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Electron Spin Resonance of Anion Radicals of Aromatic Esters. II. The Anion Radicals of Diesters of *o*-, *m*- and *p*-Phthalic Acids[1]

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The ESR spectra have been observed for the anion radicals of several diesters of *o*-, *m*- and *p*-phthalic acids. The radicals were generated by the electrolytic reduction in acetonitrile and also by the reduction with lithium, sodium, potassium and cesium metals in dimethoxyethane (DME) and tetrahydrofuran (THF). The MO calculations of spin densities were made for these radicals by using McLachlan's method, and the calculated spin densities for the anion radicals of *m*- and *p*-phthalates were in good agreement with the experimental splitting constants obtained by electrolysis. In the anion radicals of *o*-phthalates, the results of calculations taking into account the steric effect between the two ester groups revealed that the twisting angle between each ester group and the ring was 35—45°. From the spectrum of di-*t*-butyl *p*-phthalate anion radical prepared by the electrolysis in DME, the *t*-butyl ester group was found to be in a fixed orientation, probably planar with the ring. It was suggested that an ion complex was formed between the *o*- or *p*-phthalate anion radical and each alkali metal cation, and that in the *p*-phthalate-sodium system in DME or THF there existed an equilibrium between an ion complex and a completely dissociated state.

In a previous paper,[2] it was unable to observe an obvious asymmetry in the pattern of splitting constants of ring protons in the ESR spectra of several benzoate and isonicotinate anions. However, the comparison of the calculated bond orders for the ester group-ring bonds of these anions with those of the carbonyl anions,[3,4] suggested that the ester groups of these anions might be in a conformation nearly planar with the ring, as some of the aldehyde or acetyl groups in the aromatic anions.[3-7] In the nitrobenzene and benzonitrile anions prepared by the reduction with an alkali metal, the alkali metal cation has been considered to interact with the nitro and cyano groups respectively.[8,9] In the di-*p*-substituted benzene anion with two different electron-withdrawing groups ($X \neq X'$), the substituent having the larger electron-withdrawing effect may interact with the cation, while in the case of $X = X'$, except for the *p*-dinitro benzene anion in which the cation has already been known to interact with one nitro group,[8] it is interesting to study an interaction between the alkali metal cation and the anion.

This paper will report on the ESR spectra of anion radicals of several diesters of *o*-, *m*- and *p*-phthalates. Furthermore, the ion complexes between the anion and each alkali metal cation are reported for the *o*- and *p*-phthalate anions, and the temperature dependence of these spectra indicating the ion complex formation was also studied.

Experimental

The ESR spectrometer and the vacuum cells used for electrolysis are described in the previous paper.[2] In the electrolysis, acetonitrile (ACN) was employed as the solvent, and tetra-*n*-propylammonium perchlorate as the supporting electrolyte. In the alkali metal reduction, lithium, sodium, potassium and cesium metals were used as the reducing agent, and dimethoxyethane (DME) and tetrahydrofuran (THF) as the solvent.

Dimethyl, diethyl, diisopropyl and diisobutyl *o*-phthalates were purified by vacuum distillation after drying over barium oxide. Dicyclohexyl *o*-phthalate, dimethyl *m*-phthalate, and dimethyl and diethyl *p*-phthalates were recrystallized twice from benzene. Diethyl *m*-phthalate was synthesized from the corresponding acid by the Fischer method, and diisopropyl *m*-phthalate was prepared from *m*-phthaloyl chloride and isopropyl alcohol in pyridine. Diisopropyl and di-*t*-butyl *p*-phthalates were produced from dimethyl *p*-phthalate by the exchange reaction. The purification of solvents and the preparation of supporting electrolyte were described elsewhere.[2]

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[1] Presented partly at the symposium on Electron Spin Resonance, Kyoto, November, 1963.

[2] M. Hirayama, This Bulletin, **40**, 1822 (1967).

[3] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

[4] N. Steinberger and G. K. Fraenkel, *ibid.*, **40**, 723 (1964).

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

[6] A. H. Maki, *J. Chem. Phys.*, **35**, 761 (1961).

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

[8] R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1961).

[9] A. Carrington and P. F. Todd, *Mol. Phys.*, **6**, 161 (1963).

Results

***o*-Phthalates.** Dimethyl, diethyl, diisopropyl, diisobutyl and dicyclohexyl esters were investigated. Electrolysis of these compounds yielded a brown-yellow solution which displayed a well-resolved spectrum. The radicals were relatively stable at room temperature. Interpretation of the spectra is straightforward; from the similarity of them, the common two triplets were attributed to two sets of two equivalent ring protons of the one-electron reduction products of these compounds, and consequently, the residual splittings to the α-protons*[1] in two equivalent ester groups in each anion radical. The spectrum obtained by the electrolysis of diethyl *o*-phthalate is shown in Fig. 1, with its reconstruction based on the splitting constants in Table 1. The larger one of two triplet splitting constants due to the ring protons was assigned to the position 3 on the base of the MO calculation of spin densities described later.

All the five esters in contact with lithium, sodium and potassium metals in DME or THF gave

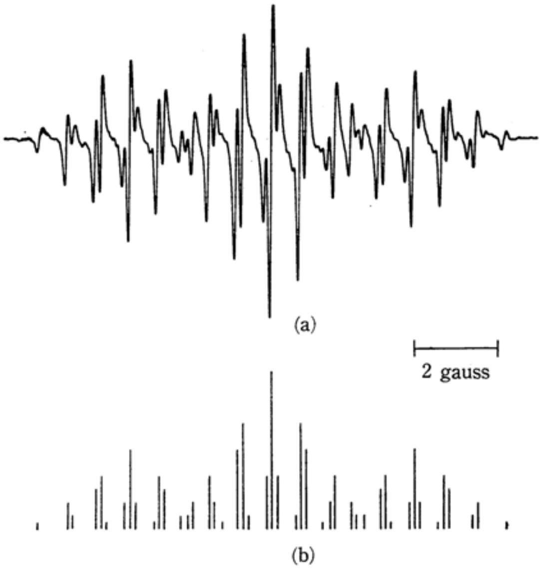

Fig. 1. The ESR spectrum of the anion radical of diethyl *o*-phthalate prepared by electrolysis in ACN (a) and its reconstruction (b).

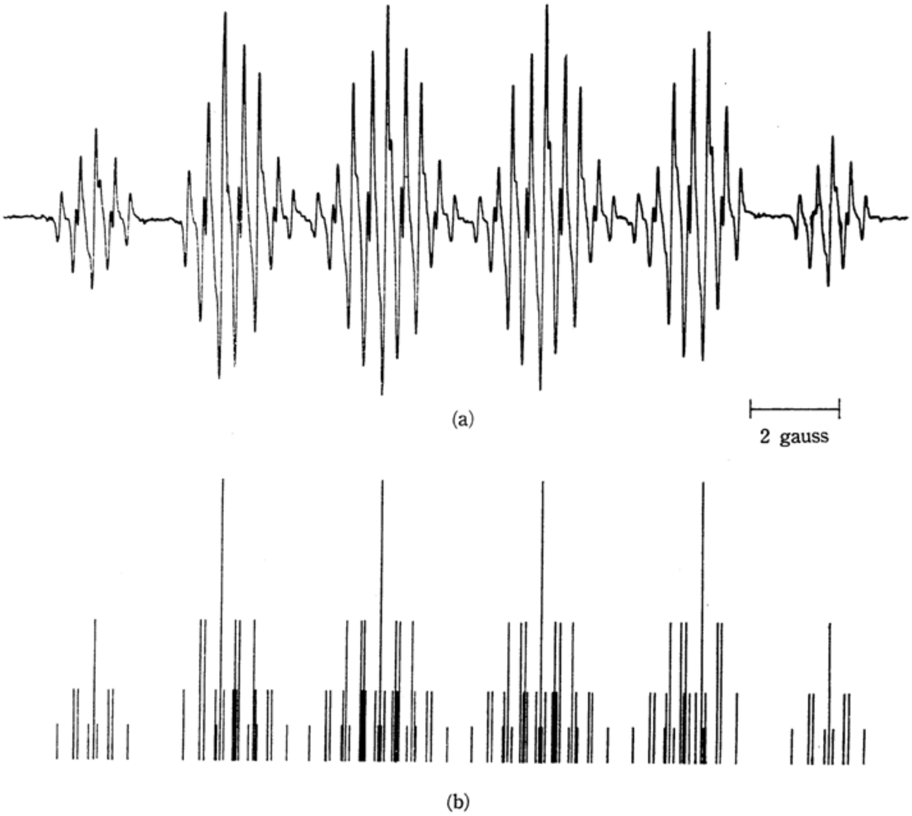

Fig. 2. The ESR spectrum of the diisopropyl *o*-phthalate - sodium complex in DME (a) and its reconstruction (b).

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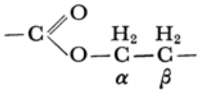
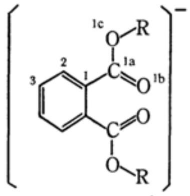
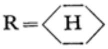
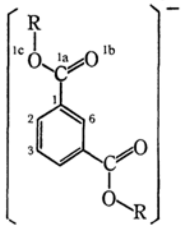
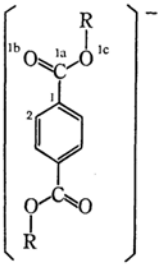
*[1] The proton position is defined by the notation:



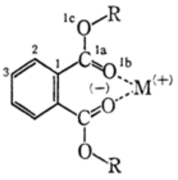
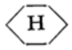
$$-C(=O)-O-\underset{\alpha}{\overset{H_2}{C}}-\underset{\beta}{\overset{H_2}{C}}-$$

TABLE 1. HYPERFINE SPLITTING CONSTANTS FOR THE ANION RADICALS PREPARED BY ELECTROLYSIS IN ACN

Anion	Hyperfine splitting constants (in gauss)				
		a_2	a_3	a_α	
	$R=CH_3$	0.83	3.45	0.74	
	$R=C_2H_5$	0.83	3.46	0.67	
	$R=CH_2CH(CH_3)_2$	0.84	3.44	0.74	
	$R=CH(CH_3)_2$	0.82	3.47	0.32	
	R= 	0.82	3.49	0.30	
		a_2	a_3	a_6	a_α
	$R=CH_3$	8.23	1.52	0.58	0.45
	$R=C_2H_5$	8.28	1.52	0.58	0.45
	$R=CH(CH_3)_2$	8.28	1.52	0.58	0.23
			a_2		a_α
	$R=CH_3$		1.56		0.78
	$R=C_2H_5$		1.56		0.78
	$R=CH(CH_3)_2$		1.56		0.42
	$R=C(CH_3)_3$		1.56 $\left\{\begin{matrix}1.57^*\\1.45^*\end{matrix}\right.$		

* In DME.

TABLE 2. HYPERFINE SPLITTING CONSTANTS FOR THE ION COMPLEXES BETWEEN THE ALKALI METAL CATION AND THE *o*-PHTHALATE ANION RADICAL IN DME

Ion complex	Hyperfine splitting constants (in gauss)				
			Sodium	Potassium	Lithium
	$R=CH_3$	a_2	0.54	0.61	**
		a_3	3.07	3.26	
		a_α	0.84	0.76	
		a^M	3.67	0.69	
	$R=C_2H_5$	a_2	0.53	0.58*	**
		a_3	3.17	3.20*	
		a_α	0.80	0.76*	
		a^M	3.88	0.74*	
	$R=CH_2CH(CH_3)_2$	a_2	0.49	0.62	**
		a_3	2.97	3.25	
		a_α	0.82	0.85	
		a^M	3.63	0.69	
	$R=CH(CH_3)_2$	a_2	0.43	0.55	0.46*
		a_3	2.90	3.19	3.03*
		a_α	0.34	0.37	0.29*
		a^M	3.67	0.76	2.02*
	R= 	a_2	0.43	**	**
		a_3	3.12		
		a_α	0.43		
		a^M	3.80		

* In THF. ** Not measured.

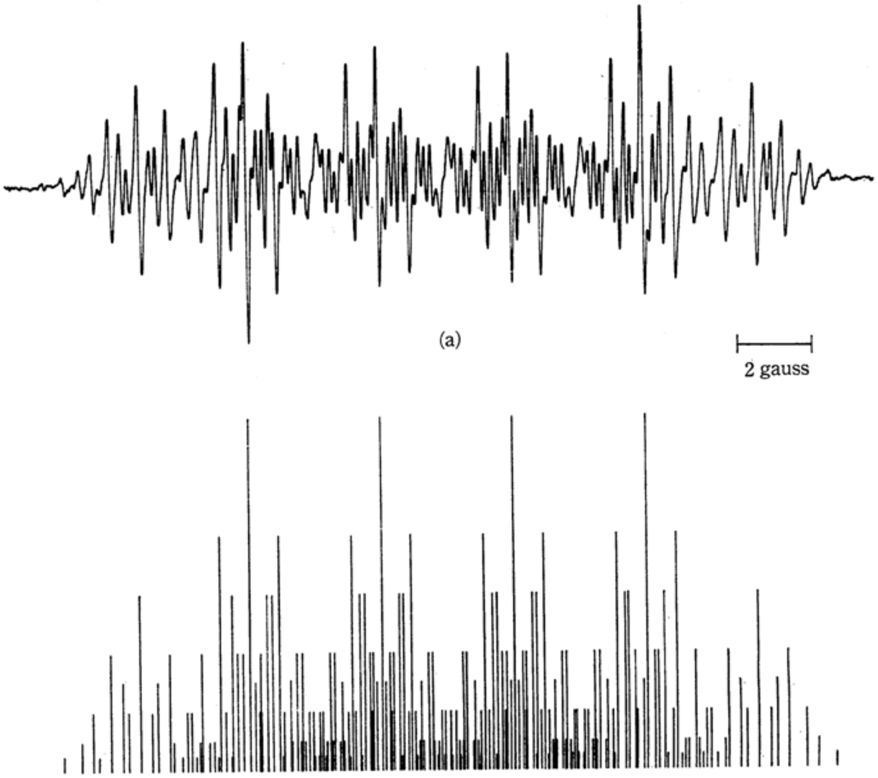


Fig. 3. The ESR spectrum of the diethyl *o*-phthalate - sodium complex in DME (a) and its reconstruction (b).

a yellow solution which displayed a markedly resolved spectrum with a much larger overall width than those of the spectrum obtained by electrolysis, while with cesium metal, a red-purple solution which gave a poorly-resolved spectrum with a very large overall width, about 30 gauss. The splitting constants measured are shown in Table 2. The radicals produced were stable at room temperature except for those with lithium metal. The analysis of spectra led apparently to the splittings corresponding to those obtained by electrolysis, and to the splitting due to an alkali metal nucleus. Both the two triplet splitting constants due to the ring protons became smaller than those obtained by electrolysis, while the α-proton splittings slightly larger. The spectra obtained by the reduction of diisopropyl ester with sodium metal in DME at room temperature and with potassium metal in THF at $-40°$C, and of diethyl ester with sodium metal in DME at room temperature, are shown in Figs. 2, 3 and 4, respectively, with each reconstruction based on the splitting constants listed in Table 2. The measurement of these anion radicals with sodium and potassium metals in DME or THF at low temperatures ($\sim -60°$C) resulted in the almost identical spectra with those observed at room temperature.

***m*-Phthalates.** The three esters were examined; dimethyl, diethyl and diisopropyl *m*-phthalates. These compounds on electrolysis yielded an orange solution which gave a very stable radical. The splitting constants given in Table 1 are consistent with those anticipated from the anion radicals of these compounds. Then, from the analogy with the spectrum of isophthalonitrile anion radical,[10] one may immediately consider that a larger triplet and two doublets with the common magnitudes of splitting constants to these spectra are attributable to the two equivalent ring protons at the positions 2 and 4, and the two unequivalent ring protons at the positions 3 and 6, respectively. Consequently, the residual ones, *i. e.*, a triplet in diisopropyl, a quintet in diethyl and a septet in dimethyl ester anions, are unequivocally interpretable as arising from two, four and six equivalent α-protons, respectively, in each anion. The larger one of two doublet splitting constants was assigned to the position 3 based on the MO calculation. The spectrum obtained by the electrolysis of diisopropyl ester is shown in Fig. 5, with its reconstruction. Several low-intensity lines

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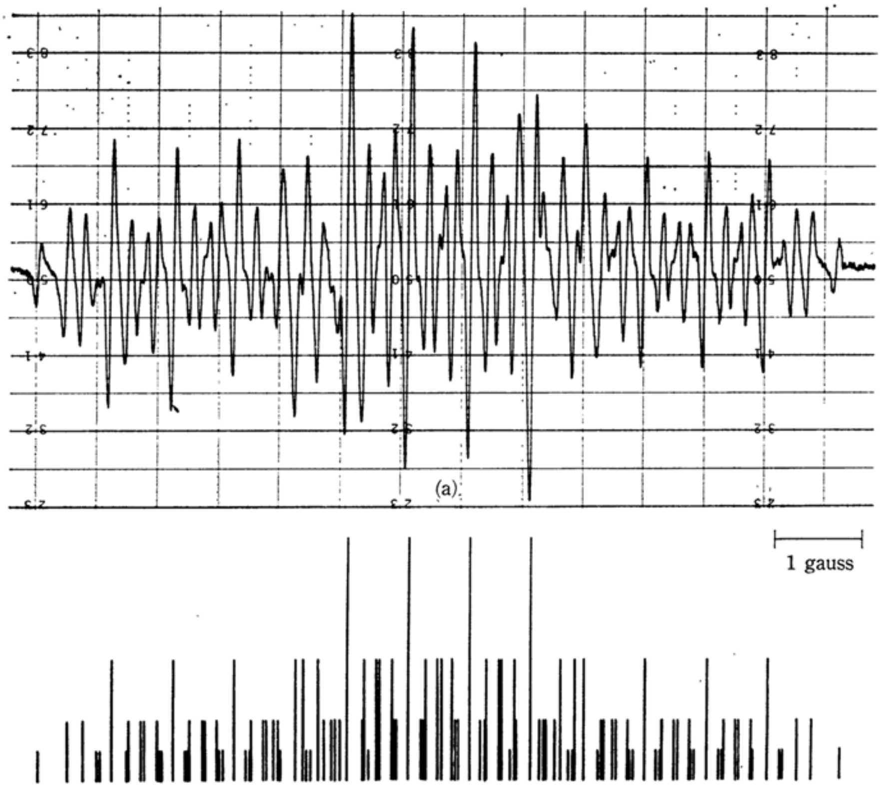
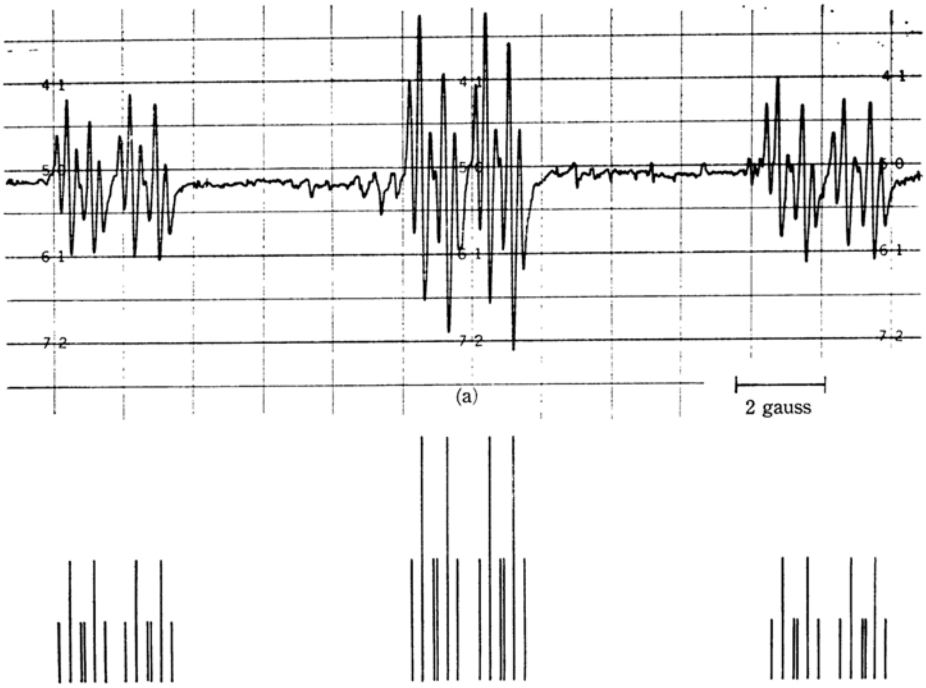
[10] P. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).



(b)

Fig. 4. The ESR spectrum of the diisopropyl *o*-phthalate - potassium complex in THF at $-40°C$ (a) and its reconstruction (b).



(b)

Fig. 5. The ESR spectrum of the anion radical of diisopropyl *m*-phthalate prepared by electrolysis in ACN (a) and its reconstruction (b).

Fig. 6. The ESR spectra of the anion radicals of di-*t*-butyl *p*-phthalates prepared by electrolysis. (a) In ACN. (b) In DME.

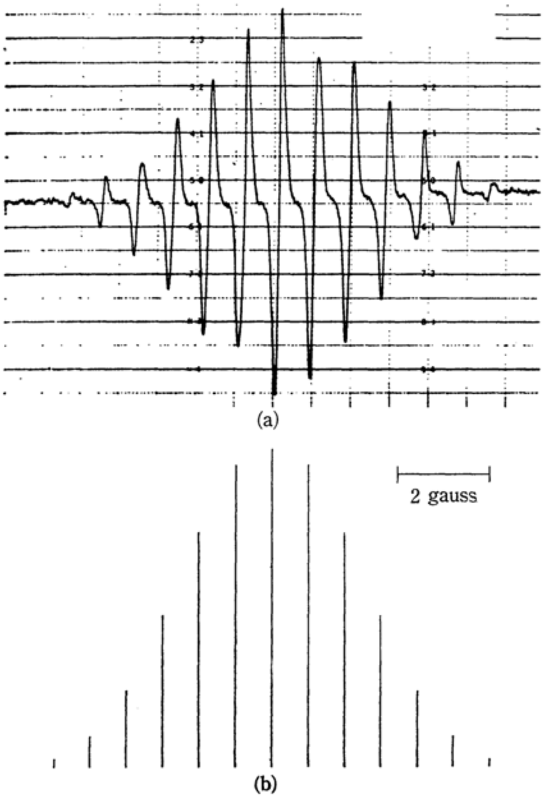


Fig. 7. The ESR spectrum of the anion radical of diethyl *p*-phthalate prepared by electrolysis in ACN (a) and its reconstruction (b).

occurring at asymmetric positions about the center of spectrum in Fig. 5 arise from the impurity of diisopropyl *p*-phthalate anion.

***p*-Phthalates.** *Electrolytic Reduction.* Dimethyl, diethyl, diisopropyl and di-*t*-butyl *p*-phthalates were investigated. The electrolytic reduction of all these esters yielded a purple-red solution which displayed a strong signal. The radicals produced were very stable at room temperature except for that obtained from di-*t*-butyl ester. In the spectrum of di-*t*-butyl ester anion, the second and fourth of the five lines are broader than the others, and although they don't split further even in a much more diluted solution of ACN, as is seen from Fig. 6(a), the line shapes of them and the occurrence of a small proton line on either side of the center line indicate that they are essentially a superposition of two unresolved lines. On the other hand, in DME solution, these lines were obviously observed to split into two lines with an equal intensity, as is shown in Fig. 6(b). Thus, one may conclude that the two *t*-butyl ester groups are at least not freely rotating. The unequivalence of ring proton splittings is probably ascribed to a little difference between the direct effects of the charges of two oxygen atoms in the ester group on the ring. It could not be clearly determined whether the spectrum observed would correspond to a cis form, a trans form or a superposition of these two forms. Also by the electrolysis of the other three esters, the splittings due to the ring and α-protons were observed for each anion radical. (Table 1) However, the small difference expected between the ring proton splittings has been not exactly estimated. The spectrum of the diethyl ester anion is shown in Fig. 7 with its reconstruction.

Li-Reduction. The reduction of these esters with an alkali metal gave also a purple-red solution. Di-*t*-butyl and diisopropyl esters were contacted

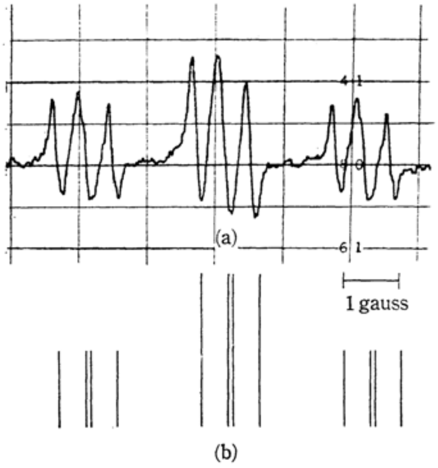


Fig. 8. The ESR spectrum of the di-*t*-butyl *p*-phthalate - lithium complex in THF $-50°C$ (a) and its reconstruction (b).

with lithium metal at a dry ice temperature and the resulting spectra were measured at low temperatures, since the radicals produced were very unstable at room temperature. The former at −50°C in THF, shown in Fig. 8, consisted of a triplet and two doublet splitting constants shown in Table 3 (Fig. 8(b)), and consequently, suggests that the ring protons included in the expected anion radical of this compound are separated into two groups. Even the single lines are broad, probably because of the existence of splitting due to a lithium nucleus. The latter in THF at −40°C was further poorly-resolved, but interpreted with a triplet splitting of 0.52 gauss, assignable to two equivalent α-protons, in addition to the similar splittings to those of the former. As the temperature was elevated above −40°C, the intensities of these two spectra became smaller, but no change in spectral pattern was observed.

Na-Reduction. Diisopropyl ester in contact with sodium metal in DME or THF at room temperature gave a stable radical, and the spectrum observed (Fig. 9(a)) was, though poorly resolved, analyzed to two triplets (in THF, the larger one is devided into two doublets) and two doublets with the splitting constants given in Table 3. From the analogy with the case of Li-reduction, two triplets were attributed to two sets of two equivalent ring

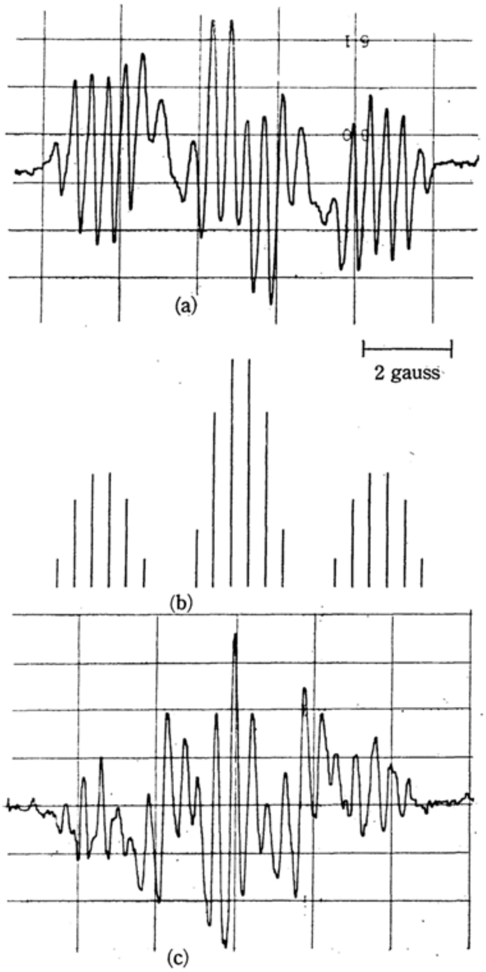


Fig. 9. The ESR spectra obtained by the reduction of diisopropyl *p*-phthalate with sodium metal in DME.
(a) Measured at 25°C. The sodium complex.
(b) The reconstruction corresponding to (a).
(c) Measured at −47°C. A superposition of (a) and the spectrum of free anion radical.

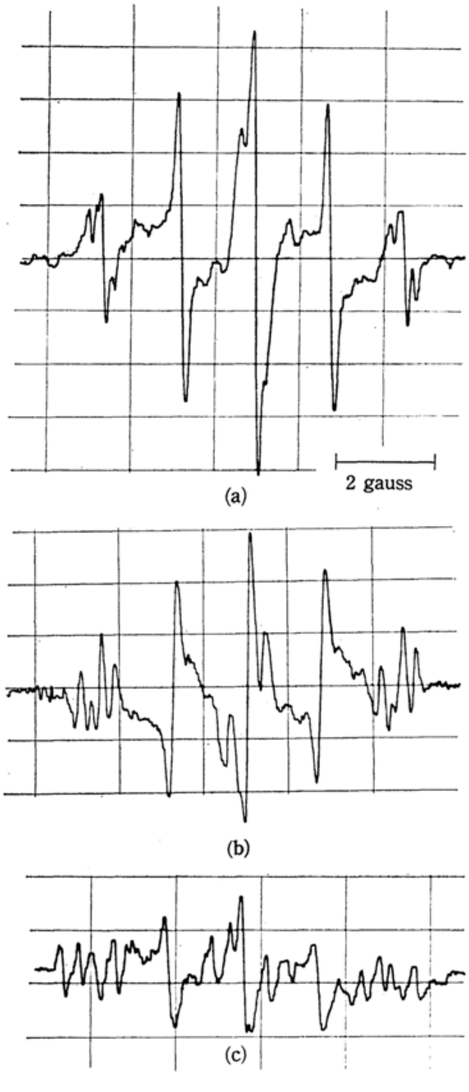
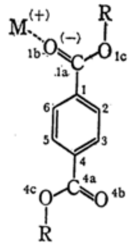


Fig. 10. The ESR spectra obtained by the reduction of di-*t*-butyl *p*-phthalate with sodium metal in DME.
(a) Measured at −60°C.
(b) Measured at −36°C.
(c) Measured at −23°C.
These spectra consist of a superposition of the spectra of free anion radical and sodium complex.

TABLE 3. HYPERFINE SPLITTING CONSTANTS FOR THE ION COMPLEXES BETWEEN THE ALKALI METAL CATION AND THE *p*-PHTHALATE ANION RADICAL IN THF

Ion complex			Hyperfine splitting constants (in gauss)			
			Lithium	Sodium		Potassium
	$R=C(CH_3)_3$	$a_{2,6}$	2.65	**		1.52*
		$a_{3,5}$	0.59 0.46			1.52*
	$R=CH(CH_3)_2$	$a_{2,6}$	2.56	3.11*	3.27 3.15	1.57
		$a_{3,5}$	0.52	0.39*	0.45	1.45
		a_α	0.52	0.77* 0.39*	0.90 0.45	0.43
		a^M	**	**	**	0.095

* In DME. ** Could not be measured.

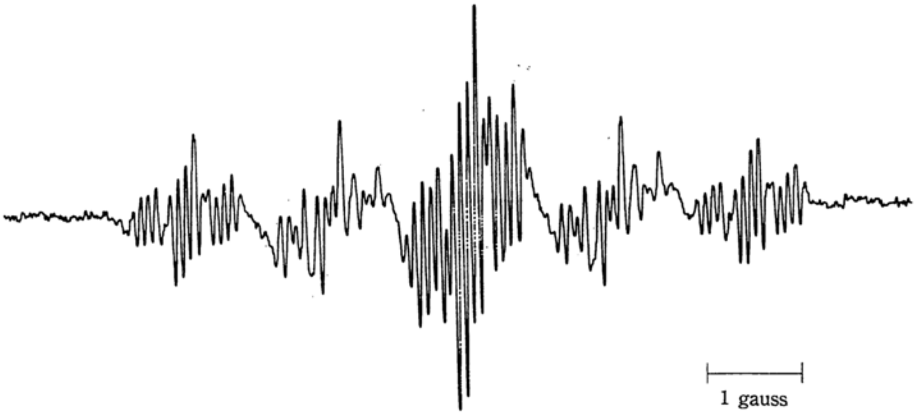


Fig. 11. The ESR spectrum of the diisopropyl *p*-phthalate - potassium complex in THF.

protons and two doublets to two α-protons in the anion radical of this ester. The assignment will be described in the section of discussion. The spectra obtained from di-*t*-butyl ester in contact with sodium metal in THF or DME at room temperature, could not be precisely measured because of unstability of the radical, but were found to be composed of three groups. Then, these esters were contacted with sodium metal at a dry ice temperature and the spectra were measured at low temperatures. Consequently, a superposition of the spectra of free anion and ion complex was observed. When the temperature was elevated above $-60°C$, the contribution from the latter increased with increasing temperature and a whole spectrum decreased, as are shown in Figs. 9 and 10.

K-Reduction. The reduction of di-*t*-butyl ester with potassium metal in DME at room temperature to $-40°C$ yielded the same spectrum as that obtained by electrolysis. The linewidth of each five line was about 0.3 gauss, and even if the solution was further diluted, all the lines did not become narrower and split. This may be ascribed to the splitting of potassium nucleus. The spectrum obtained by the reduction of diisopropyl ester in THF at room temperature contained apparently the splitting due to a potassium nucleus, as is shown in Fig. 11. The second and fourth groups in Fig. 11 are poorly resolved, because the four ring protons are not entirely equivalent.

Cs-Reduction. The radical produced by the reduction of diisopropyl ester in DME was comparatively unstable at room temperature. The spectrum observed is composed of two triplets, which may be attributed to the ring protons of the anion radical of this ester.

Discussion

The MO Calculations of Spin Densities. The MO calculations of spin densities were made by the Hückel approximation and McLachlan's method.11) The values of parameters described in the previous paper2) were used for the ester group except for $\gamma_{CC'}=1.0$ ($\gamma_{CC'}$ is the resonance integral parameter for the bond between the ester group and the ring). The calculated results are compared with the experimental spin densities obtained by the equation, $a_i^H=Q_{CH}^H\ \rho_i^\pi$, where $|Q_{CH}^H|=24.0$ gauss, in Table 4. The calculated spin densities of McLachlan for the *m*- and *p*-phthalate anions

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

TABLE 4. CALCULATED AND EXPERIMENTAL SPIN DENSITIES

Anion	Position*	Spin density		
		Calculated		Experimental***
		Hückel	McLachlan	
	1	0.1840**	0.2225**	
	2	0.0123	−0.0387	0.035
o-Phthalate anion	3	0.1245	0.1384	0.144
	1a	0.1032	0.1151	
	1b	0.0553	0.0490	
	1c	0.0206	0.0140	
	1	0.1023	0.0776	
	2	0.2475	0.3440	0.345
	3	0.0000	−0.0911	0.065
m-Phthalate anion	6	0.0000	−0.0342	0.024
	1a	0.0851	0.0927	
	1b	0.0475	0.0377	
	1c	0.0176	0.0107	
	1	0.1695	0.2011	
	2	0.0721	0.0573	0.065
p-Phthalate anion	1a	0.1010	0.1098	
	1b	0.0626	0.0583	
	1c	0.0227	0.0161	

* See Table 1 for numbering of positions.

** Calculated by using $\gamma_{CC'}=0.766$.

*** Calculated from the splitting constants obtained by electrolysis in acetonitrile, by the equation, $a_i^H=Q_{CH}^H\rho_i^\pi$, where $|Q_{CH}^H|=24.0$ gauss.

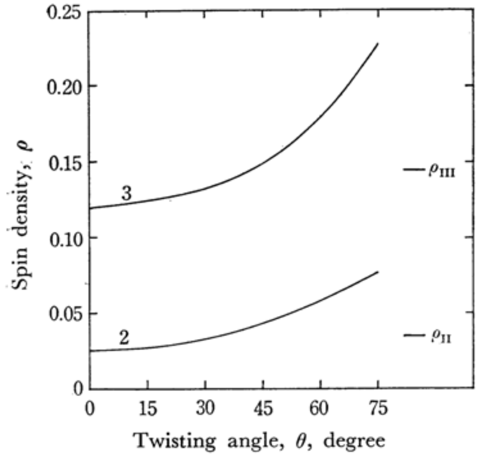

Fig. 12. Spin densities ρ calculated by the McLachlan modification of MO theory for the *o*-phthalate anion as a function of the twisting angle θ between the ester group and the ring (The spin density at the position 2 is represented as $|\rho_2|$), and experimental spin densities using $|Q_{CH}^H| = 24.0$ gauss. ρ_{II} and ρ_{III} are experimental spin densities.
The numbers on the curves indicate the positions in the radical.

are in good agreement with the experimental data obtained by electrolysis, while for the *o*-phthalate anion, those by using $\gamma_{CC'}=1.0$ disagree with the experimental splitting constants. This disagreement may be attributed to the effect of steric hindrance between two ester groups on the spin density distribution on the ring, as will be discussed in the following section.

The Steric Hindrance between Ester Groups. In order to confirm the effect of steric hindrance between two ester groups on the ring proton splittings in the *o*-phthalate anion, the spin densities were calculated with the modification that the resonance integral of the ester group-ring bond was estimated to be $\beta\cos\theta$, where θ is a twisting angle between the ester group and the ring. The dependence of the spin densities of the ring positions 2 and 3 on the twisting angle θ is shown in Fig. 12. As is seen from Fig. 12, the theoretical spin densities at the positions 2 and 3 approach each of the corresponding experimental spin densities obtained by electrolysis around $\theta=37°$ and 43°, respectively. Thus, McLachlan's calculation led to the conclusion that the two ester groups were twisted about 35—45° from the ring to the opposite direction each other. The spin densities calculated by using $\gamma_{CC'}=0.766$ corresponding to $\theta=40°$ are given in Table 4.

The Formation of Ion Complexes. *o-Phthalates.* From the large splitting due to each alkali metal nucleus, one may consider that a very tight ion complex is formed between the *o*-phthalate anion and each alkali metal cation, and these ion complexes were found to be not dissociated in the range from room temperature to −60°C. The experimental results showed that although all the

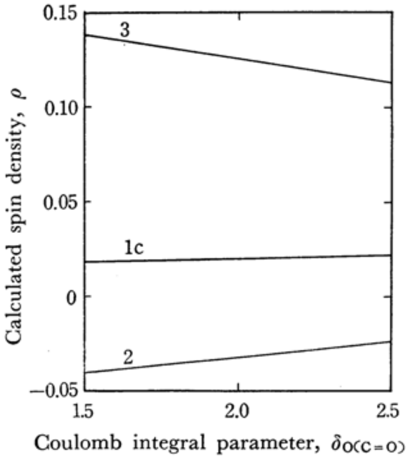

Fig. 13. Spin densities ρ calculated by the McLachlan modification of MO theory for the *o*-phthalate anion as a function of the Coulomb integral parameter for the carbonyl oxygen, $\delta_{O(C=O)}$.
The numbers on the curves indicate the positions in the radical.

TABLE 5. SPIN DENSITIES AT THE ALKALI METAL NUCLEI

	Li	Na	K	Cs
Q^M (in gauss)	143.3	316.2	82.38	820.08
a^M (in gauss)	2.02	3.67	0.76	2.00
ρ^M (a^M/Q^M)	1.41×10^{-2}	1.16×10^{-2}	9.23×10^{-3}	2.44×10^{-3}

Q^M: Splitting constant due to the free alkali metal nucleus.
ρ^M: Spin density at the alkali metal nucleus.

splittings in each anion were influenced by all the alkali metal cations, the symmetry of the pattern of the splitting constants was kept unchanged. Therefore, it seems reasonable to consider that the metal cation may exist at a symmetric position to both the ester groups. A model shown in Table 2 was thus proposed for the ion complex. In order to test the validity of this model, the MO calculation was tried with the modification that the Coulomb integral parameter for carbonyl oxygen atom, $\delta_{O(C=O)}$, was changed in the range of 1.5—2.5, assuming that the positive charge of alkali metal cation introduced a small increase in electron density on the carbonyl oxygen atom. As is illustrated in Fig. 13, the values of ρ_3 and $|\rho_2|$ were reduced with an increment of $\delta_{O(C=O)}$, while conversely, ρ_{1c} enhanced gradually. Thus, this model is supported also by the theoretical consideration. The values of the ratios, a^M/Q^M, where Q^M is the splitting constant due to a free alkali metal nucleus,[12] shown in Table 5, reveal that the magnitude of spin density on the alkali metal nucleus decreases in the order of increasing ionic radius, that is, Li>Na>K>Cs. This tendency agrees with that in the magnitude of difference of α-proton splitting constant in the ion complex from that in the anion radical produced by electrolysis, but in the case of two ring proton splittings, this difference decreases in the order of Na>Li>K.

p-Phthalates. The existence of the splitting of a potassium nucleus seems to indicate that an one-to-one ion complex is formed between the potassium cation and the *p*-phthalate anion. One may suppose that the potassium cation exists over the ring rather than near one ester group, because all the splittings are scarcely affected by the cation. In the reduction with sodium or lithium metal, the experimental results imply that one ester group (probably a carbonyl oxygen) interacts with the cation, (a model shown in Table 3 is proposed) and that this interacting ester group becomes more electron-withdrawing than the other. Consequently, in view of the superposition model proposed by Schug *et al.*,[13] the larger triplet may be interpreted as arising from two ortho ring protons to the interacting ester group. The calculation of spin densities with an increase of $\delta_{O(C=O)}$ for one ester group from 1.5 was performed, and the result is shown in Fig. 14. As is illustrated in Fig. 14, ρ_2 and ρ_{1c} (see Table 3 for numbering of position) increase with increasing $\delta_{O(C=O)}$, while ρ_3 and ρ_{4c} decrease. Thus, the assignment mentioned above is consistent with the theoretical consideration, and the larger α-proton splitting in the sodium complex can be attributed to that in the interacting ester group, as expected, while the equivalency of two α-protons in the lithium complex can not be explained by such a method.

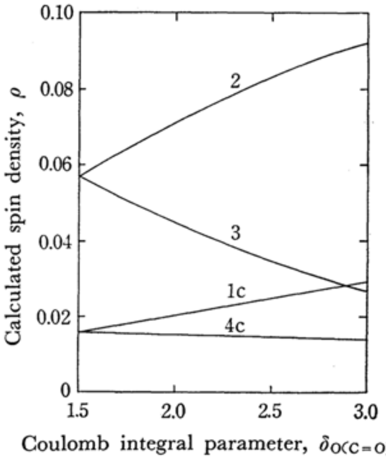

Fig. 14. Spin densities ρ calculated by the McLachlan modification of MO theory for the *p*-phthalate anion as a function of the Coulomb integral parameter for one carbonyl oxygen, $\delta_{O(C=O)}$.
The numbers on the curves indicate the positions in the radical.

From the spectra obtained with a sodium metal at low temperatures, it was suggested that there existed an equilibrium between a *p*-phthalate anion-sodium cation ion complex and a completely dissociated state in DME or THF.

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

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