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THE ESR SPECTRA OF THE NITROTROPOLONATE ANION RADICALS

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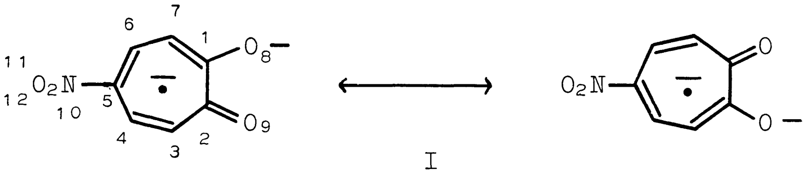
Electrolyses of 5-nitro-, 3-nitro, and 3,5-dinitro-tropolones in N,N-dimethylformamide generated the corresponding tropolonate anion radicals. Hyperfine structures in the ESR spectra of the radicals were reasonably explained by the spin density calculations. The results for the 3-nitro- and 3,5-dinitro-tropolonates suggested that the 3-nitro groups were twisted about 40 and 55°, respectively, from the ring plane.

In the previous papers[1,2] the generations and the electron spin resonance (ESR) spectra of some tropone anion radicals were reported. Since nitro-substituted aromatic compounds are readily reduced to form the stable anion radicals, generation of the anion radicals from nitrotropolones would be expected while no tropolonate anion radical has been reported. The electrolytic generations and the ESR spectra of 5-nitro-, 3-nitro-, and 3,5-dinitro-tropolonate anion radicals are reported in this paper.

5-Nitrotropolonate Anion Radical. Fig. 1 shows the ESR spectrum of the radical generated by the electrolysis of a 0.007 M solution of 5-nitrotropolone in N,N-dimethylformamide (DMF) at ca. 2.0 V, using tetra-*n*-propylammonium perchlorate as the supporting electrolyte. Hyperfine structure of the spectrum is readily interpreted by assuming the splittings arise from one nitrogen nucleus and two sets of pairs of equivalent protons. The observed splitting constants are given in Table 1. The equivalence of two sets of protons means that the radical has a symmetrical structure arising from a resonance form I.



I

The generation of the dianion radical from the tropolone is analogous to those of the nitrophenolate[3,4] and 4-cyanobenzoate anion radicals.[5]

The Hückel MO calculations with the approximate configuration interaction treatment of McLachlan were performed for the 5-nitrotropolonate anion radical in order to estimate the spin density distribution and to assist in the assignment for the splitting constants. The values of parameters used here for the nitro group were taken from the work by Rieger and Fraenkel.4) Because of the lack of the reliable MO parameters for the CO groups in the tropolonate structure, the parameters for this group were varied over the following ranges: $1.0 \leqq h_8 = h_9 \leqq 2.2$ and $1.0 \leqq k_{1,8} = k_{2,9} \leqq 2.0$, as the MO integral parameters are defined by the relation $\alpha_i = \alpha + h_i\beta$ and $\beta_{i,j} = k_{i,j}\beta$ where α and β are the Coulomb and resonance integrals, respectively, for benzene. All other bond length variations were neglected. To find out the parameters appropriate to the C=O group, the calculations were compared with the experimental splitting constants for the protons, adopting the relation $a_i = Q^H_{CH}\rho_i$, where $|Q^H_{CH}| = 23.7$ gauss. A good agreement with the experimental values was obtained by using the parameters $h_8 = h_9 = 2.0$ and $k_{1,8} = k_{2,9} = 1.8$. The spin densities are given in Table 1.

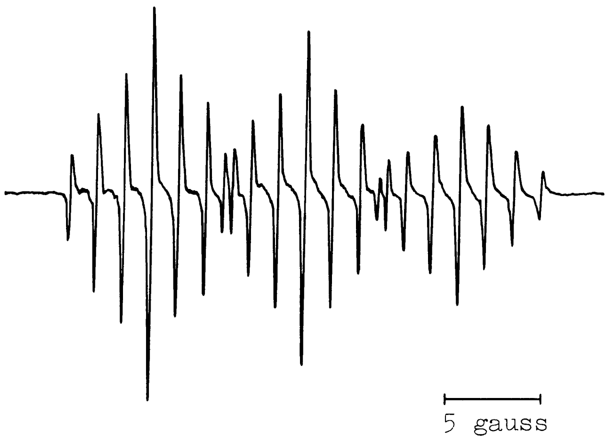


Fig. 1. ESR spectrum of the 5-nitrotropolonate anion radical generated by the electrolysis in DMF.

Table 1. Observed Splitting Constants (a_i) and Calculated Spin Densities (ρ_i) for the 5-Nitrotropolonate Anion Radical

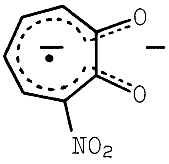
Position	a_i gauss	Spin density, ρ_i Exptl.a)	Calcd.b)
1, 2			0.1092
3, 7	1.42	0.059	-0.0472
4, 6	2.84	0.118	0.1178
5			-0.0093
8, 9 (O)			0.0477
10 (NO_2)	8.04		0.2110
11,12(NO_2)			0.1716

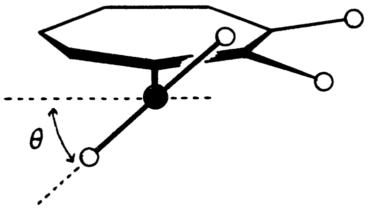
a) With the relation $a_i = Q^H_{CH}\rho_i$, in which $|Q^H_{CH}| = 23.7$ gauss was adopted.
b) Calculated by the McLachlan procedure. Parameters for the calculation: $\alpha_8 = \alpha_9 = \alpha + 2.0\beta$, $\beta_{1,8} = \beta_{2,9} = 1.8\beta$, $\beta_{C-N} = 1.2\beta$, $\alpha_N = \alpha + 2.2\beta$, $\alpha_O = \alpha + 1.4\beta$, $\beta_{N-O} = 1.67\beta$, and $\lambda = 1.2$.

The calculation of $a_N^{NO_2}$ with a relation $a_N^{NO_2} \approx Q_N\rho_N + 2Q_{ON}\rho_O$,4) where Q_N and Q_{ON} have the values of 99 ± 10 and 36 ∓ 6 gauss, respectively, was also in satisfactory agreement with the experimental splitting constant (calcd. 8.53 gauss).

3-Nitrotropolonate Anion Radical. Electrolytic reduction of 3-nitrotropolone in DMF generated the stable anion radical which exhibited the ESR spectrum shown in Fig. 2. Hyperfine structure of the spectrum is analyzed with five splitting constants given in Table 2 and is interpreted as arising from the structure IIa. However, using the same parameters with those used for the

5-nitrotropolonate anion radical, the spin density calculations did not show a good agreement with the experimental values. It was then assumed that the disagreement is caused by the twisting of the nitro group from the seven-membered ring plane, as depicted by IIIb.


IIIa



IIIb

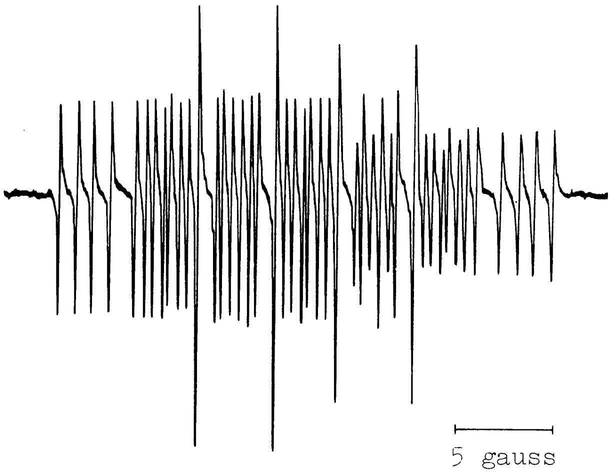


Fig. 2. ESR spectrum of the 3-nitrotropolonate anion radical generated by the electrolysis in DMF.

Table 2. Observed Splitting Constants ($\underline{a}_i$) and Calculated Spin Densities (ρ_i) for the 3-Nitrotropolonate Anion Radical

Position	$\underline{a}_i$ gauss	ρ_i Exptl.a)	Calcd.b)
1			0.1077
2			0.0114
3			0.0048
4	3.98	0.168	0.1749
5	1.76	0.074	-0.0546
6	4.51	0.190	0.1856
7	0.95	0.040	-0.0297
8			0.0447
9			0.0022
10 ($\underline{N}O_2$)	7.19		0.2140
11,12($N\underline{O}_2$)			0.1695

a) See footnote a) in Table 1.

b) Calculated by the McLachlan procedure. The values of parameters are the same with those used for the 5-nitro isomer except $\beta_{C-N} = 1.2\,\beta\cos 40^\circ$.

In order to confirm the effect of steric hindrance between the nitro group and the CO oxygen on the ring proton splittings, the spin densities were calculated with the modification that the resonance integral of the C-N bond was estimated to be $1.2\,\beta\cos\theta$, where θ is a twisting angle between the nitro group and the ring. Examining the dependence of the spin densities of the ring positions, it was indicated that the theoretical spin densities at the positions 4 and 6 approach each of the corresponding experimental spin densities around 37 and 43°, respectively. The calculated spin densities for the positions 5 and 7 with

$\theta = 40^\circ$ were also close to the corresponding experimental values though some deviations were recognized. Allowing some deviations in the calculations for such a complex molecule, it is concluded that the nitro group was twisted about 40° from the ring plane. The spin densities calculated by using $\beta_{3,10} = 0.92\ \beta$ corresponding to $\theta = 40^\circ$ are given in Table 2.

3,5-Dinitrotropolonate Anion Radical. Similar examination has been carried out for the 3,5-dinitrotropolonate anion radical generated by the electrolysis of the corresponding tropolone in DMF. The ESR spectrum of the radical is shown in Fig. 3. The spin density calculations led to the conclusion that the nitro group at 3-position is twisted about 55° from the tropolonate ring plane while the nitro group at 5-position is assumed to be coplanar with the ring. Some data are given in Table 3. The details of the present study will be reported elsewhere.

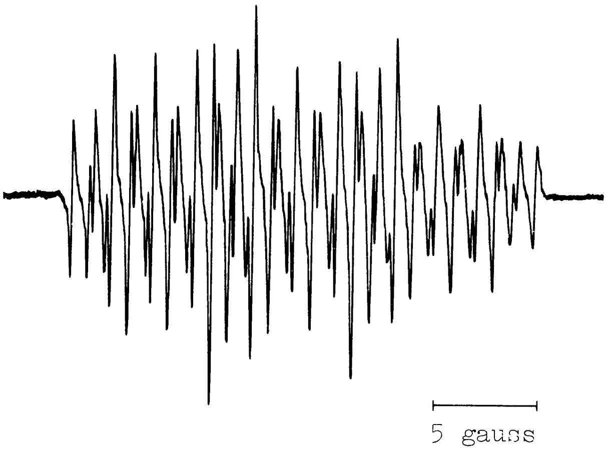


Fig. 3. ESR spectrum of the 3,5-dinitrotropolonate anion radical generated by the electrolysis in DMF.

Table 3. Splitting Constants (a_i) and Spin Densities (ρ_i) for the 3,5-Dinitrotropolonate Anion Radical

Position	a_i gauss	ρ_i Exptl.	ρ_i Calcd.[a]
4	1.94	0.082	0.0727
6	3.92	0.165	0.1500
7	1.08	0.046	-0.0527
10(3-NO_2)	0.78		0.0046
11,12(NO_2)			0.0008
13(5-NO_2)	6.78		0.1940
14,15(NO_2)			0.1576

a) McLachlan spin densities.
β_{C-N} (for 3-NO_2) = $1.2\,\beta \cos 55^\circ$.

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