BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2530—2536 (1967)

Electron Spin Resonance of Anion Radicals of Aromatic Esters. III. The Anion Radicals of Several Diesters of Biphenyl-*o*, *o*′- and -*p*, *p*′-Dicarboxylic Acids[1]

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(Received May 19, 1967)

The ESR spectra of the anion radicals of dimethyl, diethyl, and diisopropyl esters of biphenyl-*o*, *o*′- and -*p*, *p*′-dicarboxylic acids, and of the di-*t*-butyl ester of the *o*, *o*′-derivative, have been studied. The anion radicals were prepared by electrolytic reduction in acetonitrile, and also by reduction with sodium and potassium metals in dimethoxyethane and tetrahydrofuran. The MO calculations of the spin densities were made by McLachlan's method; all the splitting constants observed were assigned to the ring protons and the α-protons in the ester groups. A comparison of the experimental splittings with the calculated spin densities suggests that the anions of *p*, *p*′-derivatives are in a planar conformation, while those of *o*,*o*′-derivatives have a twisted structure in which the twisting angle between the two rings was about 35—60°. A structural model was proposed for an ion complex formed between the anion of the *o*, *o*′-derivative and a sodium or a potassium cation.

In a previous paper[2] in this series, ESR spectra have been reported for the anion radicals of several diesters of *o*-, *m*-, and *p*-phthalic acids. The present article was undertaken in an attempt to study the ESR spectra of the anion radicals of several diesters of biphenyl-*o*, *o*′- and -*p*, *p*′-dicarboxylic acids.

The MO calculation of spin densities has suggested that the biphenyl anion may be in a planar conformation.[3] Moreover, in the case of the anion radicals of some biphenyl derivatives, a discussion has been made of the orientation between the two rings; it has been suggested that the anion of *p*, *p*′-dicyano biphenyl is planar,[4,5] while the anion of *p*, *p*′-dinitro biphenyl is twisted,[5] and for the anion of *o*, *o*′-dimethyl biphenyl the twisting angle has been estimated to be 30—45°.[6] However, no anions of biphenyl-*o*, *o*′-derivatives with electron-withdrawing groups have yet been investigated.

In the present paper, the orientation between the two rings in the two series of anions will be discussed by comparing the calculated spin densities with the experimental splitting constants. The magnitude of the ring-proton splittings observed with the *o*, *o*′-derivative anion was found to vary slightly with the ester group. In view of this fact, a theoretical consideration suggests that the magnitude of steric hindrance might increase in the order of dimethyl, diethyl, diisopropyl, and di-*t*-butyl ester anions.

Experimental

The details of the ESR spectrometer and the electrolytic cell used in the present study have been described elsewhere.[7] The anion radicals were prepared by electrolysis in acetonitrile (ACN), using tetra-*n*-propylammonium perchlorate as the electrolyte, and also by alkali-metal reduction in dimethoxyethane (DME) and tetrahydrofuran (THF), using sodium and potassium metals as reducing agents.

Dimethyl, diethyl, and diisopropyl esters of biphenyl-*p*, *p*′-dicarboxylic acid were synthesized from *p*, *p*′-dicyano biphenyl, and methyl, ethyl, and isopropyl alcohols respectively. Dimethyl and diethyl esters of biphenyl-*o*, *o*′-dicarboxylic acid were prepared from diphenic acid by esterification, while diisopropyl and di-*t*-butyl esters were synthesized by the reactions of diphenic acid chloride with isopropyl and *t*-butyl alcohols respectively in pyridine.

Results

Dimethyl, Diethyl, and Diisopropyl Esters of Biphenyl-*p*, *p*′-Dicarboxylic Acid. The electrolysis of any of these esters gave a yellow solution, which in turn yielded a stable radical at room temperature. The spectrum obtained by the reduction of the diisopropyl ester, shown in Fig. 1(a), was composed of two quintets and a triplet with a ratio of splitting constants of 6 : 2 : 1; this spectrum was consistent with that to be expected from the anion radical of this compound. The two quintets may be attributed to the two

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

[2] M. Hirayama, This Bulletin, **40**, 2234 (1967).

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

[4] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

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

[6] K. Ishizu, This Bulletin, **37**, 1093 (1964).

[7] M. Hirayama, *ibid.*, **40**, 1822 (1967).

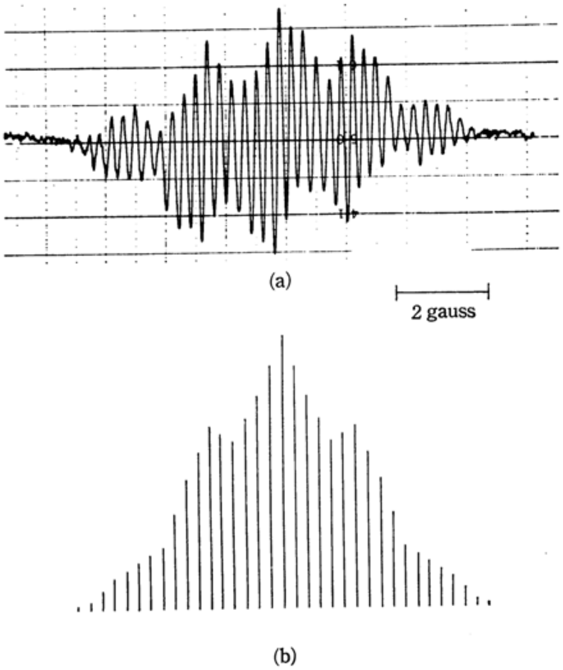
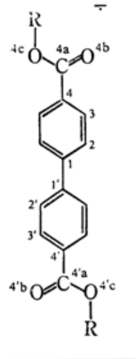


Fig. 1. The ESR spectrum of the anion radical of diisopropyl ester of biphenyl-*p*, *p*′-dicarboxylic acid prepared by electrolysis in ACN (a), and its reconstruction (b).

Table 1. Hyperfine splitting constants for the *p*, *p*′-derivative anions prepared by the electrolysis in ACN

Anion		Hyperfine splitting constants (in gauss)	
	$R=CH(CH_3)_2$	a_2	1.55
		a_3	0.52
		a_{CH}	0.28
	$R=CH_2CH_3$	a_2	1.52
		a_3	0.51
		a_{CH_2}	0.51
	$R=CH_3$	a_2	1.51
		a_3	0.51
		a_{CH_3}	0.51

sets of four equivalent ring protons, and the triplet, to the two equivalent *α*-protons[*1] in the two ester groups. The splitting constants measured are shown in Table 1. A reconstruction based on the splitting constants listed in Table 1 is given in Fig. 1(b).

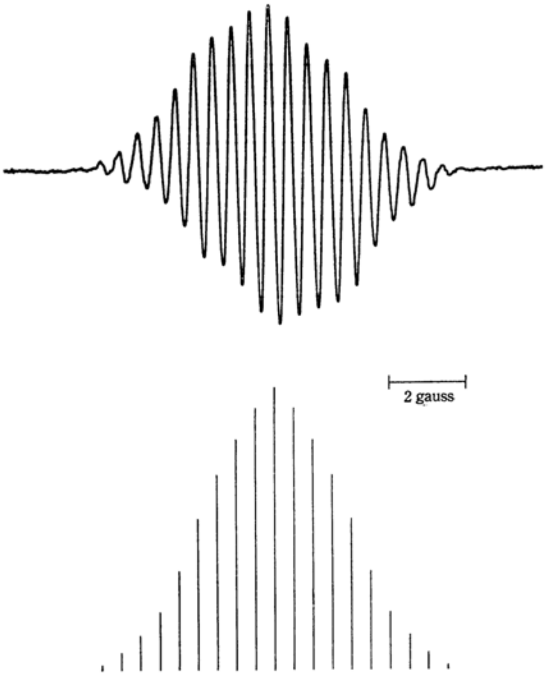


Fig. 2. The ESR spectrum of the anion radical of diethyl ester of biphenyl-*p*, *p*′-dicarboxylic acid prepared by electrolysis in ACN, and its reconstruction.

The reduction of dimethyl and diethyl esters gave spectra consisting of 23 and 21 lines respectively, with an average line-width of 0.25 gauss. The spectrum of the diethyl ester anion is shown in Fig. 2, along with its reconstruction. These two spectra were analyzed to a septet and a quintet(III) respectively, in addition to two quintets identical with those of the spectrum of the diisopropyl ester anion. The septet and quintet(III) are considered to arise from, respectively, the six and four equivalent *α*-protons in these two anions. The larger one of the two common quintets was assigned to the four equivalent ring protons ortho to the ester group; this assignment was made on the basis of a MO calculation of the spin densities to be described later.

Also, by the reduction of these esters with potassium and sodium metals in DME or THF, similar spectra were obtained.

Dimethyl, Diethyl, Diisopropyl, and Di-*t*-butyl Esters of Biphenyl-*o*, *o*′-Dicarboxylic Acid. The electrolytic reduction of all these esters gave a yellow-green solution. Since the radicals produced were relatively unstable at room temperature, no good resolved pattern of ESR hyperfine lines could be observed. The splitting constants measured are shown in Table 2. The spectrum obtained by the reduction of the diethyl ester is shown in Fig. 3, along with its reconstruction. From the similarity of the three spectra

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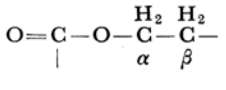
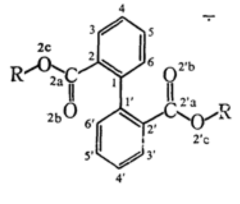
[*1] The proton position is defined by the notation:



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

TABLE 2. HYPERFINE SPLITTING CONSTANTS FOR THE o,o'-DERIVATIVE ANIONS PREPARED BY THE ELECTROLYSIS IN ACN AND FOR THE ION COMPLEXES PREPARED WITH ALKALI METALS IN DME

Anion			Hyperfine splitting constants (in gauss)		
			Electrolysis	K-reduction	Na-reduction
	$R=CH_3$	a_3	*	0.69	0.68
		a_4	1.52	3.15	3.13
		a_5	2.28	2.08	2.14
		a_6	0.15	*	0.21
		a_{CH_3}	0.53	*	*
					0.43 (a^{Na})
	$R=CH_2CH_3$	a_3	*	0.66	
		a_4	1.51	3.16	
		a_5	2.36	2.08	
		a_6	0.17	*	
		a_{CH_2}	0.51	*	
	$R=CH(CH_3)_2$	a_3	*	0.64	
		a_4	1.44	3.12	
		a_5	2.38	2.09	
		a_6	0.23	*	
		a_{CH}	0.23	*	
	$R=(CH_3)_3$	a_3	*	0.67	
		a_4	1.28	3.14	
		a_5	2.56	2.08	
		a_6	*	*	

* Could not be measured.

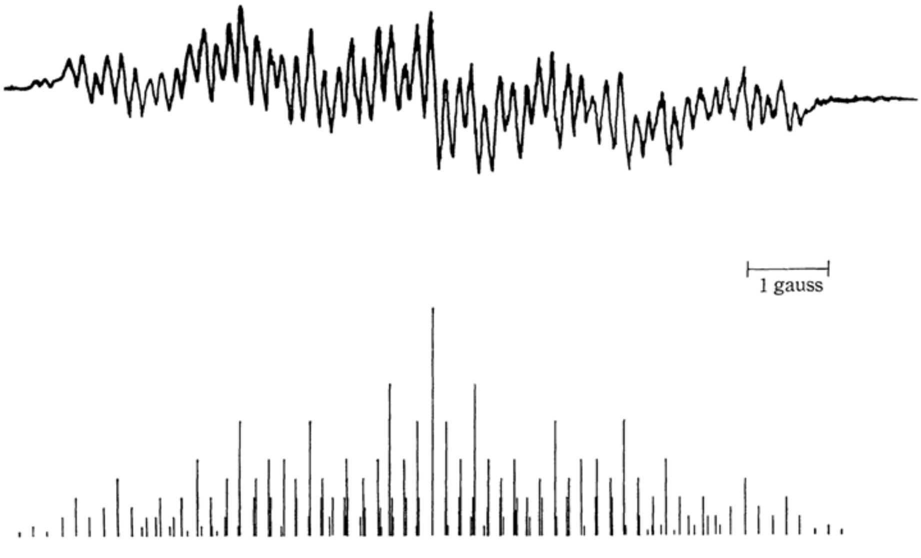


Fig. 3. The ESR spectrum of the anion radical of diethyl ester of biphenyl-o,o'-dicarboxylic acid prepared by electrolysis in ACN, and its reconstruction.

obtained from dimethyl, diethyl, and diisopropyl esters, the three triplets common to them may be attributed to the three sets of two equivalent ring protons in these anion radicals. They were assigned to the ring positions on the basis of the MO calculation of the spin densities, which will be described later. The splittings due to the residual ring protons may be covered by the line-width.

Thus, the residual splittings, *i. e.*, a triplet, a quintet, and a septet for the diisopropyl, diethyl, and dimethyl ester anions respectively, were attributed to the α-protons of two equivalent ester groups in each anion. The electrolysis of the di-*t*-butyl ester gave a poorly-resolved spectrum, which consisted of two triplets assignable to two sets of two equivalent ring protons.

The esters in contact with potassium metal in DME yielded an orange solution which displayed a strong ESR signal. However, when the solution was separated from the metal, the signal decayed slowly and the solution gradually turned red. All four esters gave almost identical poorly-resolved spectra, shown in Fig. 4, consisting of three triplets, arising from three sets of two equivalent ring protons, with much larger coupling constants than those obtained by electrolysis. The splittings due to the α-protons and the fourth ring protons could not be measured.

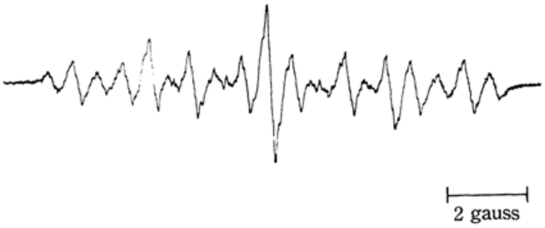


Fig. 4. The ESR spectrum of the ion complex between the anion radical of dimethyl ester of biphenyl-*o*, *o*'-dicarboxylic acid and potassium cation in DME.

The dimethyl ester in contact with sodium metal in DME gave an orange solution which displayed a well-resolved spectrum of about 80 lines (*cf.* Fig. 5). Analysis showed a small triplet arising from the fourth ring protons and a quartet due to a sodium nucleus, in addition to the three triplets identical with those obtained with potassium metal. The methyl proton splitting could not be measured, for it was much smaller than that obtained by electrolysis.

Discussion

MO Calculations of Spin Densities and Assignment of Splitting Constants. The MO calculations of spin densities were performed for the anion radicals studied here by the Hückel approximation and by McLachlan's method.3) The MO parameters used for the ester group have been described elsewhere.7) The results for the *p*, *p*'-derivative anion shown in Table 3 predict that the spin density at the position 2 will be larger than that at the position 3, as in the cases of the anions of biphenyl,3) *p*, *p*'-bipyridyl,8) and *p*, *p*'-dicyanobiphenyl.4,5) Thus, the larger one of the two ring-proton splittings was assigned to the position 2. The reduction of the resonance integral parameter for the central bond from 1.15 results in poor agreement with the experimental values, as is shown in Fig. 6. Consequently, one may consider that these *p*, *p*'-derivative anions are in a planar conformation, as are the anions of biphenyl3) and *p*, *p*'-dicyanobiphenyl.4)

In order to confirm a steric effect between the rings on the ring proton splittings in the *o*, *o*'-derivative anions, the spin densities were calculated with the modification that the resonance integral of the central bond was estimated to be $\beta\cos\theta$, where θ is a twisting angle between the two rings. The dependence of the spin density distribution on the ring on the twisting angle, θ, is shown in Fig. 7, along with the experimental spin densities for the four anion radicals. As is illustrated in Fig. 7, the theoretical spin density at the position

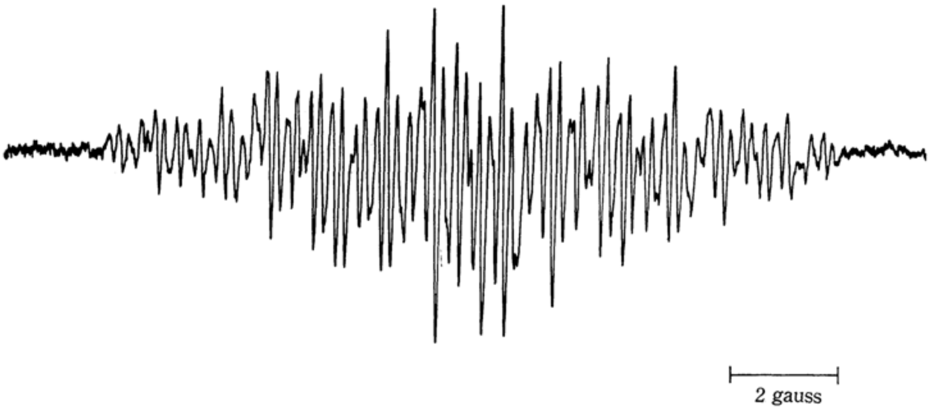


Fig. 5. The ESR spectrum of the ion complex between the anion radical of dimethyl ester of biphenyl-*o*, *o*'-dicarboxylic acid and sodium cation in DME.

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8) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 3623 (1961).

TABLE 3. CALCULATED AND EXPERIMENTAL SPIN DENSITIES

Anion	Position[*1]	Spin densities		
		Calculated		Experimental[*2]
		Hückel	McLachlan	
Anion of dimethyl ester of biphenyl-*p*,*p*′-dicarboxylic acid	1	0.0927[*3]	0.1005[*3]	
	2	0.0599	0.0625	0.063
	3	0.0370	0.0186	0.021
	4	0.1108	0.1362	
	4 a	0.0538	0.0574	
	4 b	0.0359	0.0343	
	4 c	0.0128	0.0094	
Anion of dimethyl ester of biphenyl-*o*,*o*′-dicarboxylic acid	1	0.1049[*4]	0.1291[*4]	
	2	0.1034	0.1201	
	3	0.0185	−0.0021	<0.004
	4	0.0582	0.0569	0.063
	5	0.0776	0.0921	0.095
	6	0.0059	−0.0265	0.006
	2 a	0.0730	0.0801	
	2 b	0.0428	0.0392	
	2 c	0.0157	0.0111	

[*1] See Table 1 for numbering of the position.

[*2] Calculated from the equation, $a_i^{\mathrm{H}} = Q_{\mathrm{CH}}^{\mathrm{H}}\rho_i^{\pi}$, where $|Q_{\mathrm{CH}}^{\mathrm{H}}| = 24.0$ gauss.

[*3] Calculated with $\gamma_{1-1'}=1.15$.

[*4] Calculated with $\gamma_{1-1'}=0.64$.

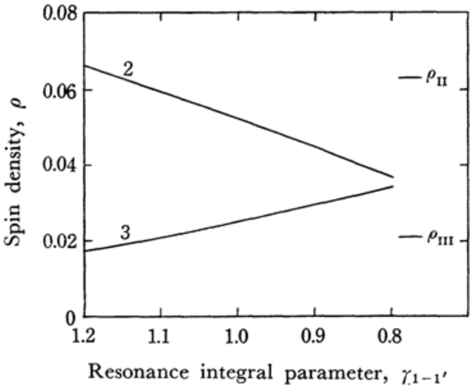

Fig. 6. Spin densities ρ on the ring calculated by McLachlan modification of MO theory for the *p*,*p*′-derivative anion as a function of the resonance integral parameter for the 1-1′ bond, and the experimental spin densities calculated using $Q_{\mathrm{CH}}^{\mathrm{H}}=-24.0$ gauss. ρ_{II} and ρ_{III} are experimental spin densities. The numbers on the curves indicate the positions in the radical.

5, ρ_5, is enhanced with an increment of θ and becomes equal to the experimental spin density, ρ_{V}, in the range of θ=52—59°, while ρ_4 is reduced and becomes equal to ρ_{IV} in the range of θ=46—52°. Furthermore, at both the 4 and 5 positions, the magnitude of θ at which the theoretical spin density agrees with the corresponding experimental spin density increases in the order of dimethyl, diethyl, diisopropyl, and di-*t*-butyl ester anions. This order is consistent with that in the steric hindrance expected for these four anions. Since the value of ρ_{VI} increases with an increment in the size of the ester group, as in the case of ρ_{V}, one can expect that the theoretical spin density corresponding to ρ_{VI} will increase with an increment in θ. Consequently, a possible theoretical spin density corresponding to ρ_{VI} is $|\rho_6|$ in the range of $\theta>20°$ or $|\rho_3|$ in the range of $\theta>52°$. However, since from $\rho_{\mathrm{VI}}>\rho_{\mathrm{III}}$, the theoretical spin density corresponding to ρ_{VI} must be larger than that corresponding to ρ_{III}, the possible theoretical spin density corresponding to ρ_{VI} is only $|\rho_6|$ in the range of $\theta>37°$, as may be seen from Fig. 7. Therefore, ρ_{III} may be assigned to the position 3, and, assuming that $\rho_{\mathrm{III}}<0.006$, $|\rho_3|$ becomes equal to ρ_{III} in the range of θ=46—57°. Thus, McLachlan's calculation led to the conclusion that the two rings were twisted about 35—60° from each other. The spin density distribution calculated with θ=50° is given in Table 3.

Formation of Ion Pair. The experimental data obtained from the alkali-metal reduction of *o*, *o*′-derivatives imply that an ion complex is formed between the alkali metal cation and the *o*, *o*′-derivative anion, and that the cation exists at a position symmetric to both the rings. MO calculations were undertaken to explain the spin density distribution considerably affected by the

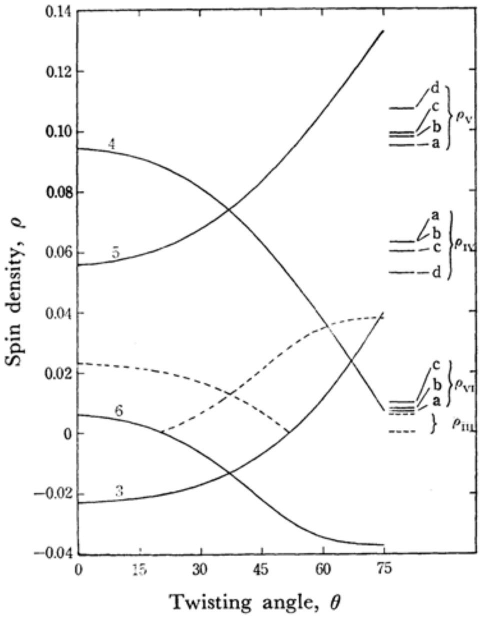

Fig. 7. Spin densities ρ calculated by McLachlan modification of MO theory for the *o, o′*-derivative anion as a function of the twisting angle θ between the rings, and the experimental spin densities calculated using $Q_{CH}^{H}=-24.0$ gauss. ρ_{III-VI} are experimental spin densities, where a, b, c, and d are those of dimethyl, diethyl, diisopropyl, and di-*t*-butyl ester anions, respectively. The numbers on the curves indicate the positions in the radical. The broken curves: $|\rho|$.

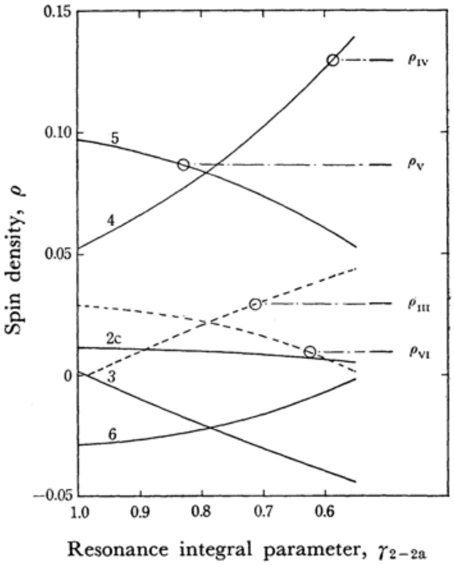

Fig. 8. Spin densities ρ calculated by McLachlan modification of MO theory for the *o, o′*-derivative anion as a function of the resonance integral parameter for the 2–2a bond (as $\gamma_{1-1'}=0.6$), and the experimental spin densities obtained from the ion complexes. ρ_{III-VI} are experimental spin densities. The numbers on the curves indicate the positions in the radical. The broken curves: $|\rho|$.

cation. The experimental data could not be explained by varying the value of the Coulomb integral parameter for the carbonyl oxygen atoms or that of the resonance integral parameter for the central bond. As is illustrated in Fig. 8, when the resonance integral parameter, γ_{2-2a}, is reduced from 1.0 (the value of $\gamma_{1-1'}$ is tentatively fixed as 0.6), ρ_4 and $|\rho_3|$ increase with a decrease in γ_{2-2a}, while ρ_5 and $|\rho_6|$ decrease, and while ρ_{2c} decreases gradually. The value of γ_{2-2a} at which the theoretical spin density becomes equal to the corresponding experimental spin density varies considerably with the position on the ring. Nevertheless, the large change in the experimental spin density distribution may be roughly interpreted by considering as follows: each ester group is twisted from the ring by the attractive force between each carbonyl oxygen and the alkali-metal cation, so that the distance between each carbonyl oxygen and the cation becomes shorter than in a structure with the ester group not twisted. If this interpretation is correct, the largest ring-proton splitting may be attributed to the 4 position; the second, to 5; the third, to 3, and the smallest, to 6. (In Table 3, each splitting constant is tentatively assigned according to this interpretation.) Thus, it may be supposed that the cation exists between the two carbonyl oxygen atoms, which approach each other in such a considerably twisted structure as is shown in Fig. 9. The magnitude of sodium splitting observed seems to reveal that the interaction between the sodium cation and the *o, o′*-derivative anion is much weaker than that between the sodium cation and the dimethyl *o*-phthalate anion.[2] In analogy with the *o*-phthalate-alkali metal system,[2] a potassium splitting of about 0.08 gauss may be expected in the present case; however,

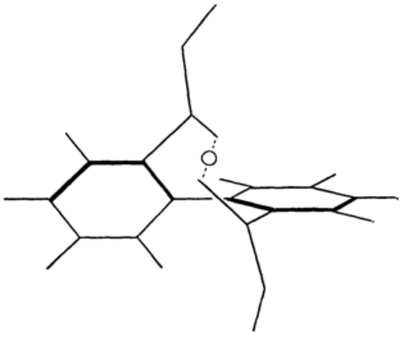

Fig. 9. A proposed structure of the ion complex between the alkali metal cation and the *o, o′*-derivative anion.
○··· The alkali metal cation.

it could not be observed because it would be covered by the large line-width.

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 through the course of this work. He is also indebted to Mrs. Masako Azumi for the synthesis of some of the samples.