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An SCF MO Treatment of Tropone Radical Anion

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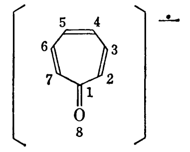
Ikegami and Seto[1] reported on the ESR spectrum of tropone radical anion.



We would like to report our calculations for tropone radical anion using "half-electron" SCF MO method of Dewar *et al.*[2] We also give a comparison between tropone radical anion and the parent compound. Calculations for tropone were performed using Dewar's variant[3] of the original Pople's SCF MO method.[4] Calculated charge densities for tropone and its radical anion and calculated spin densities for tropone radical anion together with spin densities obtained from the observed hyperfine splitting constants[5] are given in Table 1. The results suggest that spin densities on the stoms 1 and 8 are small or zero, since the highest occupied MO of tropone radical is an antisymmetric orbital. A similar conclusion is reached by HMO calculations[1], but McLachlan's procedure predicted[1] negative spin densities on these atoms even bigger in magnitude than the spin densities on the atoms 3 and 6. This was not tested by ESR study because neither atom 1 nor 8 carries a hydrogen atom. However, both sets of calculations (HMO and McLachlan's procedure)[1] reproduce qualitatively the experimental spin densities, but the quantitative agreement is not so good. If we compare, for example, the ratios of the spin densities on the atoms 2 or 7 and 4 or 5, we obtain the following results.

ρ 2,7/ρ 4,5	Method of calculation
1.56	HMO
2.02	McLachlan's procedure
1.67	our calculations
1.69	experimental value

Table 1. Calculated charge densities for tropone and tropone radical anion, and calculated and observed spin densities for tropone radical anion

Ring position	Charge density		Spin density of tropone radical anion	
	Tropone	Tropone radical anion	Calculated	Experimental[a]
1	0.6462	0.5879	0.00	—
2,7	1.0092	1.2585	0.35	0.36
3,6	0.9464	0.9588	0.04	0.004
4,5	0.9854	1.1695	0.21	0.21
8	1.4720	1.6383	0.00	—

a) Y. Ikegami and S. Seto, This Bulletin, **41**, 2225 (1968).

We would like to add that our calculations included the bond length variations (variable β).[6] This was found[7] recently to be very important in the spin density calculations of the conjugated anion radicals.

Table 2. π-Electron charge density on oxygen in tropone calculated by various authors

Author	π-Electron charge density (q_0)
Julg and Bonnet[a]	1.335
Inuzuka and Yokota[b]	1.4803
Kuroda and Kunii[c]	1.4714
Hosoya and Nagakura[d]	1.2531
Yamaguchi, Amako, and Azumi[e]	1.1431
Bertelli and Andrews, Jr.[f]	1.280
Our result	1.4720

a) A. Julg and M. Bonnet, *Tetrahedron*, **20**, 2243 (1964).
b) K. Inuzuka and T. Yokota, *J. Chem. Phys.*, **44**, 911 (1966).
c) H. Kuroda and T. Kunii, *Theoret. Chim. Acta* (Berlin), **7**, 220 (1967).
d) H. Hosoya and S. Nagakura, *ibid.*, **8**, 319 (1967).
e) H. Yamaguchi, Y. Amako, and H. Azumi, *Tetrahedron*, **24**, 267 (1968).
f) D. J. Bertelli and T. G. Andrews, Jr., *J. Amer. Chem. Soc.*, **91**, 5280 (1969).

In Table 2 is given π-electron charge distribution on the oxygen atom of tropone calculated by various authors, who all agree that a certain amount of π-electron charge is donated to the oxygen. The unpaired electron in the tropone radical ion, which occupies the π-molecular orbital contributes a certain amount of the charge to the total π-electronic charge densities of each ring carbon atom except for C_1, and to the charge density of the oxygen atoms. Such a charge density distribution may indicate that the polar character of the carbonyl group C_1–O is increased in tropone radical ion.

We have also calculated bond lengths of tropone and its radical anion. The results are given in Table 3. Our calculation of bond lengths of tropone predicts

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[1] Y. Ikegami and S. Seto, This Bulletin, **41**, 2225 (1968).

[2] M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, **90**, 1953 (1968).

[3] A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 692 (1965); M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969); M. J. S. Dewar and T. Morita, *ibid.*, **91**, 796 (1969).

[4] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[5] Observed hyperfine splitting constants (a_i^{H}) were converted into spin densities (ρ_i^{π}) using the relation $\rho_i^{\pi}=a_i^{\mathrm{H}}/Q_{\mathrm{CH}}^{\mathrm{H}}$, where $Q_{\mathrm{CH}}^{\mathrm{H}}=23.7$ Gauss.

[6] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965).

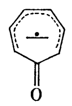
[7] H. G. Benson and A. Hudson, *Mol. Phys.*, **20**, 185 (1971).

Table 3. Calculated and observed bond lengths (in Å)

Bond	Tropone			Tropone radical anion
	Our result	Experiment[a]		
		Kuroda and Kunii	Ogasawara and Kimura	
1,8	1.259	1.270	1.23	1.279
1,2 (1,7)	1.463	1.449	1.45	1.448
2,3 (6,7)	1.355	1.369	1.36	1.392
3,4 (5,6)	1.452	1.431	1.46	1.401
4,5	1.357	1.373	1.34	1.420

a) We wish to thank the referee for information on the important work on the structure of tropone reported at the International Symposium on Non-benzenoid Aromatic Compounds held at Sendai, Japan, in August 1970.

the bond alternation within the seven-membered ring. The results of earlier structural studies on tropone agree with the value of 1.26±0.02 Å for the length of C=O bond, but CC bonds were predicted to be of an equal length (average value being 1.405±0.02 Å).[8] On the other hand, a recent structure determination of 4,5-benzotropone[9] indicated that polyenoid-type bond alternation is present in the tropone moiety. An alternation was found in the tropone ring and experimental bond lengths agree fairly well with our calculated values (Table 3).[10] Apparently tropone is a cyclic polyenoid molecule and it can be regarded as a non-aromatic compound. This was confirmed experimentally[11] and theoretically.[12] Calculated bond lengths (as well as calculated charge densities) of tropone radical anion support representation of its structure as shown below.



The C=O bond and CC bonds 1,2 and 1,7 are fixed as double and single bonds, respectively, while the remaining CC bonds are aromatic with an average bond length 1.4 Å. This is quite a different structure from that of tropone.

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8) See for example: K. Kimura, S. Suzuki, M. Kimura, and M. Kubo, *J. Chem. Phys.*, **27**, 320 (1957).

9) T. Hata, H. Shimanouchi, and Y. Sasada, *Tetrahedron Lett.*, **1969**, 753.

10) M. Ogasawara and M. Kimura reported at the International Symposium on Non-benzenoid Aromatic Compounds held at Sendai, Japan, August 1970 on "The structure of tropone determined by electron diffraction".

11) D. J. Bertelli and T. G. Andrews, Jr., *J. Amer. Chem. Soc.*, **91**, 5280 (1969); D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *ibid.*, **91**, 5286 (1969).

12) Aromatic stabilization (A_s) of tropone is calculated to be only 0.8 kcal/mol. Benzene, for example, has A_s=20.0 kcal/mol. Aromatic stabilization was calculated in the manner described by M. J. S. Dewar, A. J. Harget, and N. Trinajstić, *J. Amer. Chem. Soc.*, **91**, 6321 (1969).