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Electron Spin Resonance of Anion Radicals of Aromatic Esters. IV. The Anion Radicals of Some Substituted Methyl Benzoates*[1]

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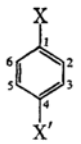
ESR spectra are observed for the anion radicals of methyl *p*-, *m*- and *o*-nitrobenzoates, methyl ester of *p*-phthalaldehydic acid, and methyl and ethyl *p*-cyanobenzoates. Both the electrolytic and alkali-metal reduction methods are used for the radical generation. The spin densities calculated by McLachlan's procedure only with the adjustment of the resonance-integral parameter for the ester group-ring bond are in good agreement with those obtained experimentally for most of the substituted positions in these radicals. The result for the methyl *o*-nitrobenzoate anion suggests that the ester group is twisted considerably by the large steric hindrance between the ester and nitro groups. The ring-proton splittings of three *p*-substituted methyl benzoate anions show that the known order of electron-withdrawing effects of the substituents, $NO_2>CHO>COCH_3>COOCH_3>CN$, holds also for these anions. And it is suggested that the electron-withdrawing power of a XM^+ group produced on the alkali-metal reduction increases in the order of free NO_2, NO_2Cs^+, NO_2K^+, NO_2Na^+ and NO_2Li^+, and that the groups $CHONa^+$ and $CHOK^+$ are more electron-withdrawing than a free CHO group. The ring-proton splittings obtained from the VB-superposition calculations for all the anions except for the *o*-derivative are in satisfactory agreement with those from the MO calculations. Structural models of ion complexes are proposed for the *p*- and *m*-nitro derivatives and methyl ester of *p*-phthalaldehydic acid with the assistance of MO calculations.

A series of the anion radicals of aromatic esters has been studied by one of the present authors.[1-3] The present paper reports the ESR spectra of the anion radicals of methyl *p*-, *m*- and *o*-nitrobenzoates, methyl ester of *p*-phthalaldehydic acid, and *p*-cyano methyl and ethyl benzoates.



The di-*p*-substituted benzene anions with electron-withdrawing groups prepared by electrolysis are known to show some interesting correlations between the relative electron-withdrawing effect of X to that of X', and the ring proton splittings;[4] in the case of $X'=NO_2$, $a_2+a_3=-2.3$ gauss, irrespective of X,[5] and in the case of $X=X'$, the larger is the electron-withdrawing effect of X, the smaller is $|a_2|$,[2,4-6] and furthermore, when the electron-withdrawing effect of X is larger than that of X', $|a_2|>|a_3|$.[4-6] All these experimental results have been discussed by using the following relation to electron-withdrawing effects

$$NO_2>CHO>COCH_3>COOCH_3>CN$$

which was determined from the ESR measurements[1,6-8] and from the theoretical consideration of monosubstituted benzene anions.[9] This order is in accord with that predicted from the valence-bond superposition model proposed by Karplus and collaborators.[10]

In the present experiments on the *p*-substituted methyl benzoate anions, the measured values of ring-proton splittings are expected to satisfy the above mentioned relations. An alkali metal cation can be considered to interact with the group having a larger electron-withdrawing effect in the unsymmetrical di-*p*-substituted benzene anion. The effect of alkali metal cation on the splittings

*1 The experimental part was presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

1) M. Hirayama, This Bulletin, **40**, 1822 (1967).
2) M. Hirayama, *ibid.*, **40**, 2234 (1967).
3) M. Hirayama, *ibid.*, **40**, 2530 (1967).
4) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).
5) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).
6) P. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Fraenkel, *ibid.*, **85**, 683 (1963).
7) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960).
8) N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).
9) P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2795 (1962).
10) J. C. Shug, T. H. Brown and M. Karplus, *ibid.*, **37**, 330 (1962).

of protons and nitrogen is discussed by the MO calculation of spin densities.

Experimental

The anion radicals studied in this work were prepared by the electrolytic reduction mainly in acetonitrile (ACN) using tetra-*n*-propylammonium perchlorate as the supporting electrolyte, and by the alkali-metal reduction mainly in dimethoxyethane (DME) and tetrahydrofuran (THF) using, sodium, potassium and cesium metals and lithium amalgam. The ESR spectra were measured with a Hitachi X-band ESR spectrometer, model MPU-3B, using a field modulation of 100 kc/s. The experimental techniques were detailed elsewhere.[1]

Methyl *p*-, *m*- and *o*-nitrobenzoates and methyl ester of *p*-phthalaldehydic acid obtained commercially were used without further purification. Methyl *p*-cyanobenzoate was prepared from silver salt of *p*-cyanobenzoic acid and methyl iodide, while ethyl ester was synthesized by the Sandmeyer method after the esterification of *p*-aminobenzoic acid.

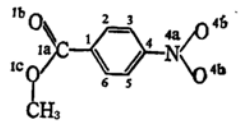
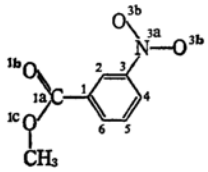
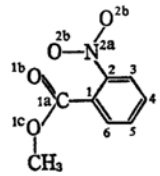
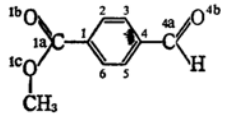
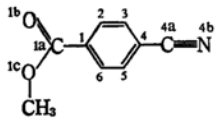
Results

The measured splitting constants are listed in Table 1.

Methyl *p*-Nitrobenzoate. A red-purple solution was obtained by both reduction methods of this compound, except for a purple solution obtained with cesium metal in THF. Dimethylformamide (DMF) was used as the solvent for electrolysis so that the spectrum could be precisely compared with those of the other *p*-substituted nitrobenzene anions measured already. The magnitude of each splitting constant observed by the electrolysis in DMF was slightly different from that measured in ACN by Maki and Geske.[5] All the radicals prepared were very stable at room temperature. The spectra observed at room temperature are shown in Fig. 1.

Methyl *m*-Nitrobenzoate. This compound yielded a green-brown solution on the electrolysis in ACN and on the reduction with lithium amalgam

Table 1. Hyperfine coupling constants

Anion		Coupling constants (in gauss)					
		a_2	a_3	a_{CH_3}	a^N	a^M	
	Electrolysis	0.64	2.99	0.32	6.50		
	Li	0.96	3.22	0.28	9.08	<0.09	
	Na	0.96	3.20	0.32	8.06	0.32	
	K	0.88	3.12	0.32	7.92	<0.12	
	Cs	0.75	3.12	0.30	7.65	2.55	
		a_2	a_4	a_5	a_6	a^N	a^M
	Electrolysis	3.04	3.46	1.10	4.10	9.09	
	Li	3.48	3.73	1.13	4.15	11.13	<0.25
	Na	3.27	3.60	1.12	4.12	10.50	0.30
	K	3.29	3.69	1.12	4.35	10.18	0.22
	Cs	3.09	3.53	1.08	4.15	10.15	2.87
		a_3	a_4	a_5	a_6	a_{CH_3}	a^N
	Electrolysis	3.18	1.11	4.02	1.11	<0.20	9.01
		a_2	a_3	a_5	a_6	a_{CH_3}	a_{CHO}	a^M
	Electrolysis	1.02	2.01	2.61	0.15	0.67	5.04	
	K(Na)	0.88	2.41	3.12	<0.16	0.56	6.40	<0.16
			a_2	a_3	a_α	a^N	
	Electrolysis	$R=CH_3$	2.73	1.07	0.84	1.07	
		$R=C_2H_5$	2.70	1.05	0.80	1.05	

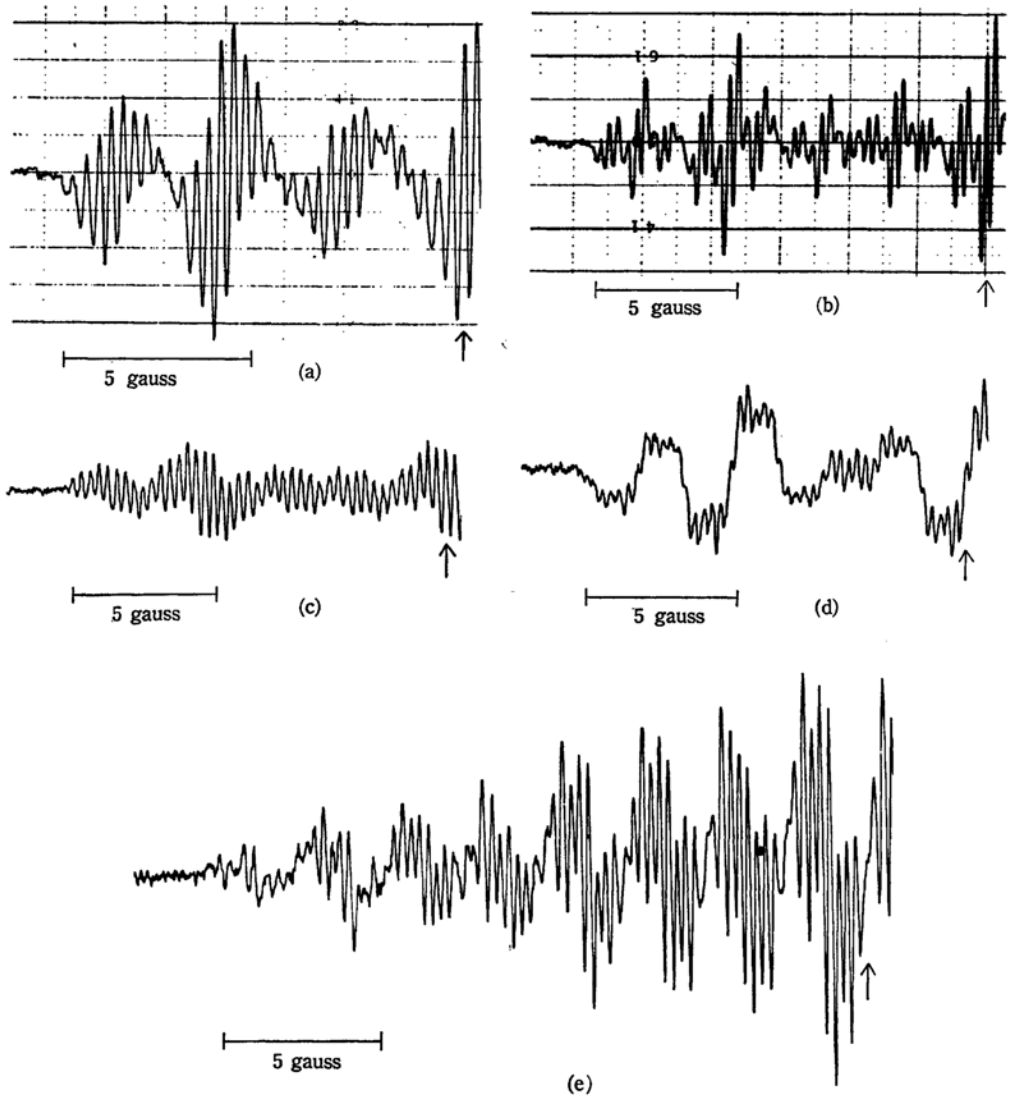


Fig. 1. Halves of ESR spectra of the methyl *p*-nitrobenzoate anions.

(a) Free anion in DMF, (b) Li-Complex in THF, (c) Na-Complex in DME, (d) K-Complex in DME, and (e) Cs-Complex in DME.
(The arrow shows the center of each spectrum.)

and potassium metal in THF, and a yellow solution with cesium metal in THF. The radicals were very stable at room temperature. The observed spectra are shown in Fig. 2.

Methyl *o*-Nitrobenzoate. A yellow-brown solution was obtained by the electrolysis of this compound in ACN. The radical prepared was comparatively stable at room temperature. The spectrum is shown in Fig. 3. No ESR signals could be observed by the reduction with sodium metal in THF.

Methyl Ester of *p*-Phthalaldehydic Acid. The electrolytic reduction of this compound in DMF gave a purple-red solution, which yielded a spectrum shown in Fig. 4(a). Although the spectrum was poorly resolved, because of instability of this radical at room temperature, the analysis was performed with reference to the result of analysis for the spectrum obtained with potassium metal (Fig. 5(b)). The result led the five doublets arising from an aldehyde proton and four unequivalent ring protons, and a quartet assignable to the three equivalent methyl protons. Since a number of lines occurred within the narrow total-width, a resolution of lines was very poor. Consequently, the reconstruction based on the coupling constants listed in Table 1 did not agree exactly with the measured spectrum, as is shown in Fig.

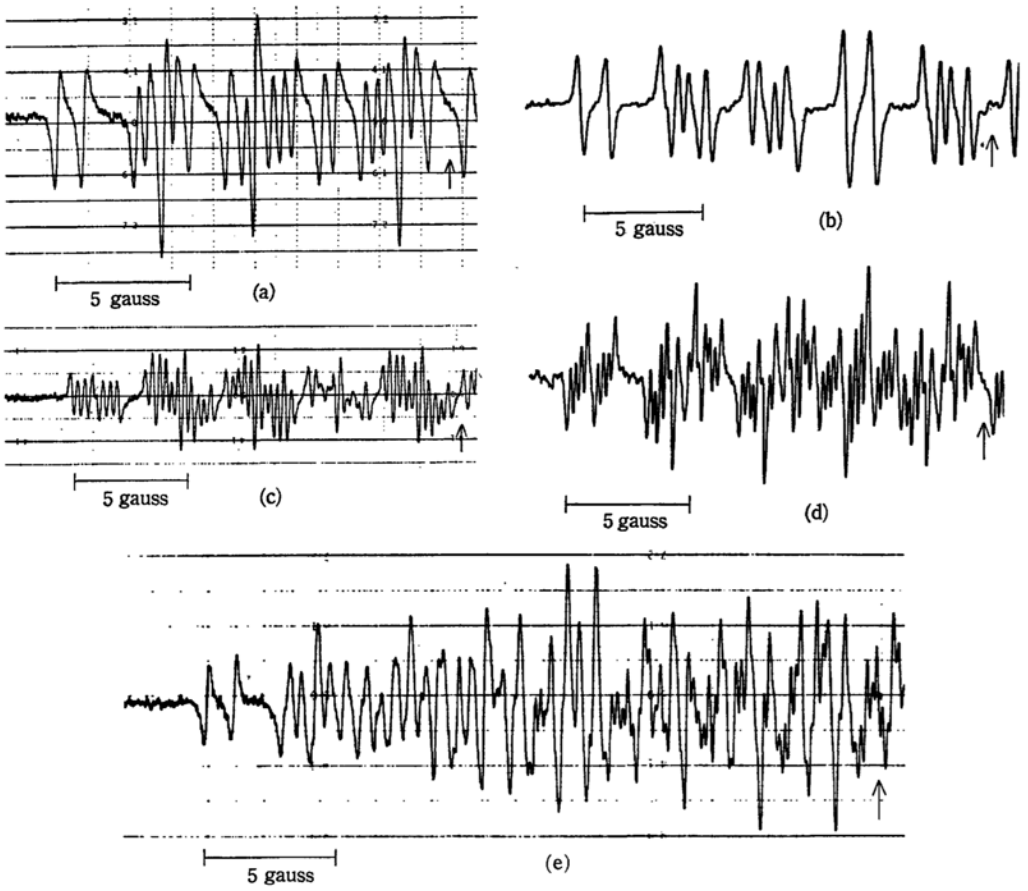


Fig. 2. Halves of ESR spectra of the methyl *m*-nitrobenzoate anions.
(a) Free anion in ACN, (b) Li-Complex in THF, (c) Na-Complex in THF, (d) K-Complex in THF, and (e) Cs-Complex in THF.
(The arrow shows the center of each spectrum.)

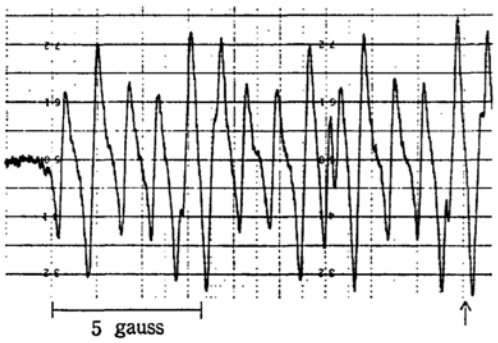


Fig. 3. Half of ESR spectrum of the methyl *o*-nitrobenzoate anion prepared by the electrolysis in ACN.
(The arrow shows the center of spectrum.)

4(b). The solution obtained by the electrolysis in ACN was liable to turn into brown from purple-red. The brown solution displayed a quite different spectrum from that measured in DMF. This spectrum has not yet been analyzed.

The spectrum obtained by the reduction with potassium metal in DME, shown in Fig. 5(a), was completely identical with that obtained with sodium metal in DME, except that the average line-width was slightly narrower than that of the latter. This spectrum was composed of four doublets and a quartet (Fig. 5(b)). A small doublet arising from the fourth ring proton may be covered within the line-width.

Methyl *p*-Cyanobenzoate. The electrolysis of this compound in ACN yielded a purple-red solution, the radical produced being not very stable at room temperature. The spectrum observed is shown in Fig. 6(a). Since 108 lines might occur within the narrow total width (about 12 gauss), they were anticipated to superpose extremely one another. The intensity of each line in the reconstruction based on the coupling constants listed in Table 1 did not agree well with that of the measured spectrum. Then, it was assumed that there was a small difference, though not measurable, between the splittings of two

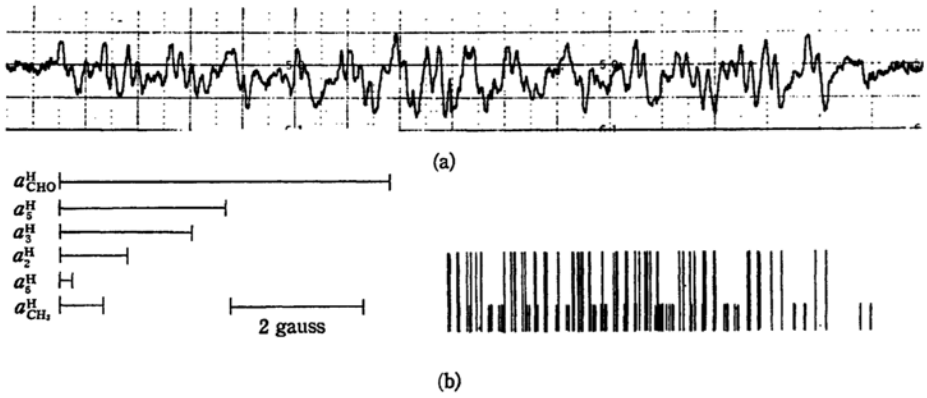


Fig. 4. ESR spectrum of the anion of methyl ester of *p*-phthalaldehydic acid prepared by the electrolysis in DMF (a) and half of its reconstruction (b).

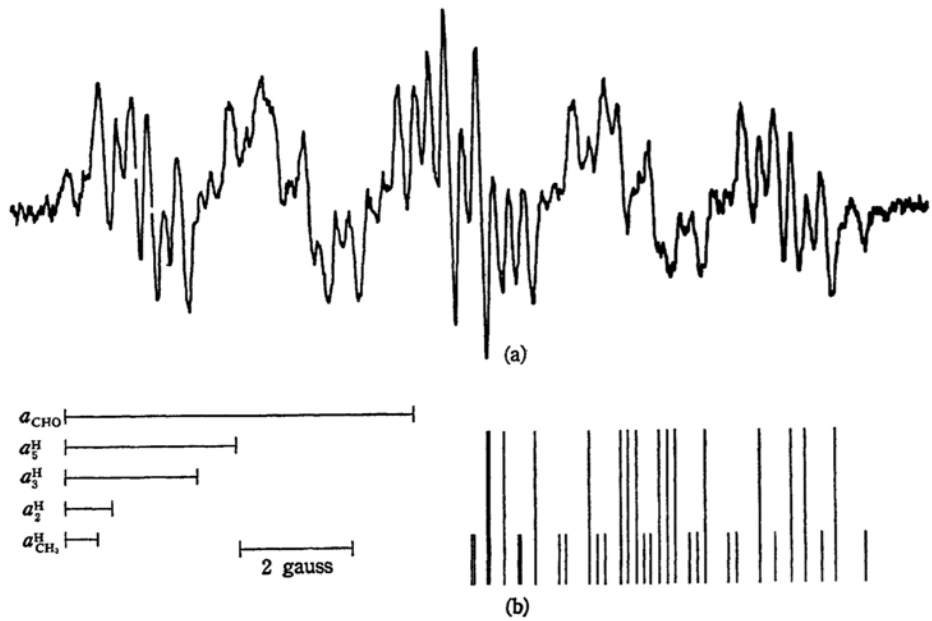


Fig. 5. ESR spectrum of the anion of methyl ester of *p*-phthalaldehydic acid prepared by the reduction with potassium metal in DME (a) and half of its reconstruction (b).

ring-protons in ortho position to the ester group, and consequently that the center line of this triplet was much broader and the peak-to-peak height of its first derivative was much smaller than in the case of a complete equivalence of these two ortho-protons. Thus, the spectrum was again reconstructed; the result is shown in Fig. 6(b), where the dotted lines show these lines of small height. As is seen from Fig. 6(b), the spectrum could be well explained by these coupling constants. This inequivalence of two protons in ortho position to the ester group may not be surprising, because in such anions having the comparatively large splittings of ring protons in ortho position to the ester group, a difference between the α-effects of two oxygen atoms in the ester group is considered to be effective to a difference between the two ortho-proton splittings.[2] In order to confirm the validity of this analysis, the spectrum of ethyl *p*-cyanobenzoate anion was measured and analyzed. Figure 7 shows that each of the splitting constants measured is equal to that of the methyl ester anion, and further that the above-mentioned technique is required for the analysis.

Also by the alkali-metal reductions of these two esters, purple-red solutions were obtained. The measured patterns of spectra were different from that obtained by electrolysis, though the total width was about 12 gauss. However, since they were further poorly-resolved, probably because of the existence of some alkali metal splittings, analyses of them were very difficult. On the

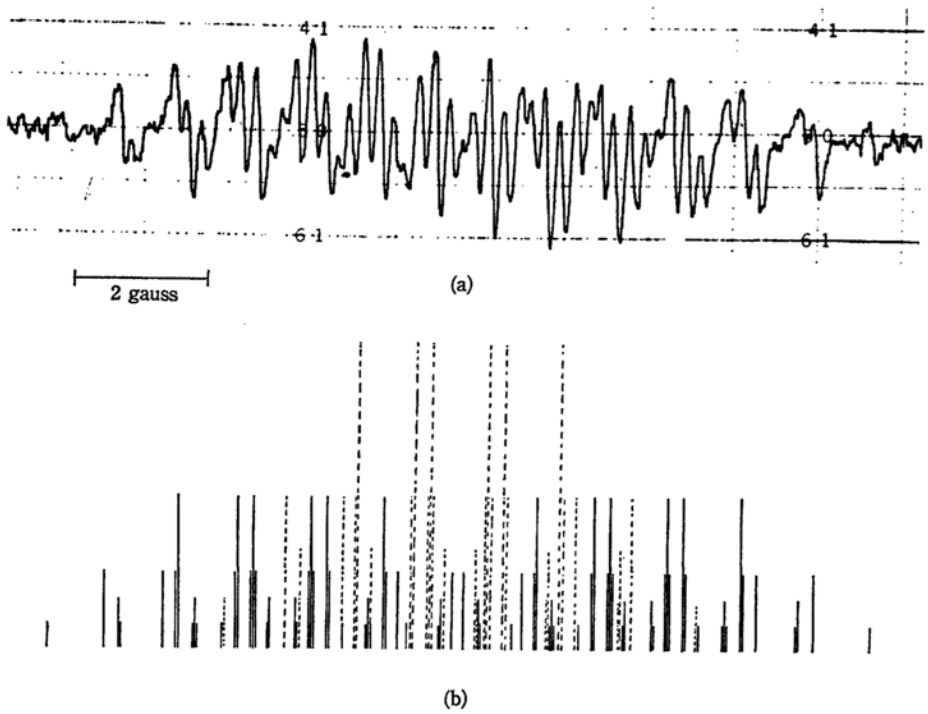


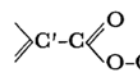
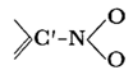
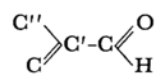
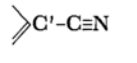
Fig. 6. ESR spectrum of the methyl *p*-cyanobenzoate anion prepared by the electrolysis in ACN (a) and its reconstruction (b).

other hand, the spectrum, measured at −45°C, of methyl ester anion prepared with sodium metal in THF was resolved better than that measured at room temperature, and was similar to that obtained by the electrolysis in ACN. This fact suggests that this ion-pair complex dissociates into a free anion and a cation under such condition.

Discussion

Molecular-Orbital Calculations of Spin Densities. Hückel molecular-orbital calculations with the approximate configuration interaction corrections of McLachlan[11] were performed for the anion radicals studied here in order to estimate the spin density distribution and to assist in the assignment of proton splittings. The values of parameters used here for the ester group, except for γ_{1-1a}, are those which have been determined to have the best fit of the calculated spin densities to the experimental ones for the methyl benzoate anion,[1] while those for the nitro, cyano, and aldehyde groups were taken from the works of Fraenkel *et al.*[8,9,12] These values of parameters are summarized in Table 2; the parameter $\lambda=1.2\beta$ was used in the correction terms. The results of calculations are given in Table 3. In the methyl

Table 2. The values of MO parameters

	$\delta_{O(C=O)}=1.5$ $\delta_{O(C-O)}=2.0$ $\gamma_{CO(C=O)}=1.6$ $\gamma_{CO(C-O)}=1.2$
	$\delta_N=2.2$ $\delta_O=1.4$ $\gamma_{NO}=1.67$ $\gamma_{NC'}=1.2$
	$\delta_O=1.5$ $\gamma_{CO}=1.6$ $\gamma_{CC'}=0.9$ $\delta_{C''}=-0.15$
	$\delta_N=1.0$ $\gamma_{CN}=2.0$ $\gamma_{CC'}=0.9$

$\delta_X=(\alpha_X-\alpha_C)/\beta_{CC}$, $\gamma_{XY}=\beta_{XY}/\beta_{CC}$

p-cyanobenzoate anion, the value of $\gamma_{1-1a}=1.2$ gave a relatively good fit to the experimental spin density at the position 2, but not at the position 3. In the anion of methyl ester of *p*-phthalaldehydic acid, the calculated result with $\gamma_{1-1a}=0.88$ was in good agreement with the experimental data, while in the methyl *p*- and *m*-nitrobenzoate anions, the values of 0.75 and 0.6 for γ_{1-1a} gave the best

11) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).
12) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

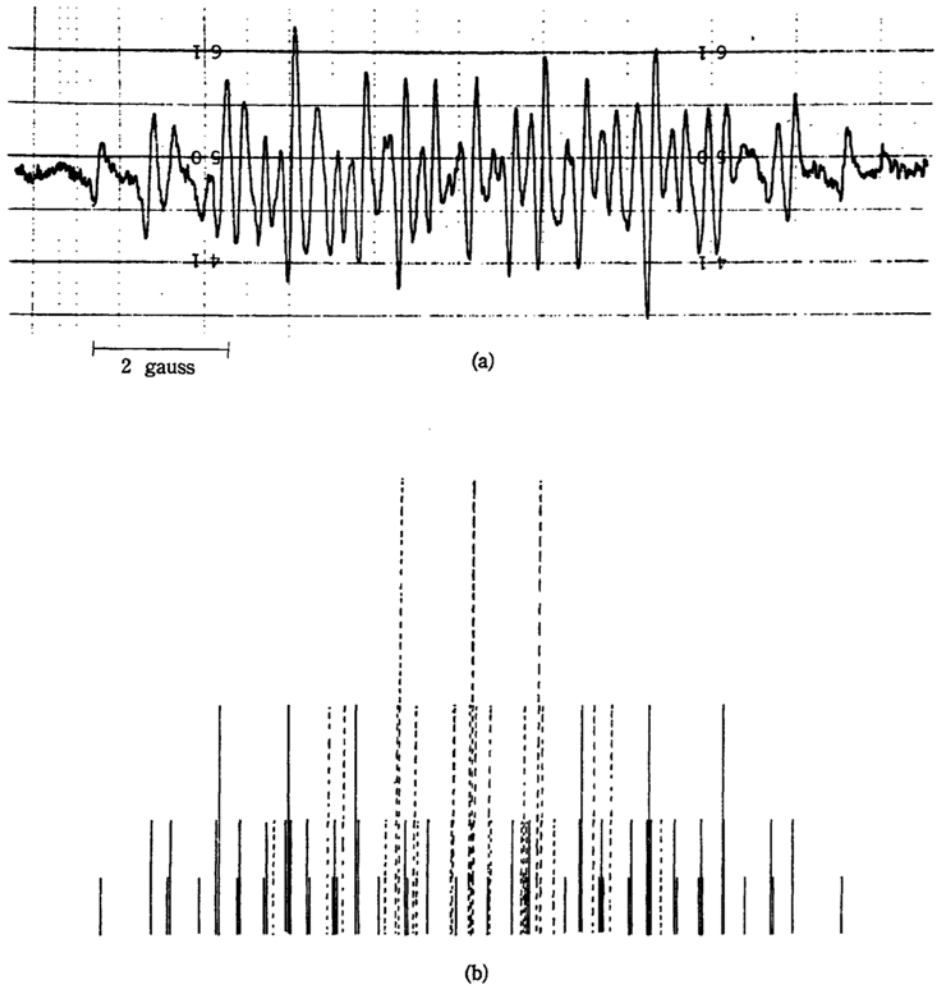


Fig. 7. ESR spectrum of the ethyl *p*-cyanobenzoate anion prepared by the electrolysis in ACN (a) and its reconstruction (b).

fits, respectively. In the methyl *o*-nitrobenzoate anion, a large steric hindrance between the ester and nitro groups may be considered to affect the spin-density distribution on the ring. Figure 8 shows that the normal value of $\gamma_{1-1a}=1.0$ does not give the fit to the experimental spin densities, and that the best fit, also for the nitrogen splitting, is obtained with $\gamma_{1-1a}=0.2$. This calculated result seems to show a structure with the ester group twisted considerably by the steric effect.

Electron-Withdrawing Effects. As is indicated in the section of introduction, the ester group has been experimentally determined to be more electron-withdrawing than the cyano group and less electron-withdrawing than the acetyl group. This has been also verified by the fact that the ring-proton splitting of dimethyl terephthalate anion in ACN, -1.56 gauss,[2] is situated between those of the terephthalonitrile and *p*-diacetylbenzene anions, *i. e.*, between -1.59[6] and -1.33 gauss.[4]*2

In a series of the *p*-substituted methyl benzoate anions, the ring-proton splittings in ortho position to the ester group, $|a_O|$, increase in the order of NO_2, CHO, $COOCH_3$ and CN derivatives, while conversely, those in meta position to the ester group, $|a_m|$, decrease in the same order, and furthermore, the methyl proton splittings increase according to this order. All these data imply that the order in the electron-withdrawing effect of the substitutents described in the introduction holds also for the anions studied here, and moreover, these data are consistent with the results from the superposition model of the valence-bond method described later. Similarly, the correlations among the ring proton splittings of each of *p*-substituted methyl benzoate anions and those of the other *p*-disubstituted benzene anions already measured[2,4-6] are approximately satisfactory in view of this order.

*2 The average value of the four ring-proton splittings in the cis and trans isomers.

TABLE 3. THEORETICAL AND EXPERIMENTAL SPIN DENSITIES

Anion	Position*1	Spin density: Theoretical: Hückel	Spin density: Theoretical: McLachlan	Spin density: Experimental*2
	1	0.1228*3	0.1600*3	
	2	0.0150	−0.0276	0.027
Methyl	3	0.0943	0.1195	0.125
p-nitro-	4	0.0534	0.0316	
benzoate	1a	0.0258	0.0269	
anion	1b	0.0192	0.0187	
	1c	0.0067	0.0050	
	4a	0.1968	0.2062	
	4b	0.1784	0.1840	
	1	0.0057*4	−0.0450*4	
	2	0.0978	0.1288	0.127
	3	0.0399	0.0068	
Methyl	4	0.1113	0.1501	0.144
m-nitro-	5	0.0045	−0.0495	0.046
benzoate	6	0.1298	0.1777	0.171
anion	1a	0.0009	−0.0002	
	1b	0.0006	−0.0019	
	1c	0.0002	−0.0006	
	3a	0.2233	0.2368	
	3b	0.1929	0.1984	
	1	0.1063*5	0.1411*5	
	2	0.0407	0.0084	
	3	0.1038	0.1370	0.133
Methyl	4	0.0055	−0.0463	0.046
o-nitro-	5	0.1236	0.1671	0.168
benzoate	6	0.0042	−0.0485	0.046
anion	1a	0.0018	0.0018	
	1b	0.0013	0.0012	
	1c	0.0004	0.0003	
	2a	0.2243	0.2379	
	2b	0.1941	0.2000	
	1	0.1671*6	0.2097*6	
	2	0.0611	0.0367	0.043
Anion of	3	0.0766	0.0745	0.084
methyl	4	0.1250	0.1320	
ester of	5	0.0947	0.1049	0.109
p-phthal-	6	0.0358	−0.0016	0.006
aldehydic	1a	0.0689	0.0749	
acid	1b	0.0426	0.0398	
	1c	0.0155	0.0110	
	4a	0.1931	0.2143	0.210
	4b	0.1195	0.1037	
	1	0.1512*7	0.1584*7	
	2	0.1074	0.1223	0.113
Methyl	3	0.0438	−0.0012	0.043
p-cyano-	4	0.1957	0.2533	
benzoate	1a	0.1357	0.1477	
anion	1b	0.0828	0.0754	
	1c	0.0301	0.0207	
	4a	0.0383	0.0300	
	4b	0.0639	0.0722	

*1 See Table 1 for numbering of the positions.
*2 The spin densities using the relation, $a_i^H = Q_{CH}^H \rho_i^\pi$, where $Q_{CH}^H = -24.0$ gauss.
*3 Calculated with $\gamma_{1-1a}=0.75$.
*4 Calculated with $\gamma_{1-1a}=0.6$.
*5 Calculated with $\gamma_{1-1a}=0.2$.
*6 Calculated with $\gamma_{1-1a}=0.83$
*7 Calculated with $\gamma_{1-1a}=1.2$.

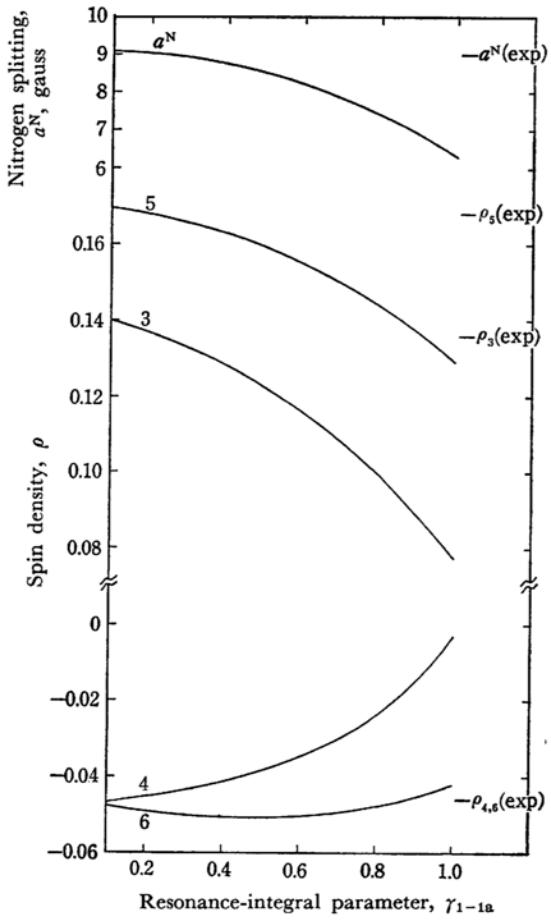


Fig. 8. Spin densities ρ and nitrogen splitting constant a^N calculated by the McLachlan modification of MO theory for the methyl *o*-nitrobenzoate anion as a function of the resonance-integral parameter for the 1-1a bond, γ_{1-1a}, and those obtained by the experiments.
The numbers on the curves indicate the positions in the radical.
The experimental values are shown in the right column.

It is reasonable to consider that the group having the larger electron-withdrawing effect in an unsymmetrical di-*p*-substituted benzene anion may interact with an alkali metal cation. Thus, regarding a group XM^+ produced on alkali-metal reduction as a new electron-withdrawing group, one may predict the effect of this group relative to the cation-free group X or to the other groups by comparing each ring proton splitting with the others. In the methyl *p*-nitrobenzoate-alkali metal ion pairs, a series of the values of a_2 and a^N in Table 1 indicates obviously that the order in the electron-withdrawing effects is $NO_2Li^+ > NO_2Na^+ > NO_2K^+ > NO_2Cs^+ >$ Free NO_2, and furthermore, the values of a_3 and a_{CH_3} seem to show that this order is reasonable within the experimental errors.

Also in the case of the methyl *m*-nitrobenzoate anion, it may be seen from a series of the values of a^N that there exists the same order of electron-withdrawing powers.

Similarly, since an aldehyde group has been decided to be more electron-withdrawing than a ester group, the aldehyde group (probably the oxygen atom) may interact with an alkali metal cation in the anion of methyl ester of *p*-phthalaldehydic acid. Thus, the $CHOK^+(Na^+)$ is compared with the free aldehyde group or the others in Table 1. One may recognize from the increment of a_{CHO} and of the splittings of ring protons in ortho position to the aldehyde group,*3 and further from the decrement of a_{CH_3}, that this group is more electron-withdrawing than the free aldehyde group. Furthermore, it may be suggested that the group $CHONa^+(K^+)$ is still slightly weaker than the free nitro group, and is strong as much as the $COOCH_3Li^+$ group[2] in the electron-withdrawing power. In the case of the methyl *p*-cyanobenzoate anion, although the spectrum of the ion pair complex could not be analyzed, the splittings in ortho position to a group $COOCH_3M^+$, may be expected to be larger than those in ortho position to the free ester group.

Valence-Bond Superposition Model. Karplus and collaborators[10] have developed an approximate valence-bond superposition theory which is applicable to the benzene anion radicals with strongly electron-withdrawing substituents; if $\rho_N(X)$ and $\rho_N(X')$ are spin densities for the monosubstituted species ϕX and $\phi X'$, respectively, the spin density ρ_N in the disubstituted anion can be written

$$\rho_N = \{k(X)\}^2\rho_N(X) + \{k(X')\}^2\rho_N(X'),$$

where $\{k(X)\}^2$ and $\{k(X')\}^2$ represent the contributions made by the ϕX and $\phi X'$ structures to the ground state of the system. By using this procedure, one of the present authors has predicted the ring proton splitting, -1.63 gauss, for the dimethyl terephthalate anion from the *m*-, and *o*-ring proton splittings of the methyl benzoate anion observed by the electrolysis in acetonitrile; this value has been in good agreement with the experimental value of -1.56 gauss.[2]

This theory has also given satisfactory results to most of the unsymmetrical di-*p*-substituted benzene anions, though inconclusive. Then, the model will be testified for the three *p*-substituted methyl benzoate anions studied here and further for the methyl *m*-nitrobenzoate anion.

At first, the relative weight of the methyl benzoate anion structure, $\{k(X)\}^2$, of each *p*-substituted methyl benzoate anion, was calculated by using the largest ring proton splitting. The calculated results are 9.2% for *p*-nitro, 36.8% for *p*-aldehyde, and 66.9% for *p*-cyano derivatives, respectively. The correlations between these values and those for the other *p*-disubstituted benzene anions having been already measured, are satisfactory in view of the order of the electron-withdrawing effects of these substituents. The predicted values of the remaining ring-proton splittings were then calculated by using the corresponding splittings of the monosubstituted benzene anions, the results being shown in Fig. 9 with those obtained from the MO calculations. These predicted values are in comparatively good agreement with the experimental values, except for the value of a_6 in the anion of methyl ester of *p*-phthalaldehydic acid and the value of a_3 in the methyl *p*-cyanobenzoate anion. These assignments are in accord with those made by the MO calculations.

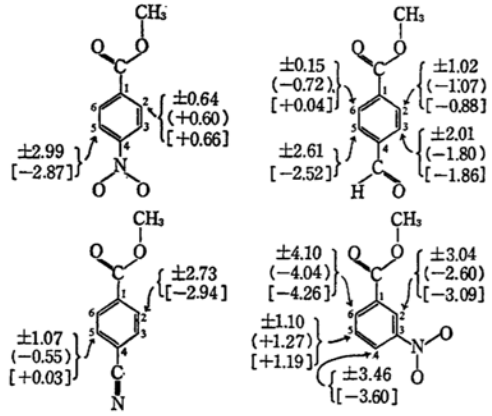


Fig. 9. Comparison of the valence-bond superposition and the molecular-orbital calculations for the ring proton splittings (gauss). Numbers not in parentheses or brackets are the experimental splittings using the MO assignments. Those in parentheses are from the valence-bond superposition procedure and those in brackets are from the MO calculation.

The spectrum of the methyl *m*-nitrobenzoate anion can be fitted comparatively well by the superposition model if the largest splitting of 4.10 gauss is assigned to the position 4. The weight of the methyl benzoate anion structure in the superposition is then 16.7%, a value of which is found to be reasonable from the comparison with the value of 22.0% predicted for the weight of the acetophenone anion structure in the *m*-nitroacetophenone anion.[4] The predicted splittings are shown in Fig. 9. However, the assignments required by the superposition model at the positions 4 and 6 are the opposite of those predicted by the MO calculations. Such the different assignments have occurred for the other meta isomers with electron-withdrawing groups.[9,12]

Interpretation of the Ion Complexes by MO Calculations. Assuming that the alkali metal cation may exist between two oxygen atoms of

*3 The average value of the splittings at the positions 3 and 5.

the nitro group, MO calculations of spin densities were performed with the modification that a small increase in the Coulomb-integral parameter of the oxygen atoms of a nitro group, $\delta_{O(NO_2)}$, was introduced. The dependence of spin density at each position on the Coulomb-integral parameter of oxygen atom is shown in Figs. 10 and 11 for methyl *p*- and *m*-nitrobenzoate anions, respectively. As is illustrated in Fig. 10, in the methyl *p*-nitrobenzoate anion, ρ_3 and $|\rho_2|$ increase with an increment of $\delta_{O(NO_2)}$ from 1.4, while conversely,

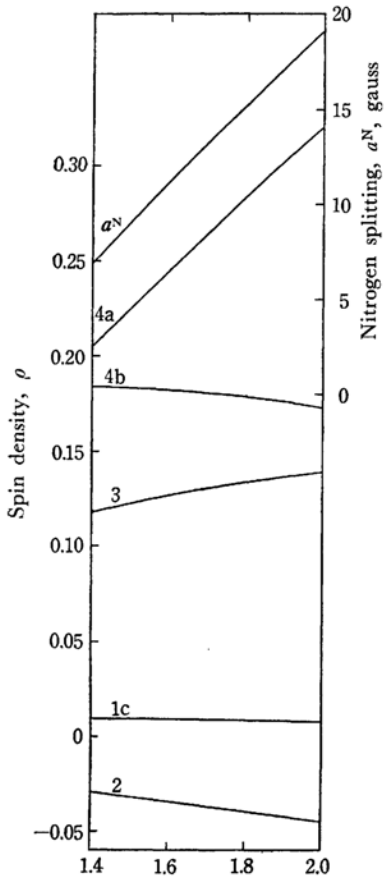


Fig. 10. Spin densities ρ and nitrogen splitting constant a^N calculated by McLachlan modification of MO theory for the methyl *p*-nitrobenzoate anion as a function of the Coulomb-integral parameter for the oxygen atom of nitro group, $\delta_{O(NO_2)}$. The numbers on the curves indicate the positions in the radical.

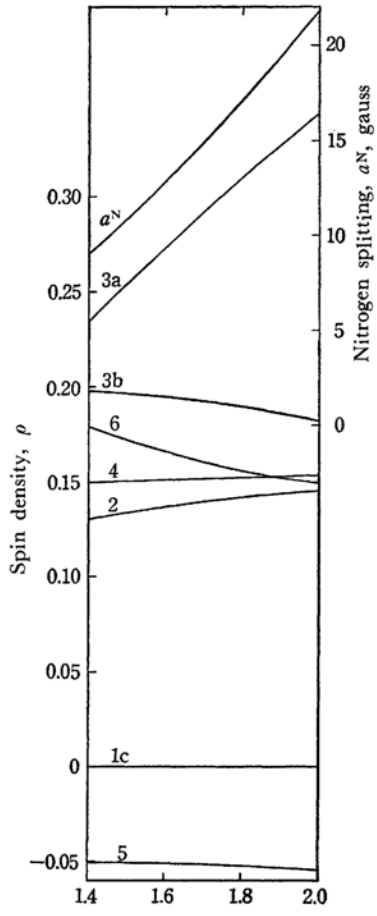


Fig. 11. Spin densities ρ and nitrogen splitting constant a^N calculated by McLachlan modification of MO theory for the methyl *m*-nitrobenzoate anion as a function of the Columb-integral parameter for the oxygen atom of nitro group, $\delta_{O(NO_2)}$. The numbers on the curves indicate the positions in the radical.

Table 4. The spin densities at the metal nuclei

	Li	Na	K	Cs
Q^M	143.3	316.2	82.38	820.08
$a^M(p)$	<0.09	0.32	<0.12	2.55
$a^M(m)$	<0.25	0.30	0.22	2.87
$a^M/Q^M(p)$	$<6.28\times10^{-4}$	1.01×10^{-3}	$<1.46\times10^{-3}$	3.11×10^{-3}
$a^M/Q^M(m)$	$<1.75\times10^{-3}$	9.48×10^{-4}	2.67×10^{-3}	3.50×10^{-3}

a^M: The splitting constant of metal nucleus.
Q^M: The splitting constans of free metal nucleus.
a^M/Q^M: The spin density at the metal nucleus.

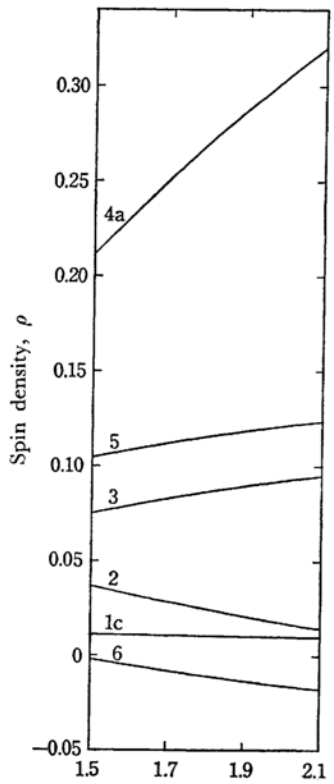


Fig. 12. Spin densities ρ calculated by McLachlan modification of MO theory for the anion of methyl ester of *p*-phthalaldehydic acid as a function of the Coulomb-integral parameter for the oxygen atom of aldehyde group, $\delta_{O(CHO)}$. The numbers on the curves indicate the positions in the radical.

ρ_{1c} decreases gradually. Furthermore, the value of a^N calculated from the values of ρ_{4a} and ρ_{4b} by using the equation proposed by Fraenkel *et al.*,[12] increases also with an increment of $\delta_{O(NO)_2}$. These results are consistent with the tendency of change of any splitting constant of the free anion to that of the ion complex listed in Table 1. Similarly, it is seen from Fig. 11 that in the methyl *m*-nitrobenzoate anion, the dependence of the values of ρ_2, ρ_4, ρ_5 and a^N on the value of $\delta_{O(NO_2)}$ is in accord with those to be expected from the experimental data, but ρ_6 is inconsistent with the experimental splitting constants.

Thus, the above-mentioned assumption on the position of the metal cation may be theoretically confirmed. Furthermore, one may determine that the smaller is the cationic radius, the stronger is the interaction between the alkali metal cation and the oxygen atoms.

On the other hand, the magnitude of spin density at the metal nucleus, a^M/Q^M,[13] increases in the order of increasing ionic radius, that is, Li<Na<K<Cs, as is shown in Table 4; this order is in contrast with that in the *o*-phthalate-alkali metal ion complexes.[2]

It seems to be plausible to consider that in the anion of methyl ester of *p*-phthalaldehydic acid the alkali metal cation may exist near the carbonyl oxygen atom. Then, a small increase in the Coulomb-integral parameter of carbonyl oxygen atom was introduced, the calculated result being shown in Fig. 12. In Fig. 12, ρ_3, ρ_5, ρ_{4a} and $|\rho_6|$ increase with an increment of $\delta_{O(CHO)}$ from 1.5, while ρ_2 decreases, and ρ_{1c} decreases gradually. These results explain very well the change in each splitting constant of the free anion to that of the ion complex, except for ρ_6. Thus, a model in which the alkali metal cation may interact with the carbonyl oxygen atom in the aldehyde group, may be supported by the theroetical consideration.

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

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13) P. Kusch and H. Taub, *Phys. Rev.*, **75**, 1477 (1949).