SE 30 columns. The purity of the recovered samples was established by analytical gas chromatography.

The radical anion solutions were prepared by *in situ* electrolytic reduction with liquid ammonia as a solvent and tetramethylammonium iodide

as an electrolyte. This technique and our apparatus have been previously described.⁸ All esr spectra were taken at 9 GHz with 100 KHz field modulation. The spectrometer was equipped with the digital data acquisition system previously described.⁹ Many of our spectra were stored on digital magnetic tape, and the spectral parameters were obtained by least-squares methods.⁹ The temperatures were measured by means of a thermocouple inside the esr cavity, but outside the electrolysis cell.

The INDO calculations were done on IBM 370/155, IBM 370/158, and CDC 6600 computers with the INDO program of Dobosh.¹⁰

RESULTS

In Table I, we give the experimentally observed coupling constants for the magnetic nuclei in the anion radicals of methyl-, methoxy-, fluoro-, cyclopropyl-, and cyanocyclooctatetraene, together with our assignments. Of these radicals, only methyl-COT⁻ has been previously reported.² The signs of the coupling constants are not determined experimentally, but are assigned on the basis of analogy and the requirement that the total pi-spin density must be unity.

In the first four radicals, the pi-spin density is concentrated on the odd ring carbons, while the last one instead has the large spin densities on the even positions. In this system, methyl, methoxy, fluoro and cyclopropyl are electron-repelling relative to hydrogen, but cyano is electron-attracting. In order of decreasing tendency to localize spin density on the odd positions, the substituents are:

fluoro > methoxy > methyl > cyclopropyl > H > cyano.

Surprisingly, the spin density distribution in fluoro-COT⁻ is consistent

Table I. Assignments of Hyperfine Coupling Constants for X-COT⁻ in Liquid Ammonia

X-	T, °C	Coupling Constants in Gauss		
		a(odd)	a(even)	a(substituent)
F-	-72	-6.500 ^c	0.326 ^b , 0.164 ^b	+13.014 ^e
CH ₃ O-	-75	-6.096 ^c	-0.431 ^b , -0.326 ^b	0.826 ^c
CH ₃ -	-77	-5.057 ^c	-1.401 ^d	+5.544 ^c
C ₃ H ₅ -	-74	-4.710 ^c	-1.676 ^d	+3.104 ^a , 0.498 ^b , 0.283 ^b
NC-	-73	+0.87 ^a , +0.53 ^b	-7.52 ^b , -6.69 ^b	0.135 ^f

^aFor 1 proton

^bFor 2 protons

^cFor 3 protons

^dFor 4 protons

^eFor ¹⁹F

^fFor ¹⁴N

with a stronger electron-repelling effect than has been found in any other monosubstituted $\text{COT}^\cdot$. Cyano- $\text{COT}^\cdot$ shows a stronger electron-attracting substituent effect than any $\text{COT}^\cdot$ derivative previously reported, and is, in fact, the only known substituted $\text{COT}^\cdot$ which unequivocally exhibits the alternation of small negative pi-spin densities with positive spin densities greater than 0.25.

The coupling constants for the substituted radicals are observed to have a temperature dependence. With our digital records of the $\text{CH}_3\text{O}-\text{COT}^\cdot$ spectra we obtained the results shown in Table II. A least-squares fit spectrum is shown in Figure 1. As one can see by the data in Table II, the digital data acquisition method and the least-squares fitting technique are remarkably successful in giving the precise fit to the spectrum which is necessary to measure small changes with temperature. The largest error in these data is probably in the temperature.

Table II. Temperature Dependence of Coupling Constants Obtained by Least-Squares Fitting of Spectra of Methoxy- $\text{COT}^\cdot$

T, °C	Spectrum Number	Coupling Constants in Gauss		
		$a_{3,5,7}$	$a_{2,8}; a_{4,6}$	$a(\text{OCH}_3)$
-75	1	-6.097	-0.432, -0.325	0.827
-75	2	-6.095	-0.431, -0.327	0.824
-75	3	-6.096	-0.431, -0.326	0.826
-62	4	-6.035	-0.467, -0.367	0.762
-62	5	-6.034	-0.468, -0.367	0.762
-46	6	-5.981	-0.503, -0.401	0.709
-46	7	-5.980	-0.503, -0.401	0.709

In Table III, we present the temperature coefficients of the ring proton coupling constants in methyl-, methoxy-, and cyclopropyl-COT⁻. In all three radicals, the coupling constants for the odd ring protons become more positive by approximately 4-5 milligauss/°C. The change at the even positions is considerably smaller and in the opposite direction; so that a_H (even) values all become more negative with increasing temperature. Concepcion and Vincow⁶ have reported similar results for 1,3,5,7-tetramethyl-COT⁻, and have rationalized the temperature effect in terms of thermal (Boltzmann) mixing of the electronic ground state with a low-lying electronic excited state having a very different spin density distribution. These authors used a Hückel MO model for COT⁻.

Table III. Temperature Coefficients of the Ring Proton Coupling Constants in XCOT⁻'s.

X-	$d a(\text{even})/dT^a$	$d a(\text{odd})/dT^a$
CH ₃ -	-1.0, -1.0	+3.8, +3.8
CH ₃ O-	-2.5, -2.6	+4.0, +4.0
C ₃ H ₅ -	-3.5, -3.5	+5.1, +5.1

^ada/dT in milligauss/degree.

DISCUSSION

Symmetry Orbitals. The highest occupied shell of a COT⁻ molecule with D_{8h} symmetry contains three electrons and is doubly degenerate. If we ignore a vibronic Jahn-Teller distortion, there are an infinite number of pairs of linear combinations of carbon p_z orbitals which constitute proper symmetry orbitals for this shell. For the unsubstituted parent anion radical, the most useful pair is:

$$\psi_4 = \frac{1}{2\sqrt{2}} (\phi_1 + \phi_2 - \phi_3 - \phi_4 + \phi_5 + \phi_6 - \phi_7 - \phi_8) \quad \text{and} \quad (1)$$

$$\psi_5 = \frac{1}{2\sqrt{2}} (\phi_1 - \phi_2 - \phi_3 + \phi_4 + \phi_5 - \phi_6 - \phi_7 + \phi_8) \quad (2)$$

When all C-C bond distances are equal, these two MO's have the same energy. However, a Jahn-Teller distortion such as shortening the 1-2, 3-4, 5-6 and 7-8 bonds increases the bonding interactions of ψ_4 , and lengthening the other four C-C bonds decreases the four antibonding interactions. As a result, this mode of distortion lowers the energy of ψ_4 . The effect on ψ_5 is precisely the opposite. The bonding interactions are weakened, the antibonding ones are strengthened, and the energy of ψ_5 is raised. Consequently, one draws the following conclusions from perturbation theory for COT⁻ itself or for any COT⁻ derivative identically substituted at both even and odd positions:^{5,11}

- (1) the minimum-energy geometry for the ring carbons will be D_{4h}, with alternating long and short C-C bonds;¹²
- (2) in the electron configuration of lowest energy, ψ_4 is filled and ψ_5 is half-filled (or vice versa); and
- (3) the unpaired electron is distributed uniformly over all eight ring carbons.

Replacement of a ring proton by another atom introduces a competing perturbation. In the absence of a Jahn-Teller distortion, it would at the same reduce the molecular symmetry from D_{8h} to C_{2v}. ψ_4 and ψ_5 are not valid MO's in the new point group. The appropriate orbitals, which correctly reflect the new molecular symmetry, are:

$$\psi_S = \frac{1}{2} (\phi_1 - \phi_3 + \phi_5 - \phi_7), \quad \text{and} \quad (3)$$

$$\psi_A = \frac{1}{2} (\phi_2 - \phi_4 + \phi_6 - \phi_8) \quad (4)$$

Clearly ψ_A has a node through C-1, and is unperturbed by a substitution at C-1 in the first approximation. ψ_S , however, has a relatively high

amplitude at C-1. An electron-repelling substituent at this position will raise the energy of ψ_S ; ψ_A will be filled and ψ_S half-filled, and the spin density will be concentrated on the odd carbons. An electron-attracting group, on the other hand, will lower the energy of ψ_S below that of ψ_A . The unpaired electron will then occupy ψ_A , and will be localized on the even positions. Provided the substituent effect is strong enough to remove the orbital degeneracy completely, the ring carbons will adopt a regular octagonal arrangement, and in any approximation which neglects the interaction of electron spins, such as HMO, spin densities of 0.25 and 0.00 should alternate around the ring. However, if the substituent perturbation is weak, there will also be a Jahn-Teller distortion of small amplitude, and the wave function for the unpaired electron will be a linear combination of ψ_S and ψ_A to which the two functions contribute unequally. In this case, smaller and larger positive pi-spin densities will alternate. Precisely this result has been observed for a number of monosubstituted COT⁻'s.^{2,3}

Three important effects remain to be considered in more detail. These are: (1) electron correlation; (2) vibronic mixing as a dynamic function of Jahn-Teller distortion; and (3) thermal (Boltzmann) mixing.

Electron Correlation. To estimate the effect of electron correlation in these COT⁻ derivatives, we performed an INDO calculation on each one, with the ring carbons at the vertices of a regular octagon and the C-C distances = 1.40 Å. The calculated spin densities are shown in Table IV. In all cases, the INDO values exhibit the alternating sign patterns predicted by considerations of electron correlation. The positive ρ 's

Table IV. Electron Correlation in Substituted COT^- 's with Regular Octagonal Geometry for the Ring Carbons

X-	INDO pi-Spin Densities				
	ρ_1	$\rho_{3,7}$	ρ_5	$\rho_{2,8}$	$\rho_{4,6}$
F^-	0.328	0.340	0.350	-0.085	-0.110
$\text{CH}_3\text{O}-$	0.331	0.335	0.345	-0.084	-0.108
CH_3-	0.343	0.337	0.338	-0.097	-0.097
C_3H_5-	0.345	0.336	0.336	-0.095	-0.095
$\text{NC}-$	-0.050	-0.111	-0.138	0.341	0.364

range from a low of 0.328 to a high of 0.364, and the negative ρ 's from -0.050 to -0.138. The spin density is predicted to be concentrated on the odd positions in fluoro-, methoxy-, methyl-, and cyclopropyl- COT^- , and on the even ones in cyano- COT^- .

As one can see from the experimental results in Table I, the spin densities as calculated by INDO are localized on the correct carbons in all five radicals. However, in contrast to predictions based on electron correlation and the INDO data, induced negative pi-spin densities are observed experimentally only for cyano- COT^- , and possibly for fluoro- COT^- . In the other three anion radicals, effects of vibronic and thermal mixing apparently predominate over correlation effects.

Jahn-Teller Distortion and Vibronic Mixing. The theoretical estimation of the spin densities in the ground state of our nearly degenerate radicals requires, in principle:

- (1) The identification of the principal Jahn-Teller-active vibrational modes.
- (2) The choice of suitable potential functions for these modes.
- (3) The determination of the vibrational eigenfunctions for these potential functions.
- (4) The calculation of the spin densities as a function of the amplitude of the vibrational distortion by an appropriate MO method.
- (5) Evaluation of the integrals for the expectation values of the spin densities.

In this section we apply a simplified version of this approach to four of the five substituted COT^- 's discussed above.

The Jahn-Teller-active vibrations of COT^- include modes of symmetry types b_{1g} and b_{2g} . These are illustrated in Fig. 2. The two b_{1g} modes involve CCC in-plane bending (Fig 2, 1a) and CH stretching (Fig. 2, 1b). The first b_{2g} mode mainly involves the stretching and compression of alternate CC bonds (Fig. 2, 2a), while the second is mainly a CCH in-plane bending (Fig. 2, 2b). The result of each of these vibronic distortions is to reduce the molecular symmetry to D_{4h} . Moss⁷ has argued that the CC stretching mode of b_{2g} symmetry is the most likely to cause vibronic effects, because it strongly affects the CC bond integrals. This system is rather similar to the four-membered ring discussed by Herzberg.¹³ To simplify the problem substantially, we neglect the less important b_{2g} CCH bending and the two b_{1g} modes, and consider only the b_{2g} CC stretching. The mode chosen retains a CH bond length of 1.08 Å, CCC angles of 135° , and CCH angles of 112.5° . The symmetry coordinate Q for this mode can be expressed as:

$$Q = 1/\sqrt{8}(q_1 - q_2 + q_3 - q_4 + q_5 - q_6 + q_7 - q_8), \quad (5)$$

where the q 's are the amplitudes of the distortions of the eight CC bonds; $q_1 = q_3 = q_5 = q_7$ and $q_2 = q_4 = q_6 = q_8$. To simplify further, we assume that $q_{\text{odd}} = q_{\text{even}}$.

The minimum-energy geometry for COT^- should be D_{4h} , with alternating long and short CC bonds,¹² as described in the first section. There are two such minima with identical energies, the two differing only in respect to which set of four CC bonds is lengthened and which is shortened (*i.e.*, with respect to the sign of the q 's). According to the Jahn-Teller theorem, the D_{8h} structure should correspond to an energy barrier between the two minima. Therefore, our simplified b_{2g} potential surface should be a symmetrical double well.

A computationally simple function appropriate for this type of surface is the Gaussian double oscillator,

$$V = \frac{1}{2}kx^2 + Ae^{-Bx^2}. \quad (6)$$

The parameter A governs the height of the barrier at the center of the potential surface, and B is a fall-off factor affecting the barrier width. Depending on the values of the parameters k , A , and B , this function can give:

- (1) a potential surface approaching a harmonic oscillator, corresponding to D_{8h} geometry and the absence of a Jahn-Teller effect;
- (2) a surface without a central barrier, but with a broadened and flattened bottom;
- (3) a double well with a low central barrier, corresponding to a dynamic Jahn-Teller effect; or
- (4) a double well with a high central barrier, inducing D_{4h} geometry and a static Jahn-Teller effect.

These possibilities are illustrated in Fig. 3, which presents plots of potential energy, as calculated by the INDO method, vs. q for COT^- , CH_3COT^- , and CH_3OCOT^- . MINDO calculations, which would be expected to be more reliable, give a central barrier of 3.6 kcal/mole for COT^- ,¹² a value which is roughly half of that given by INDO.

The application of standard vibration theory¹⁴ to the b_{2g} CC stretching mode of COT^- yields the following expression for the harmonic oscillator potential energy:

$$V = \frac{1}{2}(8F_1q_i^2 - 16F_{12}q_iq_j + 16F_{13}q_iq_k - 16F_{14}q_iq_l + 8F_{15}q_iq_m). \quad (7)$$

As all q 's have the same magnitude, substitution of an effective force constant $F'(b_{2g})$ for $(F_1 - 2F_{12} + 2F_{13} - 2F_{14} + F_{15})$ reduces Eq.(7) to:

$$V = 4F'q^2. \quad (8)$$

The potential energy of the Gaussian double oscillator for this mode of COT^- then becomes:

$$V = 4F'q^2 + Ae^{-8Bq^2}. \quad (9)$$

The vibrational Hamiltonian for the b_{2g} CC stretching mode will be written as

$$H_k = \frac{-\hbar^2}{2} \nabla_k^2 + 4F'q^2 + Ae^{-8Bq^2}. \quad (10)$$

The eigenfunctions of the Hamiltonian, χ_m , may be expanded in terms of the Hermite polynomial solutions of the harmonic oscillator problem:

$$\chi_m = \sum_j a_{mj} \phi_j. \quad (11)$$

These are:

$$\phi_j = c_j H_j(y) \exp(-y^2/2), \quad (12)$$

where:

$$y = \sqrt{8}q(4\pi^2\mu\nu/h)^{\frac{1}{2}}.$$

By applying the Rayleigh-Ritz variational method, one may find the eigenfunctions for the symmetry coordinate Q_k from the eigenvectors of the matrix H_{ij} :

$$H_{ij} = \int \phi_j^* H_k \phi_i d\tau. \quad (14)$$

Non-zero elements of the matrix H_{ij} were computed by numerical integration of Eq.(14) with the basis functions given in Eq.(12) and the matrix was diagonalized by Jacobi's method. As the ensuing discussion will show, the eigenfunctions derived by this procedure proved to be useful for the theoretical estimation of spin densities time-averaged over the b_{2g} vibration.

The perturbation argument given earlier suggests that the spin density distribution in substituted COT^- 's should be strongly dependent on q . To test this prediction in a more quantitative way, we did INDO calculations of the pi-spin densities in methyl-, methoxy-, fluoro-, and cyano- COT^- , as well as for COT^- itself, over a range of CC ring bond distances. The results are shown in Table V. Several patterns in these INDO data are worthy of comment. While all four substituted radical anions show a very pronounced even-odd alternation of spin densities with the ring carbons at the vertices of a regular octagon, in each radical the spin density distribution becomes substantially more uniform with increasing b_{2g} distortion. This behavior is predicted from symmetry-orbital arguments. The redistribution of spin density with increasing q is much more rapid in the weakly perturbed methyl- COT^- than in the more strongly perturbed fluoro- and methoxy- COT^- 's. In fact, distortion of the CC distances by 0.05 Å produces a nearly uniform spin density distribution in methyl- COT^- , while there is still an appreciable alternation in the other two radicals even at the maximum distortion studied. In general, for a given radical and a given value of

Table V. INDO Spin Densities *vs.* Amplitude of b_{2g} Distortion for $XCOT^-$'s.

$q, \text{\AA}$	Odd Positions			Even Positions	
	ρ_1	$\rho_{3,7}^a$	ρ_5	$\rho_{2,8}^a$	$\rho_{4,6}^a$
A. $F-COT^-$ ^b					
0.00	0.328	0.340	0.350	-0.085	-0.110
0.01	0.317	0.329	0.338	-0.074	-0.098
0.02	0.287	0.295	0.302	-0.041	-0.062
0.03	0.243	0.247	0.254	-0.004	-0.012
0.04	0.202	0.205	0.212	0.045	0.033
0.05	0.178	0.180	0.186	0.070	0.059
0.06	0.165	0.167	0.173	0.084	0.073
0.08	0.148	0.152	0.158	0.100	0.089
0.10	0.140	0.144	0.150	0.108	0.098
B. CH_3O-COT^- ^b					
0.00	0.330	0.355	0.345	-0.084	-0.108
0.01	0.318	0.322	0.332	-0.074	-0.092
0.02	0.288	0.288	0.296	-0.033	-0.063
0.03	0.241	0.238	0.245	0.021	-0.015
0.04	0.201	0.197	0.204	0.063	0.027
0.05	0.180	0.177	0.183	0.083	0.048
0.06	0.167	0.165	0.171	0.095	0.062
0.08	0.149	0.147	0.154	0.101	0.092
0.10	0.141	0.140	0.146	0.109	0.100
C. CH_3-COT^- ^b					
0.00	0.343	0.337	0.338	-0.099	-0.095
0.01	0.322	0.316	0.316	-0.076	-0.074
0.02	0.230	0.221	0.220	0.019	0.024
0.03	0.167	0.158	0.156	0.084	0.088
0.04	0.145	0.135	0.132	0.107	0.112
0.05	0.138	0.128	0.125	0.115	0.118
0.06	0.136	0.125	0.122	0.119	0.120

cont'd.

Table V, cont'd.

D. NC-COT⁻ b

0.00	-0.050	-0.111	-0.138	0.341	0.364
0.01	-0.036	-0.090	-0.114	0.320	0.343
0.02	0.014	-0.025	-0.044	0.257	0.278
0.03	0.061	0.032	0.017	0.201	0.219
0.04	0.087	0.062	0.049	0.171	0.187
0.05	0.101	0.077	0.065	0.157	0.170
0.06	0.111	0.085	0.073	0.149	0.158
0.08	0.121	0.092	0.079	0.143	0.148
0.10	0.129	0.095	0.079	0.142	0.140

- a) Because of the two equivalent distortions possible for the ring carbons, on a time-averaged basis $\rho_2 = \rho_8$, $\rho_3 = \rho_7$, and $\rho_4 = \rho_6$. The ρ values given are the averages for the two positions as calculated by the INDO method.
- b) Bond distances, except for those of the ring, and bond angles are standard values taken from pp. 111-112 of J. W. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill Book Co., New York, 1970. To avoid severe nonbonded interactions with the neighboring ring protons in CH₃OCOT⁻, we take the plane defined by C-1, O and the methyl C as perpendicular to the plane of the ring.

60 11 24 7 0 10 5 2
-15-

ρ_1 , ρ_3 , ρ_7 , and ρ_5 are approximately equal; similarly, $\rho_{2,8}$ is roughly equal to $\rho_{4,6}$. Thus, despite the reduction in symmetry with substitution, the INDO results suggest that the use of linear combinations of the D_{8h} symmetry orbitals ψ_S and ψ_A for substituted COT^- 's is a reasonable approximation.

In an actual anion radical, of course, the observed spin densities represent averages over the various nuclear positions assumed by the vibrating molecule. The effects of the substituents on the vibrational eigenfunction and on the spin density distributions determine the extent to which the competing effects of electron correlation and vibronic coupling cancel each other. In view of the spin density data given in Table V, it is likely that the outcome of this competition is a sensitive function of the electronic nature of the substituent.¹⁵

The INDO spin densities can be reproduced with good accuracy by polynomials $S(q)$ in even powers of q . Theoretical estimates of the spin densities as time-averaged over the b_{2g} vibration can then be obtained from the expression:

$$\langle \rho_{\mu,i} \rangle = \int X_i S_{\mu,i}(q) X_i dq, \quad (15)$$

where $\langle \rho_{\mu,i} \rangle$ is the expectation value of the pi-spin density at ring carbon μ in the i^{th} vibrational state, and X_i is the eigenfunction for this state.

The reduced mass μ for the b_{2g} stretching mode equals¹⁴ $m_C/(2-2\cos\theta)$, where m_C is the mass of the carbon atom, and θ is the CCC angle of 135° . These give $\mu = 5.841 \times 10^{-24}$ g. The force constant F' has not been reported, and a value for it must be assumed. Adopting the benzene force field, we calculate the $F' = 3.98$ md/ $\text{\AA}$, a value nearly identical with that of the closely related b_{2u} mode of benzene.¹⁶ For a harmonic oscillator, the frequency ν would be 4.154×10^{13} Hz.

In Table VI we give the expectation values $\langle \rho_\mu \rangle$ for the pi-spin densities at carbons 2 through 5 of the radical anions F $^-$, CH₃O $^-$, CH₃ $^-$, and NC-COT $^-$. Values of $\langle \rho_\mu \rangle$ are presented for the first four harmonic oscillator vibrational states, ϕ_0 - ϕ_3 . The experimental pi-spin densities, calculated from the McConnell equation with $Q = -26.224$ gauss, are also given. As the data in Table VI show, the even-odd alternation of the $\langle \rho_\mu \rangle$ values for the harmonic oscillator ground state ϕ_0 is sharper than that of the experimental spin densities for all four radicals. Vibronic averaging over the b_{2g} mode in ϕ_0 does, as expected, partially cancel the effect of electron correlation, but not sufficiently to give satisfactory agreement between the theoretical and experimental spin densities. The model also yields the reasonable results that vibronic averaging in ϕ_0 is considerably more effective for the weakly perturbed CH₃-COT $^-$ than that for the more strongly perturbed F $^-$, CH₃O $^-$, and NC-COT $^-$'s.

Vibronic averaging in the higher vibrational levels ϕ_1 , ϕ_2 , and ϕ_3 is more extensive, and the spin density distributions in these states are far more uniform than in ϕ_0 . Consequently, the mixing of higher states with ϕ_0 leads to better agreement between the calculated and the experimental values. Use of the Gaussian double oscillator model - that is, the application of equations 10 through 14 - leads to mixing of ϕ_0 with ϕ_2 , ϕ_4 , etc., provided appropriate values of the parameters A and B are chosen. In addition to the $\langle \rho_\mu \rangle$ values for the harmonic oscillator states of the four monosubstituted radical anions, Table VI also lists the $\langle \rho_\mu \rangle$'s for the double oscillator ground state for the parameters $F' = 3.98$ md/Å, $A = 8 \times 10^{-13}$ erg, and $B = 125$ Å⁻²; ϕ_0 is 71.6% χ_0 , 28.32% ϕ_2 , and 0.08% higher states. The agreement between theory and experiment is quite good for the χ_0 state for

Table VI. π -Spin Densities for X-COT $^-$'s in Harmonic Oscillator States and with Vibronic Mixing

State ^a	Odd Positions		Even Positions	
	$\langle\rho_{3,7}\rangle$	$\langle\rho_5\rangle$	$\langle\rho_{2,8}\rangle$	$\langle\rho_{4,6}\rangle$
A. F-COT $^-$				
ϕ_0	+ .2999	+ .3082	- .0476	- .0675
ϕ_1	+ .2410	+ .2480	+ .0077	- .0053
ϕ_2	+ .2172	+ .2241	+ .0331	+ .0199
ϕ_3	+ .2073	+ .2138	+ .0440	+ .0305
χ_0	+ .2764	+ .2843	- .0247	- .0427
Exptl. ^b	+ .2479	+ .2479	.0063 or .0124 ^c	.0124 or .0063 ^c
B. CH ₃ O-COT $^-$				
ϕ_0	+ .2929	+ .3018	- .0405	- .0658
ϕ_1	+ .2339	+ .2412	+ .0233	- .0089
ϕ_2	+ .2123	+ .2193	+ .0452	+ .0140
ϕ_3	+ .2069	+ .2100	+ .0526	+ .0250
χ_0	+ .2700	+ .2784	- .0162	- .0432
Exptl. ^b	+ .2325	+ .2325	+ .0164 or +.0124 ^d	+ .0124 or +.0164 ^d
C. CH ₃ -COT $^-$				
ϕ_0	+ .2597	+ .2591	- .0208	- .0175
ϕ_1	+ .1746	+ .1726	+ .0672	+ .0709
ϕ_2	+ .1697	+ .1675	+ .0724	+ .0754
ϕ_3	+ .1630	+ .1626	+ .0802	+ .0818
χ_0	+ .2342	+ .2331	+ .0057	+ .0089
Exptl. ^b	+ .1928	+ .1928	+ .0534	+ .0534
D. NC-COT $^-$				
ϕ_0	- .0483	- .0694	+ .2793	+ .3006
ϕ_1	+ .0251	+ .0098	+ .2072	+ .2248
ϕ_2	+ .0377	+ .0224	+ .1951	+ .2107
ϕ_3	+ .0464	+ .0316	+ .1870	+ .1999
χ_0	- .0239	- .0433	+ .2554	+ .2749
Exptl. ^b	- .0202	- .0332	+ .2551 or +.2868 ^d	+ .2868 or +.2551 ^d

cont'd.

Table VI, cont'd.

- a) ϕ_i is the i^{th} vibrational state of the harmonic oscillator, and χ_0 is the ground state of the Gaussian double oscillator. $A = 8 \times 10^{-13}$ ergs and $B = 125 \text{ \AA}^{-2}$ in the double oscillator calculations; $F' = 3.98 \text{ md/\AA}$ in all calculations.
- b) Calculated from the ring proton coupling constants by the McConnell equation, with $Q = -26.224$ gauss.
- c) Signs of these spin densities not known. Assignments ambiguous.
- d) Assignments ambiguous.

the χ_0 state for NC-COT^- . The $\langle \rho_{\text{odd}} \rangle$ values for χ_0 for F^- , CH_3O^- , and $\text{CH}_3\text{-COT}^-$ are significantly larger than the experimental ones, however, and the $\langle \rho_{\text{even}} \rangle$'s are underestimated.

An increase in the barrier height and width by appropriate variation of the parameters A and B results in more uniform distribution of the spin densities and better agreement with experiment. However, only barriers substantially higher and wider than those calculated by INDO or MINDO¹² methods lead to quantitative agreement. The model presented in this section tends to exaggerate the alternation of pi-spin densities on the ring carbons of substituted COT^- 's. In the next section we introduce a further improvement in the model, and discuss some of the sources of error.

Temperature Dependence and Thermal Mixing. A further important characteristic of the double potential well, as compared to the harmonic oscillator, is that the energy difference E_{01} between the ground and first excited vibrational levels decreases rapidly as the height of the central barrier is increased. For barrier heights comparable to those calculated for COT^- by the INDO or MINDO¹² methods, E_{01} is comparable to the thermal energy at 200K. Consequently, the first excited vibrational state might well be significantly populated at this temperature. The vibronic mixing model of the preceding section can readily be modified to include this thermal (Boltzmann) mixing. The equation is that of Concepcion and Vincow:⁶

$$\langle \rho_{\mu}^T \rangle = \frac{\langle \rho_{\mu}^G \rangle + \langle \rho_{\mu}^E \rangle \exp(-E_{01}/kT)}{1 + \exp(-\Delta E_{01}/kT)}, \quad (16)$$

where $\langle \rho_{\mu}^T \rangle$ is the pi-spin density at the carbon C_{μ} and at temperature T. In our application, $\langle \rho_{\mu}^G \rangle$ and $\langle \rho_{\mu}^E \rangle$ are the expectation values of the spin densities at C_{μ} in the ground and first excited vibrational states.

Equation(16) requires that thermal mixing increase with increasing T , and since the average amplitude of b_{2g} distortion is greater in the first excited state than in the ground state, the spin density distribution in the higher state will be more uniform. If ΔE_{01} is not too large, an increase in T should decrease the even-odd alternation of spin density around the ring.

The experimentally observed temperature dependence of the coupling constants in methyl-, methoxy-, cyclopropyl-, 1,5-dimethyl,⁵ and 1,3,5,7-tetramethyl-COT⁻⁶ establishes the occurrence of Boltzmann mixing in these radicals. Theoretical estimates of the temperature dependence $d a_{\mu}/dT$ can be obtained from values of $\langle \rho_{\mu}^T \rangle$ at two or more temperatures. One simply multiplies $d \langle \rho_{\mu}^T \rangle /dT$ by Q , the proportionality constant of the McConnell equation. Table VII lists values of $\langle \rho_{\mu}^T \rangle$ for positions 2 through 5 of F-, CH₃O-, CH₃-, and NC-COT⁻, together with the $d a_{\mu}/dT$'s for CH₃O- and CH₃-COT⁻. The parameters used in these calculations were $F' = 3.98 \text{ md/\AA}$, $A = 8 \times 10^{13} \text{ erg}$, and $B = 125 \text{ \AA}^{-2}$, giving $E_{01} = 0.81 \text{ kcal/mole}$ and a barrier height of 5.5 kcal/mole .

For this set of parameters, the alternation of spin densities calculated for F-, CH₃O-, and CH₃-COT⁻ is again somewhat too sharp. Vibronic and thermal mixing together still do not sufficiently counteract electron correlation. The agreement for NC-COT⁻ is quite good. In this one case, the model gives a spin density distribution which is too uniform; however, the overestimate of mixing is slight. The average error in the ρ_{odd} values for the four radical anions is 0.0255.

Any model based on D_{8h} or D_{4h} symmetry orbitals predicts that $a_{2,8}$ exactly equals $a_{4,6}$, and $a_{3,7}$ exactly equals a_5 . Such a model cannot account

Table VII. Calculated Thermal Mixing in X-COT⁻ Radical Anions.^a

A. $\langle \rho_{\mu}^T \rangle$.

X-	$\langle \rho_{2,8} \rangle$	$\langle \rho_{3,7} \rangle$	$\langle \rho_{4,6} \rangle$	$\langle \rho_5 \rangle$	T
F-	-.0205	+.2719	-.0379	+.2797	201
CH ₃ O-	-.0113	+.2656	-.0389	+.2738	198
CH ₃ -	+.0127	+.2274	+.0159	+.2263	196
NC-	+.2496	-.0179	+.2688	-.0369	200

B. $d a_{\mu}/dT$.^b

X-	2,8	3,7	4,6	5	T
CH ₃ O-	-1.13	+1.03	-1.00	+1.07	198,227
CH ₃ -	-1.66	+1.61	-1.67	+1.63	196,229

a) Calculated for $A = 8 \times 10^{-13}$ erg, $B = 125 \text{ \AA}^{-2}$, and $F' = 3.98 \text{ md/\AA}$.

b) $d a_{\mu}/dT$ in milligauss/degree.

for inequalities within these pairs of coupling constants. Our approach is capable of accounting for such differences. In fact, we find differences of 0.0174 or greater between the $\langle \rho^T \rangle$'s for the two types of even positions for F-, CH₃O-, and NC-COT⁻, as well as between those for the two types of odd positions in the cyano radical. These are precisely the four cases in which the two experimental coupling constants differ measurably. The $\langle \rho_{\text{odd}}^T \rangle$ values in F-, CH₃O-, and CH₃-COT⁻, as well as those of $\langle \rho_{\text{even}}^T \rangle$ for the methyl radical differ by only 0.0011 to 0.0082, and in these four cases the odd pairs of coupling constants are identical within experimental error.

The calculated $d a_{\mu}/dT$ values all have the correct sign and are of the right order of magnitude. However, our model underestimates the temperature coefficients for the odd positions by factors of 2.4 to 3.9. The agreement is better for the even positions, but is still not quantitative. The calculations of Moss⁷ for CH₃-COT⁻, which includes both electron correlation and vibronic mixing, gives results essentially identical with ours. An alternative approach, which includes neither electron correlation nor vibronic mixing, and considers only the thermal mixing of a low-lying electronic excited state, gives quite good results for the odd positions of 1,3,5,7-tetramethyl-COT⁻,⁶ but overestimates the absolute magnitude of $d a_{\text{even}}/dT$ by a factor of five. It also over-estimates all four temperature coefficients for each of the three radical anions in our study.

Any changes in the parameters A and B which decrease the barrier height decrease both vibronic and thermal mixing, thus increasing the alternation of spin densities and decreasing the calculated temperature coefficients. Both changes result in poorer agreement with experiment.

Parameters which give higher barriers increase mixing and lead to better agreement between the theoretical and experimental spin densities.

However, because the contribution of ϕ_2 to the vibronic ground state is increased, the calculated temperature coefficients are again reduced.

The inability of our model to duplicate the experimental temperature coefficients may be a consequence of any of a number of assumptions and approximations, such as: (1) the use of the Born-Oppenheimer approximation in a problem involving vibronic mixing; (2) the choice of a force constant based on the benzene force field (lowering the force constant results in more uniform spin density distributions and larger temperature coefficients); or (3) the use of the INDO method, which often gives good results when vibrational motion is neglected, but may not be suitable when vibronic mixing is taken into account.

Finally, the substantial differences between the absolute values of $d a_{\text{odd}}/dT$ and $d a_{\text{even}}/dT$ are important. In all probability, these differences reflect the leakage of positive spin density directly into the $1s$ orbitals of the ring protons as a consequence of Boltzmann mixing of excited states for one or more out-of-plane vibrations. Such bending modes of the COT^- ring may well be quite facile, as they reduce the angle strain.¹⁷ The possibility that the temperature dependence of the coupling constants of COT^- derivatives results from an out-of-plane bending vibration deserves serious consideration.

SUMMARY. The esr spectra of five anion radicals of singly substituted cyclooctatetraene have been analyzed and the coupling constants have been assigned. All five radicals show an even-odd alternation of pi-spin densities, the spin density being concentrated on the odd carbons in four and on the even carbons in cyano-COT⁻. A redistribution of spin density from the odd to the even carbons with increasing temperature has been observed for methyl-, methoxy-, and cyclopropyl-COT⁻.

Our INDO calculations have elucidated the roles of electron correlation, Jahn-Teller distortion, and vibronic mixing in these COT⁻ derivatives. Our model for the estimation of pi-spin densities in substituted COT⁻'s combines a Gaussian double oscillator potential function for the b_{2g} vibration with spin densities calculated by the INDO method. With the inclusion of Boltzmann mixing of the first excited vibrational level, the model accounts qualitatively for the observed substituent effects and for the temperature dependence of the coupling constants. However, our parameters would have to be rather grossly adjusted to give both larger temperature coefficients and smaller even-odd hyperfine differences. Future work should include out-of-plane vibrations in the calculations.

Our results do show that the extent of vibronic mixing in a substituted COT⁻ is a sensitive function of the nature of the substituent, and that dynamic vibronic coupling effects are primarily responsible for the widely differing spin density distributions in COT⁻ derivatives.¹⁵

REFERENCES and NOTES

1. T. J. Katz and H. L. Strauss, J. Chem. Phys., 32, 1873 (1960);
H. L. Strauss, T. J. Katz, and G. K. Fraenkel, J. Am. Chem.
Soc., 85, 2360 (1963).
2. A. Carrington and P. F. Todd, Mol. Phys., 7, 533 (1964)
and 8, 299 (1964).
3. a.) G. R. Stevenson and I. Ocasio, J. Am. Chem. Soc., 98,
890 (1976); b.) G. R. Stevenson and J. G. Concepcion, J.
Phys. Chem., 78, 90 (1974); c.) G. R. Stevenson, J. G.
Concepcion, and L. Echegoyen, J. Am. Chem. Soc., 96, 5452
(1974).
4. R. D. Rieke and R. A. Copenhafer, Tetrahedron Lett., 4097
(1971).
5. J. H. Hammons, C. T. Kresge, and L. A. Paquette, J. Am.
Chem. Soc., 98, 8172 (1976).
6. J. G. Concepcion and G. Vincow, J. Phys. Chem., 79, 2042
(1975).
7. R. E. Moss, Mol. Phys., 10, 501 (1966).
8. D. H. Levy and R. J. Myers, J. Chem. Phys., 41, 1062 (1964).
9. A. Bauder and R. J. Myers, J. Mol. Spectrosc., 27, 110
(1968).
10. This program is available from the Quantum Chemistry Pro-
gram Exchange, Department of Chemistry, Indiana University.
11. N. L. Bauld, F. R. Farr, and C. E. Hudson, J. Am. Chem.
Soc., 96, 5634 (1974).
12. M. J. S. Dewar, A. Harget, and E. Haselbach, J. Am. Chem.
Soc., 91, 7521 (1969). MINDO calculations indicate that
a D_{4h} structure with CC distances of 1.383 and 1.442 Å,
and all CCC angles 135° , is lower in energy than D_{8h}
structures, but that a nonplanar D_{2d} structure with all
CCC angles = 132.2° is the most stable one for COT^- .
13. G. Herzberg, "Molecular Spectra and Molecular Structure,"
vol. III, D. Van Nostrand Co., Inc., 1966, p.41.
14. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Mole-
cular Vibrations," McGraw-Hill Book Co., New York, 1955.

15. In contrast to our treatment, other authors have used a model in which vibronic mixing in the ground state is the same for all substituted $\text{COT}^{\cdot-}$'s. See references 3 and 6.
16. A. C. Albrecht, J. Mol. Spectrosc., 5, 236 (1960).
17. The neutral molecule, of course, has a tub-shaped (D_{2d}) structure, and, according to the MINDO calculations of Dewar et al., ref. 12, the radical anion should also be nonplanar.

Figure Captions

- Fig. 1. ESR spectrum of $\text{CH}_3\text{-COT}^-$ *Top*: experimental. *Bottom*: computer simulated.
- Fig. 2. Approximate carbon or hydrogen motions for the b_{1g} and b_{2g} vibrational modes.
- Fig. 3. INDO potential energies *vs.* b_{2g} CC stretching distortion for COT^- , $\text{CH}_3\text{-COT}^-$ and $\text{CH}_3\text{O-COT}^-$
- (a) COT^-
 - (b) $\text{CH}_3\text{-COT}^-$
 - (c) $\text{CH}_3\text{O-COT}^-$

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1.) b_{1g}

a.) CCC Bending

b.) CH Stretching

2.) b_{2g}

a.) CC Stretching.

b.) CCH Bending

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