# An Electron Spin Resonance Study of the Anion Radicals of Some Nitrotropolonates and 2-Methoxy-5-nitrotropone

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The anion radicals of 5-nitro-, 3-nitro-, and 3,5-dinitro-tropolonates and of 2-methoxy-5-nitrotropone were generated electrolytically in *N,N*-dimethylformamide. Hyperfine structures of these ESR spectra were reasonably interpreted with 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.

Studies on the anion radicals of tropone[1)] and its some derivatives[2)] revealed that the anion radicals of tropone derivatives are usually unstable and could only be generated by the electrolytic reductions for some tropones under the presence of a large amount of supporting electrolyte. Since nitro-substituted aromatic compounds are easily reduced to form the stable anion radicals, the generation of the anion radicals of nitro-substituted tropone derivatives will be expected. As a part of the electron spin resonance (ESR) study on the nonbenzenoid aromatic radicals, the electrolytic generations of the anion radicals from 5-nitro-, 3-nitro-, and 3,5-dinitro-tropolones and 2-methoxy-5-nitrotropone have been successfully examined. This paper reports the ESR spectra and the structures of these radicals. The McLachlan calculation[3)] was adopted to the spin density estimation in order to interpret the ESR hyperfine structures.

## Results and Discussion

*5-Nitrotropolonate Anion Radical.* Figure 1 shows the ESR spectrum of the radical generated by the electrolysis of a 0.007 M solution of 5-nitrotropolone in degassed *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 in terms of splitting from one nitrogen nucleus and two sets of pairs of equivalent protons. The observed splitting constants are given in Table 1. Since tropolones are usually strong acid like phenols, the formation of radicals would be understood in a similar manner to the formation of phenolate and benzoate anion radicals, such as nitrophenolate and 4-cyanobenzoate anion radicals,[4—6)] which were produced by the electrolyses of the corresponding phenols and benzoic acids in the presence of a large amount of supporting electrolyte. Accordingly, the equivalence of two sets of protons in the radical produced should be explained with the assumption that the radical has a symmetrical structure arising from a resonance form I, rather than a structure of tropolone anion radical in which a highly mobile tautomerism with the jump of the hydroxylic proton would be required.

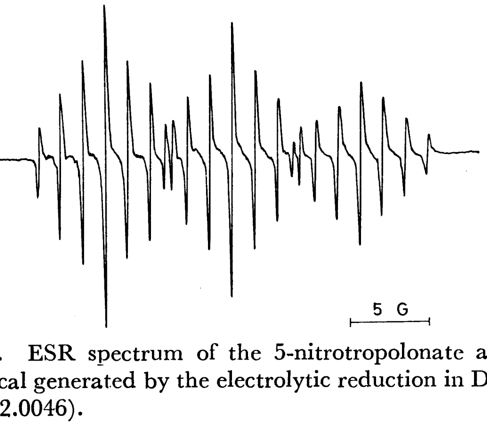
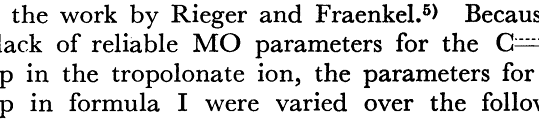


Fig. 1. ESR spectrum of the 5-nitrotropolonate anion radical generated by the electrolytic reduction in DMF ($g$=2.0046).

Table 1. Splitting constants ($a_i$) and spin densities ($\rho_i$) for the 5-nitrotropolonate anion radical

| Position | $a_i$ G | $\rho_i$ Exptl[a)] | $\rho_i$ Calcd[b)] |
|---|---|---|---|
| 1, 2 | | | 0.1092 |
| 3, 7 | 1.42 | 0.060 | −0.0472 |
| 4, 6 | 2.84 | 0.120 | 0.1178 |
| 5 | | | −0.0093 |
| 8, 9 (C$\underline{\mathrm{O}}$) | | | 0.0477 |
| 10 ($\underline{\mathrm{N}}\mathrm{O}_2$) | 8.04 | | 0.2110 |
| 11, 12 ($\mathrm{N}\underline{\mathrm{O}}_2$) | | | 0.1716 |

a) With the relation $a_i = Q^{\mathrm{H}}_{\mathrm{CH}}\rho_i$, in which $|Q^{\mathrm{H}}_{\mathrm{CH}}|=23.7$ G was adopted. b) Calculated by the McLachlan procedure. The following parameters were adopted: $\alpha_8=\alpha_9=\alpha+2.0\beta$, $\beta_{1,8}=\beta_{2,9}=1.8\beta$, $\beta_{\mathrm{C-N}}=1.2\beta$, $\alpha_{\mathrm{N}}=\alpha+2.2\beta$, $\alpha_{\mathrm{N}\underline{\mathrm{O}}}=\alpha+1.4\beta$, $\beta_{\mathrm{N-O}}=1.67\beta$, and $\lambda=1.2$.



I

The Hückel MO calculations with the approximate configuration interaction treatment of McLachlan were carried out for the 5-nitrotropolonate anion radical in order to estimate the spin density distribution and to assist in assigning the splitting constants. The values of parameters used here for the nitro group were taken from the work by Rieger and Fraenkel.[5)] Because of the lack of reliable MO parameters for the C$\cdots$O group in the tropolonate ion, the parameters for this group in formula I were varied over the following ranges: $\alpha+1.0\beta \leqq \alpha_8=\alpha_9 \leqq \alpha+2.2\beta$ and $1.0\beta \leqq \beta_{1,8}=\beta_{2,9} \leqq 2.0\beta$, where $\alpha$ and $\beta$ are the Coulomb and resonance integrals, respectively, for benzene. All other bond length variations were neglected, since the bond alternation in the seven-membered anion ring was not worthy of consideration even for the tropone anion radical.[1)] 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 $|Q^H_{CH}| = 23.7$ G. A good agreement with the experimental values was obtained by using the parameters $\alpha_8 = \alpha_9 = \alpha + 2.0\beta$ and $\beta_{1,8} = \beta_{2,9} = 1.8\beta$.[7] The spin densities are given in Table 1. The calculation of $a_N^{NO_2}$ with a relation $a_N^{NO_2} \approx Q_N\rho_N + 2Q_{ON}\rho_{O'}$,[5] where $Q_N$ and $Q_{ON}$ have the values of 99±10 and 36±6 G, respectively, was also in satisfactory agreement with the experimental value (calcd 8.53 and exptl 8.04 G).

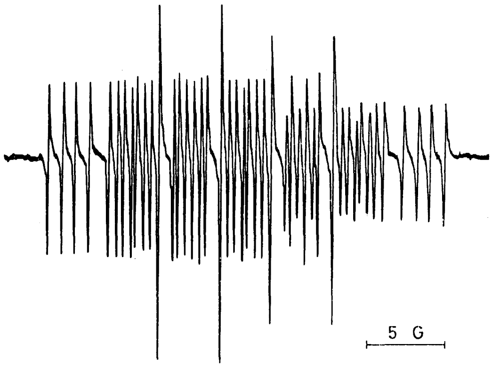


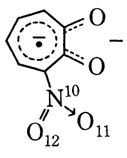
Fig. 2. ESR spectrum of the 3-nitrotropolonate anion radical generated by the electrolytic reduction in DMF ($g = 2.0039$).

TABLE 2. SPLITTING CONSTANTS ($a_i$) AND SPIN DENSITIES ($\rho_i$) FOR THE 3-NITROTROPOLONATE ANION RADICAL

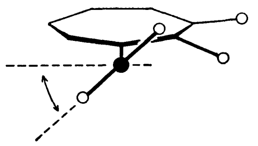
| Position | $a_i$ G | $\rho_i$ Exptl[a] | $\rho_i$ Calcd[b] |
|---|---|---|---|
| 1 | | | 0.1077 |
| 2 | | | 0.0114 |
| 3 | | | 0.0048 |
| 4 | 3.98 | 0.168 | 0.1749 |
| 5 | 1.76 | 0.074 | −0.0546 |
| 6 | 4.51 | 0.190 | 0.1856 |
| 7 | 0.95 | 0.040 | −0.0297 |
| 8 | | | 0.0447 |
| 9 | | | 0.0022 |
| 10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

a) See the footnote a) in Table 1. b) Calculated by the McLachlan procedure. The values of parameters are the same as those used for the 5-nitro isomer except $\beta_{C-N} = 1.2\beta \cos 40°$.

*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 this spectrum is analyzed with five splitting constants given in Table 2 and is interpreted as arising from the structure IIa. The McLachlan calculation was then applied to this structure. Using the same parameters with those for the 5-nitro isomer, however, 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 IIb.



IIa



IIb

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 $\theta$ is a twisting angle between the nitro group and the ring. The dependence of the spin densities at the ring positions 4, 5, 6, and 7 on the angle $\theta$ is shown in Fig. 3. As seen from the figure, 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 values for the positions 5 and 7 with $\theta = 40°$ were not far from the corresponding experimental values though some deviations are recognized. Allowing some deviations in the calculations from the experimental values, the McLachlan calculation led to the conclusion 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 this twisting angle are given in Table 2.

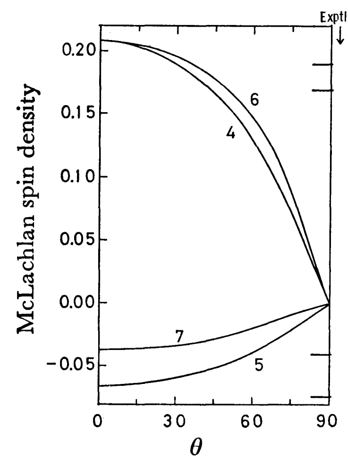


Fig. 3. Spin densities ρ calculated for the 3-nitrotropolonate anion radical by the McLachlan procedure as a function of the twisting angle θ between the ring and the nitro group. The numbers on the curves indicate the positions in the radical. See the footnote in Table 2 for the parameters in the calculation.

*3,5-Dinitrotropolonate Anion Radical.* The 3,5-dinitrotropolonate anion radical was produced by the electrolysis of the corresponding tropolone in DMF, similarly to the above 5- and 3-nitrotropolonates. The ESR spectrum of the radical shown in Fig. 4 is analyzed with five splitting constants, two of which represent the couplings with two different nitrogen atoms and the others the couplings with three different hydrogen atoms.

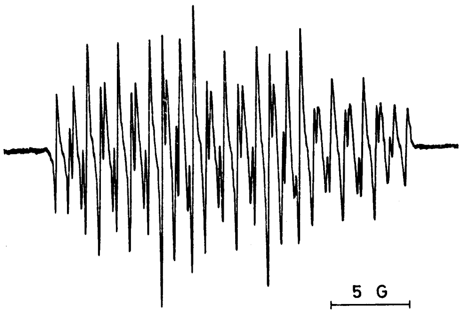
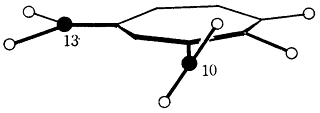


Fig. 4. ESR spectrum of the 3,5-dinitrotropolonate anion radical generated by the electrolytic reduction in DMF ($g$=2.0043).

With reference to the structures of the 5- and 3-nitrotropolonate anion radicals, it is readily assumed that the nitro group at 3-position is twisted considerably from the ring plane while the nitro group at 5-position is co-planar with the ring, as depicted by III. In order to confirm the twisting of the nitro group and to assist in assigning the splitting constants, the spin density calculations were carried out with the modification in which the resonance integral of the C–N bond at 3-position was estimated to be $1.2\beta \cos \theta$. The nitro group at the position 5 was treated to be co-planar with the ring. Figure 5 shows the dependence of the spin densities at ring positions 4, 6, and 7 and at the nitrogen atoms. As seen from the figure, the theoretical spin densities at the positions 4 and 6 approach each of the corresponding experimental values around 58 and 50°, respectively. Allowing some deviations in the MO calculation for such a complex molecule, it may be concluded that the nitro group at 3-position is twisted about 55° from the ring plane. The spin densities calculated with $\beta_{3,10}$=$0.69\beta$ corresponding to this angle are given in Table 3. A remarkable difference of the splitting constants at 3- and 5-nitrogen atoms is reasonably understood from the contrast between the calculated spin densities at 3- and 5-nitro groups.



III

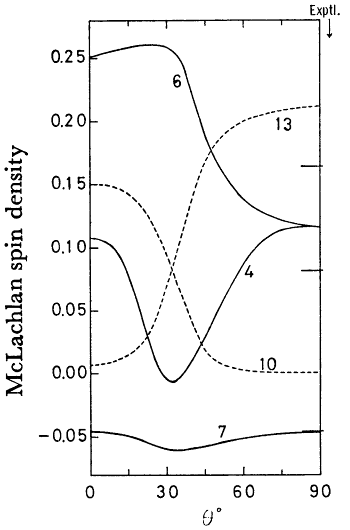


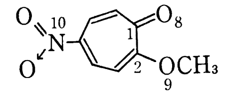
Fig. 5. Spin densities ρ calculated for the 3,5-dinitrotropolonate anion radical by the McLachlan procedure as a function of the twisting angle θ between the ring and the nitro group at 3-position.

Table 3. Splitting constants ($a_i$) and spin densities ($\rho_i$) for the 3,5-dinitrotropolonate anion radical

| Position | $a_i$ G | $\rho_i$ Exptl[a] | $\rho_i$ Calcd[b] |
|---|---|---|---|
| 1 | | | 0.1311 |
| 2 | | | 0.1160 |
| 3 | | | −0.0347 |
| 4 | 1.94 | 0.082 | 0.0727 |
| 5 | | | −0.0089 |
| 6 | 3.92 | 0.165 | 0.1500 |
| 7 | 1.08 | 0.046 | −0.0527 |
| 8 | | | 0.0582 |
| 9 | | | 0.0529 |
| 10 (3-$\underline{N}O_2$) | 0.78 | | 0.0046 |
| 11, 12 | | | 0.0008 |
| 13 (5-$\underline{N}O_2$) | 6.78 | | 0.1940 |
| 14, 15 | | | 0.1576 |

a) See the footnote a) in Table 1. b) McLachlan spin density. The values of parameters are the same as those used for the 5-nitrotropolonate anion radical except $\beta_{C-N}$ (for 3-NO$_2$)$=1.2\beta \cos 55°$.

*2-Methoxy-5-nitrotropone Anion Radical.* Treatment of 2-methoxy-5-nitrotropone (IV) with lithium or sodium metal in degassed 1,2-dimethoxyethane showed neither change in its color nor the appearance of ESR signal. On the other hand, the electrolytic reduction of IV in DMF showed a strong ESR signal, while the yellow color of the solution turned dark brown gradually during the electrolysis. The ESR spectrum is shown in Fig. 6 and the hyperfine structure was analyzed with six splitting constants listed in Table 4. The analysis was confirmed by the spectral simulation assuming a half-width of 100 milligauss for the lines.



IV

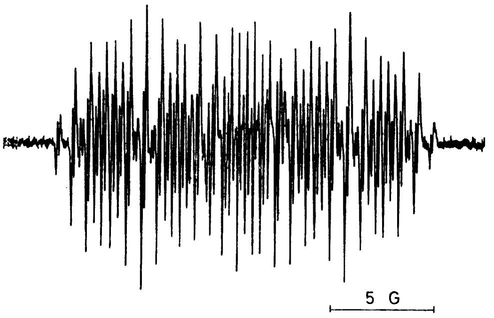


Fig. 6. ESR spectrum of the 2-methoxy-5-nitrotropone anion radical generated electrolytically in DMF ($g$=2.0035).

TABLE 4. SPLITTING CONSTANTS ($a_i$) AND SPIN DENSITIES ($\rho_i$) FOR THE 2-METHOXY-5-NITROTROPONE ANION RADICAL

| Position | $a_i$ G | $\rho_i$ | |
|---|---|---|---|
| | | Exptl[a)] | Calcd[b)] |
| 1 | | | 0.0050 |
| 2 | | | 0.3255 |
| 3 | 1.46 | 0.062 | −0.0595 |
| 4 | 6.42 | 0.271 | 0.2655 |
| 5 | | | 0.0220 |
| 6 | 0.12 | 0.005 | −0.0188 |
| 7 | 1.10 | 0.046 | 0.0354 |
| 8 (C=$\underline{\mathrm{O}}$) | | | 0.0249 |
| 9 ($\underline{\mathrm{O}}$–$CH_3$) | 0.75 | | 0.0258 |
| 10 ($\underline{\mathrm{N}}O_2$) | 3.36 | | 0.1293 |
| 11, 12 ($N\underline{\mathrm{O}}_2$) | | | 0.1225 |

a) See the footnote a) in Table 1. b) McLachlan spin densities calculated with the following parameters: $\alpha_8=\alpha+1.2\beta$, $\beta_{1,8}=1.8\beta$, $\alpha_9=\alpha+2.0\beta$, $\beta_{2,9}=0.8\beta$, $\alpha_N=\alpha+2.2\beta$, $\alpha_{N\underline{O}}=\alpha+1.4\beta$, $\beta_{C-N}=1.2\beta$, $\beta_{N-O}=1.67\beta$, and $\lambda=1.2$.

The nitrogen splitting constants (4.88 G) was readily assigned according to the type of splitting. Other assignments were given on the basis of the spin density calculation.

On account of the complexity of the molecule IV, choice of the parameters for the calculation affects very much on the spin density distribution. But, the treatments for the nitrotropolonates above-mentioned, 2-methoxytropone,[2)] and 2-methoxyazulene[8)] anion radicals may be helpful to the selection of the parameters, except those for the carbonyl group which could not be evaluated appropriately in the study on the tropone anion radical.[1)] Therefore, the parameters for the carbonyl group in IV were varied over the following ranges: $\alpha+1.0\beta\leqq\alpha_8\leqq\alpha+2.0\beta$ and $1.0\beta\leqq\beta_{1,8}\leqq2.0\beta$. The values $\alpha_9=\alpha+2.0\beta$ and $\beta_{2,0}=0.8\beta$ were chosen for the methoxy group. Assuming the co-planarity of the nitro group with the ring plane, a satisfactory agreement between the calculated and experimental spin densities was finally obtained when the parameters, $\alpha_8=\alpha+1.2\beta$ and $\beta_{1,8}=1.8\beta$, were adopted. The values are given in Table 4. Thus, the ESR hyperfine structure of the 2-methoxy-5-nitrotropone anion radical was reasonably interpreted.

During the course of the electrolytic generation of the anion radical of IV in DMF, the gradual transformation of the radical into a second paramagnetic species was observed in the ESR spectrum. The ESR spectrum of the second species fits in well with that shown in Fig. 1. This indicates that the electrolysis of IV for a long period led to the demethylation forming the 5-nitrotropolonate anion radical. The reaction may be interpreted on the analogy of the demethylation of 2,4,6-trinitroanisole in the presence of triethylamine and an aprotic solvent.[9)]

## Experimental

The materials, 5-nitrotropolone, mp 154 °C, 3-nitrotropolone, mp 197 °C, 3,5-dinitrotropolone, mp 174 °C, and 2-methoxy-5-nitrotropone, mp 232 °C, were prepared by the method of Nozoe *et al.*[10)] and each recrystallized from methanol. *N,N*-Dimethylformamide (DMF) was degassed by at least five freezing-pumping cycles after being purified and distilled on to a molecular sieve which had been flame-dried in a vacuum.

Electrolytic generation of each free radical was performed by using a cell with platinum electrodes at room temperature. Tetra-*n*-propylammonium perchlorate was used as the supporting electrolyte.

The ESR spectra were measured with a Hitachi X-band ESR spectrometer, model 771, using a field modulation of 100 MHz. Analyses of the ESR hyperfine structures were confirmed by spectral simulation, for which a JEOL spectrum computer, JEC-5, was used. Numerical calculations were carried out at the Computer Center of Tohoku University.

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7) Other choice of the MO parameters such as $h_8=1.5$ and $k_{1,8}=1.7$ or $h_8=1.8$ and $k_{1,8}=1.8$ are also permitted to the calculation for the 5-nitrotropolonate anion radical. However, the values chosen in the text are applicable more satisfactorily to the calculations for the 3-nitro- and 3,5-dinitro-tropolonate anion radicals.

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