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Electron Spin Resonance of Anion Radicals of Aromatic Esters. I. The Anion Radicals of Methyl, Ethyl and Isopropyl Benzoates, and of Methyl and Ethyl Isonicotinates[1]

Masatoshi HIRAYAMA

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira-cho, Sendai

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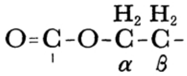
The ESR spectra of the anion radicals of methyl, ethyl and isopropyl benzoates, and of methyl and ethyl isonicotinates were observed. When the spin densities of these anions were calculated by using McLachlan's method, the results were in good agreement with the experimental data. It has been found that the electron-withdrawing effect of the ester group is situated between those of the cyano and acetyl groups, and that the ester group may be locked into the benzene plane. Comparatively large splittings due to the α-protons in the ester group were observed. The proton position is defined by the notation:



$$\mathrm{O{=}\underset{|}{C}{-}O{-}\underset{\alpha}{\overset{H_2}{C}}{-}\underset{\beta}{\overset{H_2}{C}}{-}}$$

An equation, $a^{H}_{CH_3} = Q^{H}_{OCH_3}\rho^{\pi}_{O}$, was assumed, and for these anion radicals values of $|Q^{H}_{OCH_3}|$ much larger than 27.2 gauss for the C-CH_3 hyperconjugation were evaluated.

The benzene anion radical, with some electron-withdrawing groups, is generally known to be stable in an aprotic solvent at room temperature; therefore, a number of ESR spectra of these anions with such substituents as nitro, cyano, aldehyde, amide, acetyl, and trimethylacetyl groups have been measured by several groups of workers.[2-10] The spin densities of these anions have been calculated by MO methods; the results obtained by McLachlan's method are generally in better agreement with the experimental splitting constants than those obtained by the Hückel approximation.[11,12] Furthermore, from the ESR studies of these anions, interesting information has been obtained about the effect of a substituent on the spin distribution of the benzene ring, the intramolecular motion of a substituent,[7-10,13,14] and the ion pair produced by alkali metal reduction.[15-18]

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1) Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

2) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

3) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

4) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

5) I. Bernal and G. K. Fraenkel, *ibid.*, **86**, 1671 (1964).

6) P. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Fraenkel, *ibid.*, **85**, 683 (1963).

7) A. H. Maki, *J. Chem. Phys.*, **35**, 761 (1961).

8) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2811 (1962).

9) N. Steinberger and G. K. Fraenkel, *ibid.*, **40**, 723 (1964).

10) E. W. Stone and A. H. Maki, *ibid.*, **38**, 1999 (1963).

11) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2795 (1962).

12) P. H. Rieger and G. K. Fraenkel, *ibid.*, **39**, 609 (1963).

13) J. H. Freed and G. K. Fraenkel, *ibid.*, **37**, 1156 (1962).

14) J. H. Freed, P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 1881 (1962).

15) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1960).

16) R. L. Ward, *J. Chem. Phys.*, **36**, 1405 (1962).

117) A. Carrington and P. F. Todd, *Mol. Phys.*, **6**, 61 (1962).

18) P. B. Ayscough and R. Wilson, *Proc. Chem. Soc.*, **1962**, 229.

For instance, Rieger and Fraenkel[8,9] found, from an analysis of the hyperfine patterns of the spectra, that many of the aldehyde and acetyl groups were locked into a conformation planar with the benzene ring. However, with regard to the aromatic compounds with some ester groups as electron-withdrawing groups, ESR studies of the anion radicals have not yet been systematically performed, with some exceptions.[4,19]

Therefore, the present author attempted to prepare the anion radicals of a series of aromatic esters and to study the ESR of these anions. The present paper will report on the ESR spectra of the anion radicals of methyl, ethyl, and isopropyl benzoates, which are the most fundamental of the aromatic esters, and of methyl and ethyl isonicotinates.

Experimental

The radicals were prepared by using two kinds of reduction methods, the electrolytic and alkali metal reduction methods. In the electrolytic reduction, two types of high vacuum cells were employed in order to make it possible to control the radical concentration. Both of them were a little different from the cells designed by Rieger *et al.*,[6] by Bolton *et al.*,[20] and by Harriman *et al.*[21] One of them (cell A) had mercury electrodes and a fine-fritted glass disk between the cathode and anode compartments and was designed in such a way that the electrolysis was performed outside the cavity. It was used for the preparation of radicals stable at room temperature. The other cell (cell B), with platinum electrodes, was designed so that the electrolysis could be performed within the cavity for the preparation of radicals unstable at room temperature. This cell is similar to that designed by Maki and Geske except that the distance between the two electrodes is very short and the cell is highly evacuated.

In the electrolytic reduction, acetonitrile (ACN) was mainly used, while *N, N*-dimethylformamide (DMF) and 1, 2-dimethoxyethane (DME) were partly used as solvents. Tetra-*n*-propylammonium perchlorate (T*n*PAPC) was used as the supporting electrolyte in ACN and DMF, while tetra-*n*-butylammonium perchlorate (T*n*BAPC) was used in DME. The alkali metal reduction was performed by the usual method, using sodium and potassium metals as the reducing agents. The ESR spectra were measured with a Hitachi X-band ESR spectrometer, model MPU-3B, using a field modulation of 100 kc/s.

All the samples used here were purified by vacuum distillation after having been dried over barium oxide for two days. DMF and ACN were purified by repeated vacuum distillations from calcium hydride and phosphorus pentoxide respectively after having been dried over potassium hydroxide. T*n*PAPC and T*n*BAPC were prepared from the corresponding hydroxides. DME and THF were purified by the method of Weissman *et al.*[22]

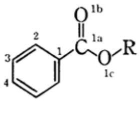
Results

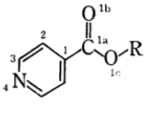
Methyl, Ethyl and Isopropyl Benzoates. The electrolytic reduction of these esters yielded brown-yellow solutions, which gave ESR spectra consisting of the hyperfine splitting constants listed in Table 1. The spectrum of the methyl benzoate anion is shown in Fig. 1. The interpretations of these three spectra were straightforward because of their similarity; a doublet and two sets of triplet splittings of common magnitudes, arising from a para proton, two ortho, and two meta protons respectively. Consequently, it is reasonable to assign the residual coupling constants, *i. e.*, a doublet in the isopropyl ester, a triplet in the ethyl ester, and a quartet in the methyl ester, to the α-protons in each ester group. The assignment of two sets of triplet splittings to the ortho and meta positions was based on the MO calculations of the spin densities, which will be described later.

When the DME solutions of these esters were brought into contact with potassium metal at the temperature of dry ice, red-purple solutions were yielded; these solutions gave, at room temperature,

TABLE 1. HYPERFINE SPLITTING CONSTANTS (in gauss)[a]

Methyl benzoate anion radical			
a_2^H	a_3^H	a_4^H	$a_{CH_3}^H$
4.20	0.94	7.64	0.94
Ethyl benzoate anion radical			
a_2^H	a_3^H	a_4^H	$a_{CH_2}^H$
4.19	0.89	7.63	0.89
Isopropyl benzoate anion radical			
a_2^H	a_3^H	a_4^H	a_{CH}^H
4.19	0.89	7.63	0.40
Methyl isonicotinate anion radical			
a_2^H	a_3^H	a^N	$a_{CH_3}^G$
3.16	0.81	5.15	1.03
3.37[b]	0.67[b]	5.04[b]	1.16[b]
3.30[c]	0.75[c]	4.96[c]	1.14[c]
Ethyl isonicotinate anion radical			
a_2^H	a_3^H	a^N	$a_{CH_2}^H$
3.16	0.85	5.06	0.85





a) The splitting constants of anions prepared by electrolysis in ACN.

b) The splitting constants of anions prepared by reduction with potassium metal in DME at −70°C.

c) The splitting constants of anions prepared by reduction with potassium metal in THF at −60°C.

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19) P. B. Ayscough, F. P. Sargent and R. Wilson, *J. Chem. Soc.*, **1963**, 5418.

20) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.* **40**, 3307 (1964).

21) J. E. Harriman and A. H. Maki, *ibid.*, **39**, 778 (1963).

22) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

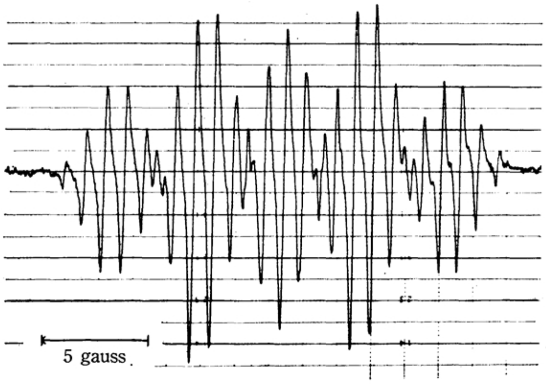

Fig. 1. The ESR spectrum of methyl benzoate anion radical prepared by electrolysis in ACN.

a well-resolved spectrum with a number of hyperfine lines, but with a much smaller magnitude of total splitting, about 10 gauss, than those obtained by the electrolytic reduction of these compounds. However, these spectra could not be analyzed, since these paramagnetic species were unstable at room temperature and since the shapes of the end parts of the spectra were too obscure to be analyzed. The contact of DME solutions of these esters with sodium metal gave orange solutions, which exhibited spectra with only a single line, and their intensity decreased in a moment.

Methyl and Ethyl Isonicotinates. The electrolytic reduction of these compounds resulted in brown-yellow solutions which gave ESR spectra containing a number of hyperfine lines. These two spectra were composed of a nitrogen splitting, two triplet splittings due to two sets of two equivalent protons, and the α-proton splittings. The splitting constants, as measured in ACN, are presented in Table 1. As in the case of the benzoate anions, the assignment to the ring positions was made by MO calculation.

The contact of DME and THF solutions of these compounds with potassium metal at the temperature of dry ice yielded yellow solutions which gave a strong ESR signal. The spectra measured at $-70°C$ to $-40°C$ were almost identical (with only a small difference in the coupling constants) with those obtained by the electrolytic reduction of these compounds; thus, these spectra can be attributed to the anion radicals of these compounds. The spectrum of the methyl isonicotinate anion radical, as measured at $-70°C$, is shown in Fig. 2. As the temperature was elevated above $-40°C$, the intensity of the spectrum of the methyl isonicotinate anion became smaller and the linewidth became larger; the spectral pattern changed slightly, but the total width of the spectrum remained unchanged, as the temperature changed. The spectrum measured after warming has not yet been well interpreted. The splitting constants of the anions produced by reduction with potassium metal in DME and THF are listed in Table 1.

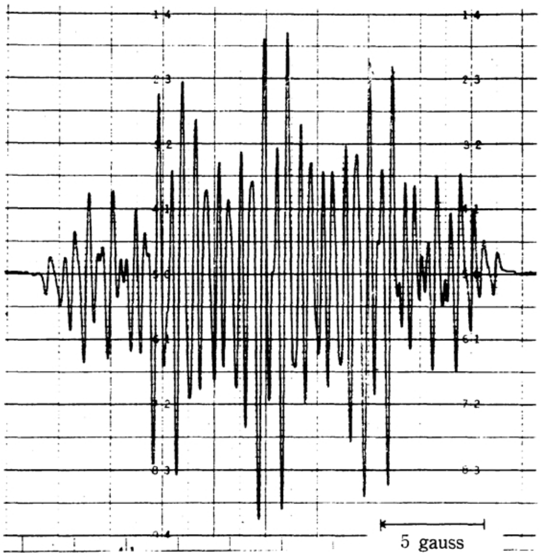

Fig. 2. The ESR spectrum of methyl isonicotinate anion radical prepared by the reduction with potassium metal in DME (measured at $-70°C$).

Molecular Orbital Calculations of Spin Densities

The calculations of the spin densities were made using the Hückel theory and the approximate configuration interaction treatment of

TABLE 2. EXPERIMENTAL AND CALCULATED SPIN DENSITIES

Anion radical	Position[a]	Spin density Calculated Hückel	Spin density Calculated McLachlan	Spin density Experimental[b]
Methyl benzoate anion	1	0.1491	0.1406	
	2	0.1394	0.1770	0.175
	3	0.0221	−0.0490	0.039
	4	0.2190	0.3012	0.318
	1a	0.1745	0.1924	
	1b	0.0980	0.0858	
	1c	0.0362	0.0239	
Methyl isonicotinate anion	1	0.1774	0.1935	
	2	0.1098	0.1154	0.132
	3	0.0645	0.0265	0.034
	4	0.2112	0.2653	
	1a	0.1408	0.1527	
	1b	0.0897	0.0833	
	1c	0.0323	0.0225	

a) See Table 1 for numbering of positions.

b) Spin densities using the relation, $a_i^H = Q_{CH}^H \rho_i^\pi$, where $|Q_{CH}^H| = 24.0$ gauss.

McLachlan.[23] At first, the six MO parameters on the ester group were adjusted: the three Coulomb-integral parameters, $\delta_{O(C=O)}$, $\delta_{O(C-O)}$ and $\delta_{C_{1a}}$, and the three resonance-integral parameters, $\gamma_{CO(C=O)}$, $\gamma_{CO(C-O)}$ and $\gamma_{C_1C_{1a}}$. The δ_x Coulomb-integral parameter and the γ_{xy} resonance-integral parameter are defined in the equations, $\alpha_x=\alpha+\delta_x\beta$ and $\beta_{xy}=\gamma_{xy}\beta$, where α and β are the Coulomb and resonance integrals for benzene respectively. These parameters varied over the following ranges: $1.0\leq\delta_{O(C=O)}\leq 2.0$, $1.5\leq\delta_{O(C-O)}\leq 2.5$, $0\leq\delta_{C_{1a}}\leq 0.2$, $1.0\leq\gamma_{CO(C=O)}\leq 1.6$, $0.6\leq\gamma_{CO(C-O)}\delta_{CO(C-O)}\leq 1.2$ and $0.8\leq\gamma_{C_1C_{1a}}\leq 1.2$. The λ parameter in McLachlan's procedure was kept fixed at the value $\lambda=1.2\,\beta$ for all the calculations. Good agreement with the experimental splitting constants in the methyl benzoate anion was obtained by McLachlan's method, using the following values for these parameters: $\delta_{O(C=O)}=1.5$, $\delta_{O(C-O)}=2.0$, $\delta_{C_{1a}}=0$, $\gamma_{CO(C=O)}=1.6$, $\gamma_{CO(C-O)}=1.2$ and $\gamma_{C_1C_{1a}}=1.2$. The spin densities calculated by using these values are given in Table 2. The calculation of the methyl isonicotinate anion was made by using the parameter for a heterocyclic nitrogen, $\delta_N=0.6$, in addition to the six parameters listed above.

Discussion

Several suggestions have been made by Fraenkel *et al.*[11] for correlating the electron-withdrawing effect of a substituent with the magnitudes of the splitting constants of the ring protons in a benzene anion radical with an electron-withdrawing substituent. One of them shows that the ratio of the spin density ortho to that at the para position, ρ_o^π/ρ_p^π, is a simple function of the energy of the molecular orbital occupied by the unpaired electron (in the Hückel approximation); if the energy of the singly-occupied level is small (a strong electron-withdrawing group), the ratio approaches unity, while if it is large (a weakly electron-withdrawing group), the ratio is smaller than unity. This result is in agreement with the ratio of the experimental splitting constants, a_o^H/a_p^H.[2,6,8,9]

All the experimental ratios for methyl, ethyl, and isopropyl benzoate anions were 0.550; this value was found to be situated between those for the acetophenone and benzonitrile anions, *i. e.*, between 0.603[9] and 0.430[6]. On the other hand, it may be suggested, on the basis of the experimental data, that the electron-withdrawing effect of a substituent in a monosubstituted benzene anion radical is also related to the total spin density at the ring positions, although no theoretical analysis has yet been carried out. Assuming that a_o^H and a_p^H are negative, and that a_m^H is positive, the total ring proton splitting constants of these three benzoate anions may be said to be -14.16, -14.16 and -14.23 gauss respectively; these values were also found to be situated between those for the acetophenone and benzonitrile anions, *i. e.*, between -12.62[9] and -15.08 gauss[6]. Thus, these data imply that the ester group is less electron-withdrawing than the acetyl group, but more electron-withdrawing than the cyano group.

The splitting constants listed in Table 1 show that the spin density distribution in the rings of all the anions observed has a twofold symmetry about the bond connecting the ester group to the ring. Even if the ester group is locked into an orientation planar with the benzene ring, it may be difficult to observe a lack of twofold symmetry in the spin density distribution, as in the case of the aldehyde and acetyl groups in the benzaldehyde and acetophenone anions,[9] because the α-effects of the two oxygen atoms of the ester group on the nearest ring carbon atoms may be expected to be almost identical, and the small differences between two ortho proton splittings and between two meta proton splittings may be within the linewidth.

On the other hand, a measure of the conjugation of the substituent group with the ring can be obtained from the calculated bond order for the substituent group-ring bond. It has been found by Fraenkel *et al.* that the carbonyl groups, which have not been experimentally confirmed to be locked into the molecular plane, have much smaller bond orders than those which may be locked, as is shown in Table 3. Therefore, the bond orders of the ester group-ring bonds for the methyl benzoate and methyl isonicotinate were calculated, with $\gamma_{C_1C_{1a}}=1.0$, to be 0.3393 and 0.3386 for the neutral molecules, and 0.5124 and 0.5024 for the anion radicals. From a comparison of these values for the anions with those of a series of carbonyl anions shown in Table 3, one may suppose that

TABLE 3. CALCULATED BOND ORDERS OF THE CARBONYL GROUP-RING BOND IN THE CARBONYL ANIONS[8]

Compound	Bond order		Experimental result
	Neutral molecule	Anion radical	
Acetophenone	0.326	0.500	Locked[9]
Terephthalaldehyde	0.334	0.469	Locked
4-Acetylpyridine	0.317	0.490	Locked
4-Nitrobenzaldehyde	0.333	0.419	Locked
3-Nitroacetophenone	0.326	0.334	Freely rotating
4-Nitroacetophenone	0.323	0.407	Pertial*

* The interchange of the acetyl group from one planar conformation to the other occurs at an intermediate rate in DMF, so that the line width alternation is observed.

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23) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

these ester groups are locked by the strong conjugation in a conformation nearly planar with the benzene ring.

The splittings due to the protons of methyl group bonded to an oxygen atom have been measured in ESR spectra in only a few cases,[24] and these splittings have not yet been calculated. It seems reasonable to consider that the comparatively large splittings of the α-protons in the ester groups listed in Table 1 are due to the hyperconjugation of the methyl group. Then, assuming the equation, $a^{\mathrm{H}}_{\mathrm{CH_3}}=Q^{\mathrm{H}}_{\mathrm{OCH_3}}\rho^{\pi}_{\mathrm{O}}$, for the methyl proton splittings, where $Q^{\mathrm{H}}_{\mathrm{OCH_3}}$ is the methyl proton splitting parameter between the oxygen and the methyl group, and where ρ^{π}_{O} is the π-electron spin density on the oxygen atom, the $Q^{\mathrm{H}}_{\mathrm{OCH_3}}$ values were evaluated by means of the values of ρ^{π}_{O} calculated by McLachlan's method and the methyl proton splittings. However, the results gave two values far from each other, 39.3 and 45.8 gauss, both of which values were much larger than that of 27.2 gauss generally used for the C-CH_3 hyperconjugation, for the methy benzoate and methyl isonicotinate anions respectively.

As may be seen from Table 1, the values of the $a^{\mathrm{H}}_{\mathrm{CH_2}}/a^{\mathrm{H}}_{\mathrm{CH_3}}$ ratio is 0.95 for the ethyl benzoate anion and 0.83 for the ethyl isonicotinate anion, while $a^{\mathrm{H}}_{\mathrm{CH}}/a^{\mathrm{H}}_{\mathrm{CH_3}}$ is 0.43 for the isopropyl benzoate anion. These data obviously reveal that, in the methyl ester anions, the methyl group freely rotates about the oxygen-carbon single bond, while in the ethyl and isopropyl ester anions the rotation of these alkyl groups about the oxygen-carbon single bond may be restricted.

The numerical calculations were carried out on the NEAC 2230 at the Computation Center, Tohoku University.*

The author wishes to thank Professors Taro Isobe and Masamoto Iwaizumi for their helpful discussions and encouragement.

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[24] K. Umemoto, Y. Deguchi and H. Takaki, This Bulletin, **36**, 560 (1963).

* Also in the paper reported previously by the present author (M. Hirayama, This Bulletin, **40**, 1557 (1967)), the NEAC 2230 Computer was used for the numerical calculations.