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An Electron Spin Resonance Study of the Tropone Anion Radical

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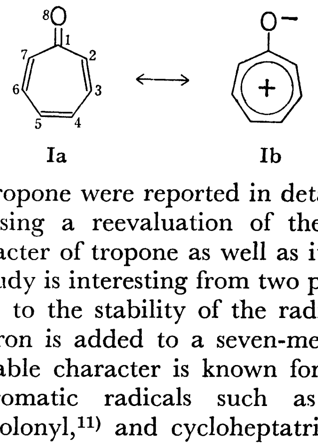
The ESR spectrum of the tropone anion radical has been examined. The radical was generated from the neutral species by the electrolytic reduction in *N,N*-dimethylformamide. Splitting constants are satisfactorily explained in terms of the calculated spin densities by the McLachlan procedure, confirming that the unpaired spin orbital belongs to an a_2 symmetrical species. The complete delocalization of the π-electrons was assumed for the anion radical.

The physico-chemical properties of tropone (I) have been studied by means of various techniques such as dipole moment,[1] vapor-phase electron diffraction,[2] ionization potential,[3] and infrared and Raman spectra.[4] Theoretical treatments of the electronic spectrum have also been discussed by some investigators.[5–6] It has been clarified from the above results and the chemical properties of troponoid compounds[7] that tropone has a planar C_{2v} symmetrical structure possessing both the unsaturated character as a conjugate ketone (Ia) and the aromatic character of a 6π-electron ring system (Ib) caused by the polarization of the carbonyl group. The magentic resonance of tropone, however, has been little studied until recently.[8] The measurement and analysis of the nuclear magnetic resonance of tropone were reported in detail by Bertelli *et al.*,[9] proposing a reevaluation of the question of aromatic character of tropone as well as its derivatives.



Ia Ib

The ESR study is interesting from two points of view. One is related to the stability of the radical in which an extra electron is added to a seven-membered ring. Since the instable character is known for some seven-membered aromatic radicals such as cycloheptatrienyl,[10] tropolonyl,[11] and cycloheptatriene anion,[12] the stability would be related to whether the radical has a ketyl structure as seen in the stable benzophenone radical anions. The other point is the expectation that the splitting constants, if observed, might be related to the calculated spin densities at the carbon atoms of the radical. This would be a good approach to getting the relationship between the experiments and the molecular orbital calculations.

We have measured the ESR spectrum of the tropone

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anion radical.[13] Details of the study will be reported.

Results and Discussion

Generation and ESR Spectrum of Tropone Anion Radical. Treatment of tropone with lithium, sodium, or potassium metal in degassed tetrahydrofuran or 1,2-dimethoxyethane caused immediate change in color to reddish violet at temperatures above −40°C. However, no ESR signal was observed at temperatures above −75°C. On the other hand, the electrolytic reduction of tropone solution in degassed *N,N*-dimethylformamide (DMF) at room temperature gave the spectrum shown in Fig. 1. The radical was not stable so that the signal intensity decreased to one half during 15 minutes at room temperature after the current was turned off. The color of the solution changed gradually to a reddish brown during the electrolysis. The use of acetonitrile as the solvent did not favor the generation of the radical.

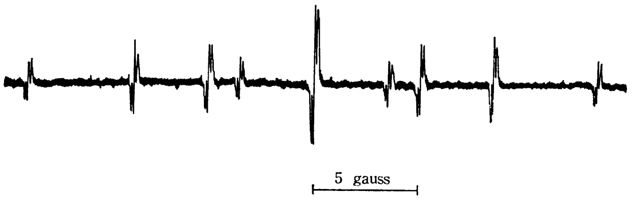

Fig. 1. ESR spectrum of tropone anion radical generated by electrolytic reduction of tropone in DMF at room temperature.

Hyperfine structure of the spectrum is readily analyzed with three splitting constants as expected for the symmetrical structure of I. Assignments for the constants are reasonably made by comparison with calculated spin densities. The observed splitting constants and the experimental spin densities calculated by the relation, $a_i^{\mathrm{H}}=Q_{\mathrm{CH}}^{\mathrm{H}}\rho_i$,[14] where $|Q_{\mathrm{HC}}^{\mathrm{H}}|=23.7$ gauss, are given in Table 1.

Table 1. Observed splitting constants (a_i) and calculated spin densities (ρ_i) for tropone anion radical

Position	a_i gauss	Spin density, ρ_i			
		Exptl[a)]	Calcd		
			Hückel	McLachlan[b)] (1)	McLachlan[b)] (2)
1			0	−0.0562	−0.0571
2, 7 (2H)	8.578	0.3619	0.2716	0.3741	0.3726
3, 6 (2H)	0.10	0.004	0.0538	−0.0186	−0.0200
4, 5 (2H)	5.050	0.2131	0.1746	0.1861	0.1849
8			0	−0.0270	−0.0179

a) Spin densities using the McConnell relation.[14]

b) The Coulomb and resonance integral parameters for the carbonyl group of tropone were chosen as:

(1) $\beta_{1,8}=1\beta$ and $\alpha_8=\alpha+\beta$,

(2) $\beta_{1,8}=1.4\beta$ and $\alpha_8=\alpha+2\beta$.

The λ-parameter in McLachlan procedure was fixed at the value $\lambda=1.2$.

Calculation of Spin Densities. Calculation of unpaired spin densities (ρ_i) for the anion radical was carried out by employing the Hückel MO theory and the approximate configuration interaction treatment proposed by McLachlan.[15] The bond alternation parameter k was introduced in order to represent the aromaticity of the tropone molecule. It is defined by $k=\beta_s/\beta_d$, where β denotes the resonance integral parameter, and the subscripts s and d the single and double bond in Ia, respectively. $k=1$ means complete delocalization and $k=0$ complete localization of π-electrons. The Coulomb and resonance integral parameters for the carbonyl group were chosen.

It was shown from the calculations that, if $k=1$, the calculated spin densities by the Hückel MO theory are independent of the Coulomb and resonance integral parameters for the carbonyl group, because the unpaired spin orbital for the radical belongs to an a_2 symmetrical species of C_{2v} symmetrical structure. The effects of the carbonyl parameters appear slightly at second hand in the McLachlan spin densities. Two calculations using different parameters for the carbonyl group are included in Table 1 togehter with the Hückel spin densities. The McLachlan procedure showed better values than by Hückel MO calculation.

Dependence of the orbital energies of tropone on k-parameter is shown in Figs. 2a and 3a for the cases of two different Coulomb integral parameters. It is assumed that $\beta_{\mathrm{C=O}}=\beta_{\mathrm{C=C}}$. These figures disclose that the reduction of k-parameter replaces the unpaired spin orbital by the b_2 symmetrical one. The replacement of the orbitals is unavoidable unless one adopts the unusually small parameter α_8 for the carbonyl oxygen. The spin density at the carbonyl group in the b_2 orbital is so large that the total extent of the ESR spectrum can not be rationalized. It is thus concluded that the k-parameter must be close to 1, which means the complete delocalization of π-electrons in the tropone anion radical.

Total Binding Energy. The above conclusion for the anion radical is inconsistent with the considerations

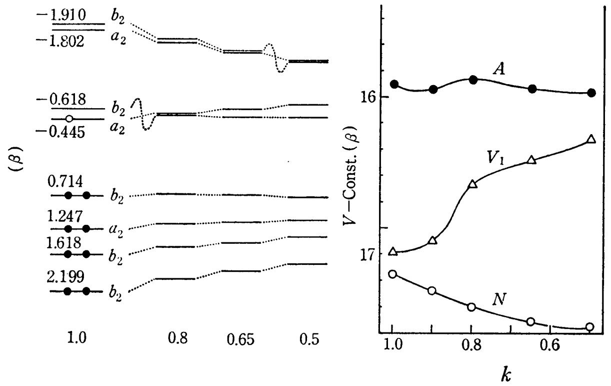

Fig. 2. Dependence of the Hückel molecular orbitals and total binding energy (V) on the bond alternation parameter k. $\beta_{1,8}=1\beta$, $\alpha_8=\alpha+1\beta$.
(a): Orbital energy. (b): V-k Curves for tropone (N), the lowest excited state (V_1), and tropone anion radical (A). All the energies are in terms of β.

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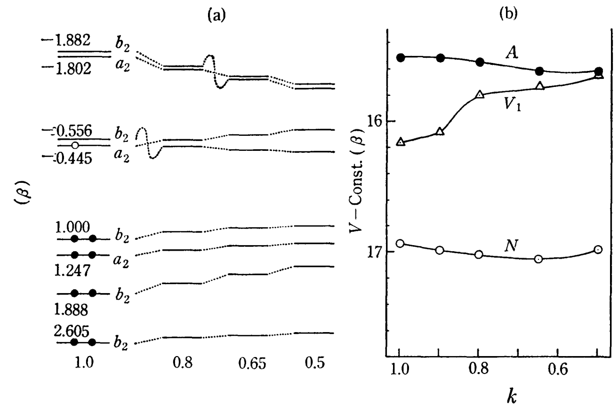


Fig. 3. Dependence of the Hückel molecular orbitals and total binding energy on the bond alternation parameter. $\beta_{1,8}=1\beta$, $\alpha_8=\alpha+2\beta$. Representation is the same as for Fig. 2.

for the neutral molecule by Yamaguchi *et al.*[6] and Bertelli *et al.*[9] who emphasized the reduced delocalization of the π-electrons in tropone. It is considered that a comparison between the *V*-*k* curves for tropone and the anion radical might provide information on the difference in the bond alternations. The *V*-*k* curve depicts the dependence of the total binding energy on *k*-parameter. We thus examined the curves for both species. The total binding energies (V) were calculated by the procedure by Longuet-Higgins and Salem,[16] adapted to non-benzenoid aromatic compounds by Nakajima and Katagiri.[17] The procedure is as follows.

Bond lengths *r* are given by

$$r(\text{in Å}) = 1.520 - ap$$

$$a = 0.186$$

where *p* designates the bond orders. Resonance integral $\beta(r)$ is given as an exponential function of the form

$$\beta(r) = \beta \exp[b(1.397-r)]$$

with

$$b = 4.599\,\text{Å}^{-1}.$$

The total binding energy of the molecule is given by

$$V = E_\pi + E_\sigma = (2/ab)\sum_{i<j}\beta_{ij} + \sum_i q_i\alpha_i + \text{const}$$

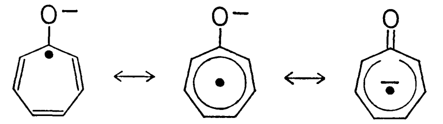
with

$$\alpha_i = \alpha + \omega(1-q_i)\beta$$

in which α designates the Coulomb integral parameter, q_i the electron density, and ω a proportionality coefficient here taken to be unity. β_{ij} corresponds to the $\beta(r)$ calculated for the bond between the *i*- and *j*-atoms. Calculations using the above equation afforded the *V*-*k* curves shown in Figs. 2b and 3b for the ground states of the neutral molecule (N) and the anion radical (A). For comparison, the curves for the lowest excited states (V_1) are included in the figures.

It is to be noticed in that the total binding energy of the anion radical is little affected by the bond alternation parameter *k*, while the other two states, *N* and V_1, show a distinct dependency like that for some non-benzenoid aromatic molecules.[17] Since the variation of the energy with *k*-parameter for the anion radical is estimated to be few kilocalories which can be covered by thermal energy at normal temperature, the calculations do not permit assumption of the stable electronical configuration for the anion radical. This implies that the electronical configuration of the radical is largely affected by the counter-ion and the supporting electrolyte.

Conclusion. It is clear that the unpaired spin orbital belongs to an a_2 species and the spin is located mainly on the seven-membered ring. Thus the structure IIc is predominant over the ketyl forms IIa and IIb for the radical. As the radical was generated at room temperature, it is more stable than the cycloheptatriene anion radical,[12] which could only be generated at low temperature and was assumed to have a nonplanar boat conformation. The considerable stability of the tropone anion radical might be attributed to the environmental factors besides the complete delocalization of π-electrons in a planar tropone structure.



IIa IIb IIc

Experimental

Tropone was carefully purified by distillation in a high vacuum. *N*,*N*-Dimethylformamide was degassed by at least five freezing-pumping cycles after being purified and distilled on to a Molecular Sieve 4A which had been flame-dried in a vacuum.

The technique employed in the electrolytic generation of the free radical is similar to that used by Hirayama.[18] A cell with platinum electrodes was constructed so that electrolysis could be performed within a cavity for the preparation of radical unstable at room temperature. Electrolysis was performed with a concentration less than 0.7% in DMF, using tetra-*n*-propylammonium perchlorate as a supporting electrolyte.

The ESR spectrum was measured with a Hitachi X-band ESR spectrometer Model MPU-3B using a field modulation of 100 kHz.

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