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ESR Study of the Ion Pairs of the Phthalonitrile Anion with Alkali Metals

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From the ESR spectroscopic point of view, there are two distinct species of ion pairs of the phthalonitrile anion with the lithium ion in ethereal solvents. One corresponds to the locating of the cation in close proximity to a cyano group. Its ESR spectrum exhibits the loss of twofold symmetry in the spin distribution on the anion (spectrum I) or an alternating line width (spectrum II), depending on the transfer rate of the cation between the two cyano groups. The other species refers to the locating of the cation probably in the spacing between the two cyano groups. The appearance of its spectrum (spectrum III) is similar to that of the free anion. The DME or THF solution gives spectrum II; the ethyl ether solution, spectrum III, and the THP or MeTHF solution, the superposition of spectrum I or II upon III. A similar two species are found in the sodium ion pair. The negative spin density at the meta-carbon atom to the cyano group where the cation is located has been found. The solvent and the temperature effects on the alkali metal splittings, a semi-quantitative treatment of the alternating line width, and the variations in the proton and nitrogen coupling constants are also described.

In a previous paper1) (hereafter referred to Paper I), it was described that, when the alkali metal cation formed an ion pair with the terephthalonitrile anion, the cation was transferred between two cyano groups, and in what manner the transfer rate of the cation depends on the solvent, the temperature, and the species of cation. In an earlier stage of studying the cation-anion interaction of the phthalonitrile-alkali metal system, we reproted the finding of the sodium hyperfine lines.2) The further study of this system displayed many interesting features of cation-anion interaction.

Some of them were similar to the observations of the terephthalonitrile-alkali metal system, but others were unique in exhibiting the effect of the close proximity of a pair of cyano groups.

In the present paper, emphasis has been placed on this ortho-effect.

Experimental

Unless otherwise stated, the apparatus and materials used in this work were the same as those described in Paper I. Phthalonitrile was a commercial product; it was used without further purification.

Results and Discussion

The Existence of Two Species of Ion Pairs. From the ESR spectroscopic point of view, there exist two species of ion pairs of the phthalonitrile anion with lithium or sodium ions: the species are distinguished by the relative location of the cation to the anion.

When phthalonitrile was reduced with lithium, depending on the solvent and the temperature three types of spectra were obtained; those spectra arose from the lithium ion pairs. Two of them (spectra I and II) were attributed to the same species of the ion pair, in which the lithium ion was transferred back and forth between the two cyano groups; these two types of spectra were similar in nature to the corresponding spectra of the terephalonitrile ion pair reported in Paper I. The other (spectrum III) was unique in suggesting a possible location of the lithium ion other than in "the proximity of either of the two cyano groups."

The characteristic features of each type are as follows.

Spectrum I. This denoted the spectrum exhibiting the localization of the lithium ion at a cyano group. Since this localization resulted in the loss of the twofold symmetry in the spin distribution on the anion, the spectrum was interpreted in terms of four proton coupling constants and two nitrogen coupling constants. An example of this spectrum is presented in Figs. 1(a) and (b), the spectrum of the MeTHF solution at −40°C and the corresponding reconstruction respectively.

Spectrum II. This denoted the spectrum exhibiting an alternating line width, corresponding to the transfer rate of the lithium ion being in the range of $t \fallingdotseq |\gamma(a_{1'}-a_{1''})|^{-1}$, $\fallingdotseq |\gamma(a_{2'}-a_{2''})|^{-1}$ or

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1) K. Nakamura, This Bulletin, to be published.

2) K. Nakamura and Y. Deguchi, *ibid.*, **36**, 359 (1963).

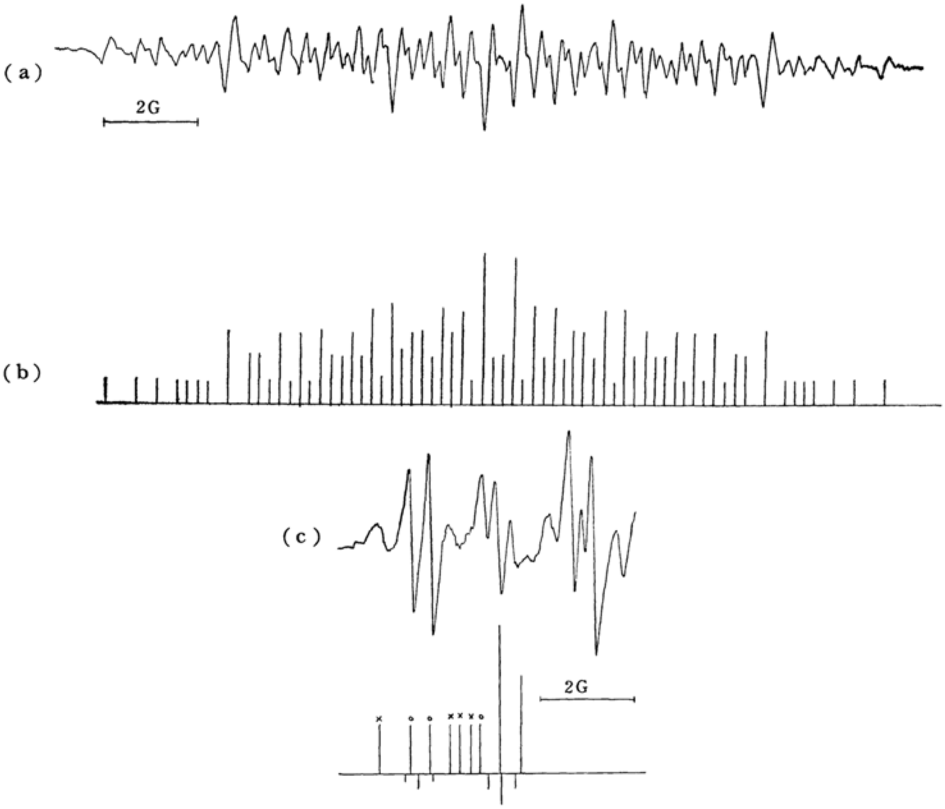


Fig. 1. The phthalonitrile-lithium system in MeTHF.
(a) The ESR spectrum at −40°C (spectrum I).
(b) The reconstruction corresponding to (a).
(c) The low-field end part at 20°C, and its reconstruction (the superposition of spectra I and III).
In (c), the upper and the lower parts of the reconstruction express spectra I and III, respectively.
× : lines for ($M_{2'}=+1$, $M_{2''}=-1$) or ($M_{2'}=-1$, $M_{2''}=+1$), which disappear when the spectrum varies from spectra I to II.
○ : lines for ($M_{1'}=+1$, $M_{2''}=+1$) or ($M_{2'}=-1$, $M_{2''}=-1$), which remain unchanged in spectrum II.

TABLE 1. THE COUPLING CONSTANTS OF THE PHTHALONITRILE ANION

Specie	Type of spectrum	Absolute value of coupling constant (in gauss)					Δg (×10^5)
		a_1		a_2		a_N	
Free anion		4.165		0.385		1.715	0
Potassium ion pair		4.035		0.357		1.726	−3
Sodium ion pair	(II)	4.013		0.323		1.743	−4.5
	(III)	4.013		0.323		1.743	−4.0
Lithium ion pair	(II)	3.995		0.210*		1.730	−6.5
	(III)	3.995		0.295		1.754	−6.0
	(I)	$a_{1'}$	$a_{1''}$	$a_{2'}$	$a_{2''}$	a_{N1}	a_{N2}
		5.42	2.57	1.08	0.66	1.94	1.51

The signs of proton coupling constants are assumed to be negative with exception of that of 2′′-proton, and those of nitrogen coupling constants to be positive.
a_1, $a_{1'}$, $a_{1''}$, *etc.*: see (I).
Δg: g(the ion pair) − g(the free anion). The g value of the free anion = 2.0026.
* This value varies with the solvent and the temperature. The one in THP at 20°C is listed here (see Table 3).

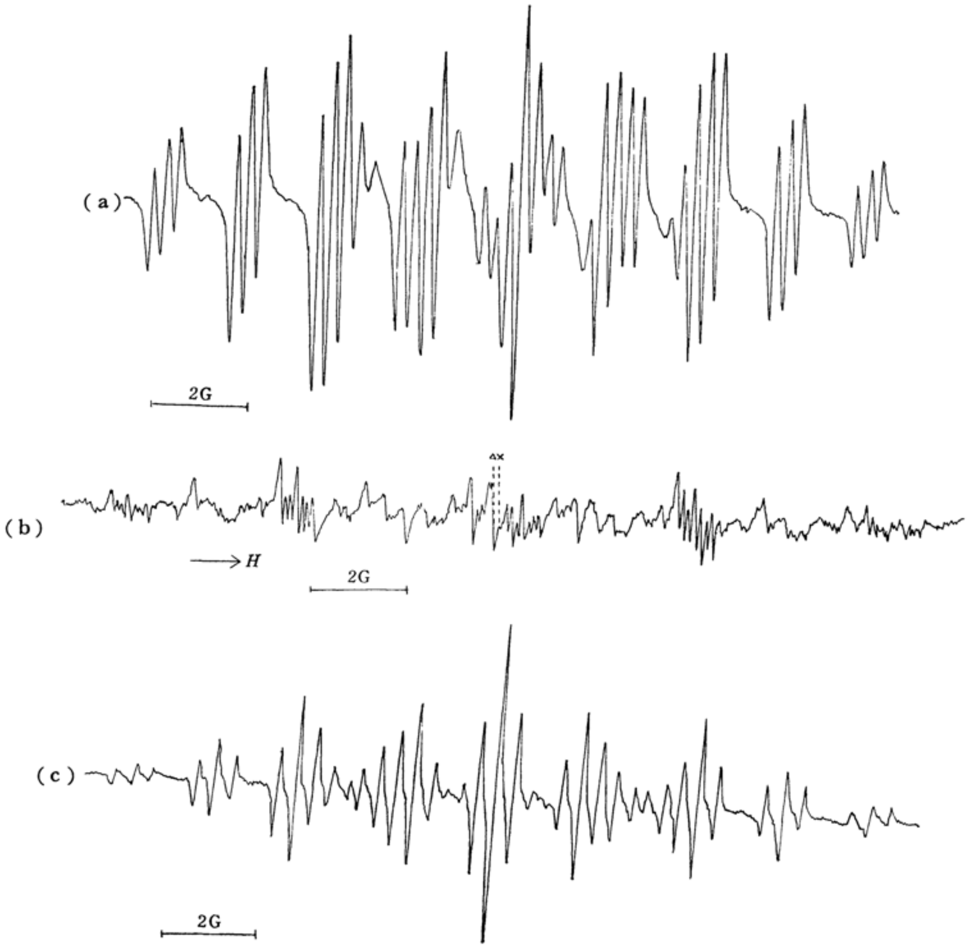


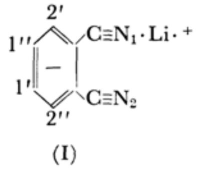
Fig. 2. The ESR spectra of the phthalonitrile-lithium system in DME.
(a) at 20°C (spectrum II).
(b) at −50°C (the superposition of spectrum II and the one of the free anion).
(c) at −80°C (the free anion).
In (b), the intensity ratio of spectrum II to the spectrum of the free anion is about 4, and several lines for $M_N=0$ or ±1 are splitted into four due to the lithium hyperfine interaction.
×: the center of spectrum II.
△: the center of the spectrum of the free anion.

$\doteqdot|\gamma(a_{N1}-a_{N2})|^{-1}$, where t is equal to a duration of the stay of the lithium ion in the proximity of the same cyano group. Examples are shown in Figs. 2(a) and 3(a) and (b), the spectra of the DME solution at 20°C and of the THF solution at 20°C and −70°C respectively. In comparison with the spectrum of the free anion in Fig. 2(c), these spectra clearly displayed decreases in the amplitudes of the particular lines.

Spectrum III. As is shown in Fig. 4, the spectrum of ethyl ether solution is similar in appearance to the spectrum of the free anion. The coupling constants and the g value obtained from this type. however, displayed a marked departure from those of the free anion, being near those of spectrum II.

The coupling constants and g values obtained from these spectra are listed in Table 1 (see (I)), while the solvent dependence of each type is presented in Table 2.

As Table 2 indicates, the spectrum in MeTHF or THP consists of a superposition of spectrum I or II upon III. Examples of such superposed spectra are presented in Figs. 1(c) and 5. The coexistence of the well-defined spectra gives evidence



(I)

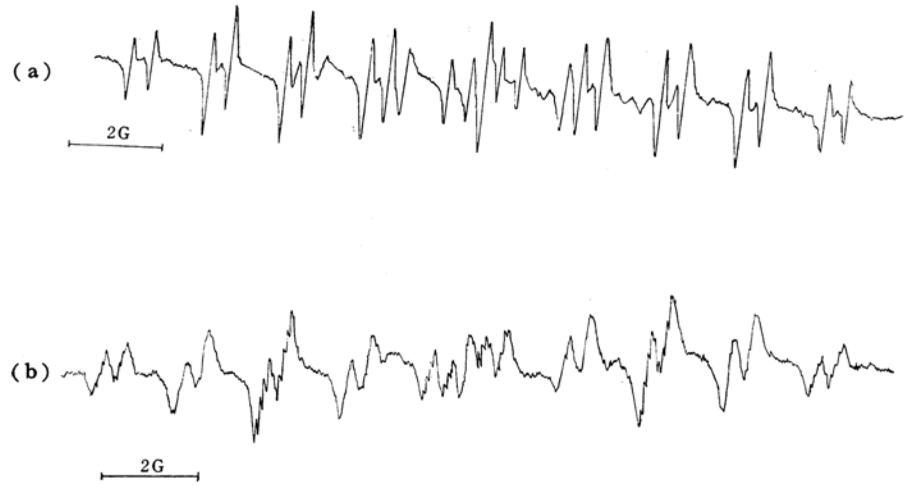


Fig. 3. The ESR spectrum of the phthalonitrile-lithium ion pair in THF (spectrum II).
(a) at 20°C. (b) at −70°C.

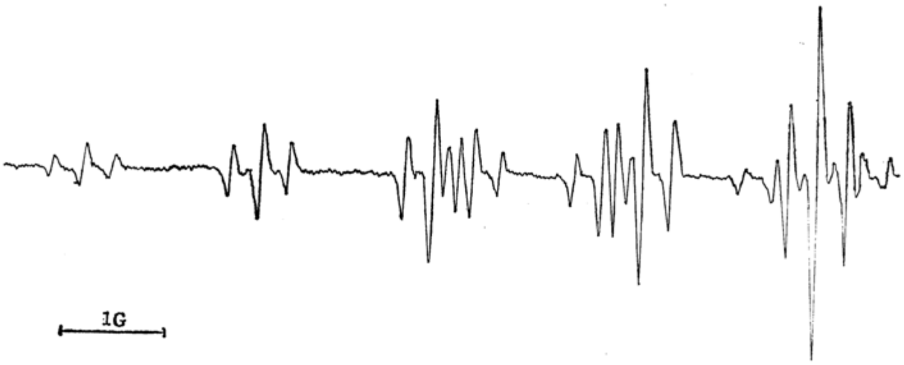


Fig. 4. The ESR spectrum of the phthalonitrile-lithium ion pair in ethyl ether at 20°C (spectrum III).

Table 2. Solvent dependences of spectra I, II and III at 20°C

Solvent	Types of spectra	
	lithium ion pair	sodium ion pair
DME	II (F)	II (F)
THF	II	II
THP	II+III (I+III)	II+III
MeTHF	I+III (I)	II+III
Ethyl ether	III	III

The sign, +, denotes the superposition of two types of spectra.
Parentheses show types of spectra at a lower temperature.
F denotes the spectrum of the free anion, which is obtained at a temperature lower than −50°C. The dissociation was observed only in DME.

to confirm the assumption that the ion pair exhibiting spectrum III is different from one exhibiting spectrum I or II. The intensity of spectrum III in the superposed spectrum diminishes with a lowering of the temperature.

Two types of the spectra arising from the sodium ion pairs were also observed. One exhibited the sodium hyperfine lines, and the other did not. No alternating line width was observed with them. This made it difficult to relate these spectra to the type found in the lithium ion pairs. However, when the spectrum with sodium hyperfine lines was assigned to spectrum II, and the one without sodium hyperfine lines, to spectrum III, then there existed a correct parallelism between the solvent effects on the spectra of the lithium ion pairs and of the sodium ion pairs, as is shown in Table 2. This assignment implies that the spectrum with sodium hyperfine lines corresponds to the limit of the fast transfer of the sodium ion between two cyano groups. Figures 6, 7 and 8 represent spectrum II in THF, spectrum III in a 1 : 1 mixture of THP and ethyl ether, and the superposed spectrum in THP respectively. Contrary to the case with the lithium ion pair, the

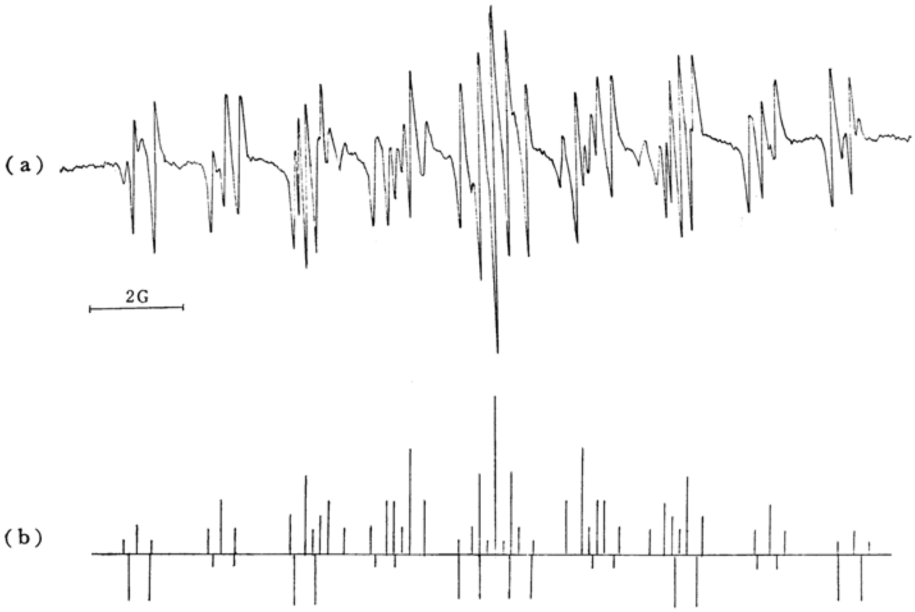


Fig. 5. (a) The ESR spectrum of the phthalonitrile-lithium ion pair in THP at 20°C (the superposition of spectra II and III).
(b) The reconstruction corresponding to (a).
In (b), the upper and lower parts represent spectra III and II, respectively, with the intensity ratio estimated from (a).

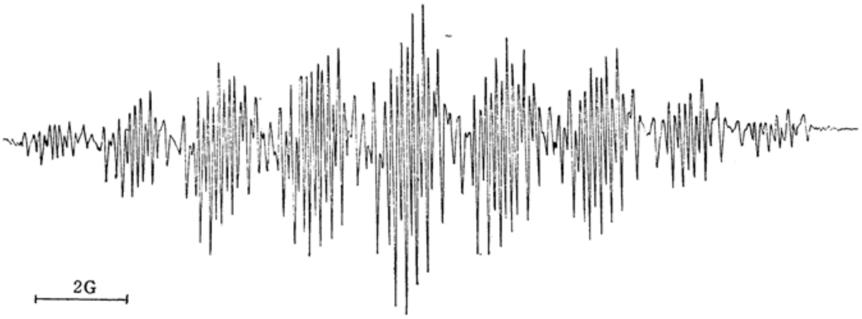


Fig. 6. The ESR spectrum of the phthalonitrile-sodium ion pair in THF at −40°C (spectrum II).

intensity of spectrum III in the superposed spectrum seemed to slightly increase with a lowering of the temperature.

The Sign of 2''-Proton Coupling Constant. Among the coupling constants listed in Table 1, one thing to be explained is the sign of the 2''-proton coupling constant. When the transfer rate of the lithium ion increased, the four proton splitting (5.42, 2.56, 1.08 and 0.66 gauss) for spectrum I were averaged into two pair proton splittings (3.99 and 2.10 gauss) for spectrum II. The relations were $(5.42+2.56)/2=3.99$ and $(1.08-0.66)/2=0.210$ (in gauss). The latter relation led to the conclusion that the sign of 0.66 gauss was inverse to those of 1.08 and 0.210 gauss.

The valence bond or C. I. molecular orbital treatment has shown that the effect of a strong electron-attracting group linking to the benzene ring was to induce a negative spin density at the meta carbon atom to that group. Further, Schug *et al.*[3] showed that the spin distribution on the benzene derivative linked by two strong electron-attracting groups was approximately explained in terms of the superposition of the effects of these two groups. This treatment of the phthalonitrile anion predicted the spin densities at 2-carbon atom would be positive.[3] In the present case, the localization of the lithium ion at a cyano group will increase its electron-attracting ability, resulting in an increased negative spin density at the meta carbon atom (the 2''-carbon atom in

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[3] J. C. Shug, T. H. Brown and M. Karplus, *J. Chem. Phys.*, **37**, 330 (1962).

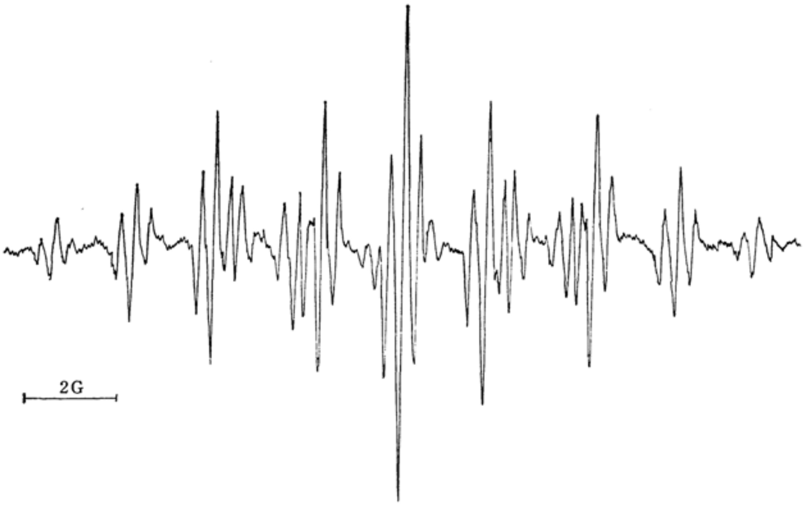

Fig. 7. The ESR spectrum of the phthalonitrile-sodium ion pair in a 1 : 1 mixture of THP and ethyl ether at 20°C (spectrum III).

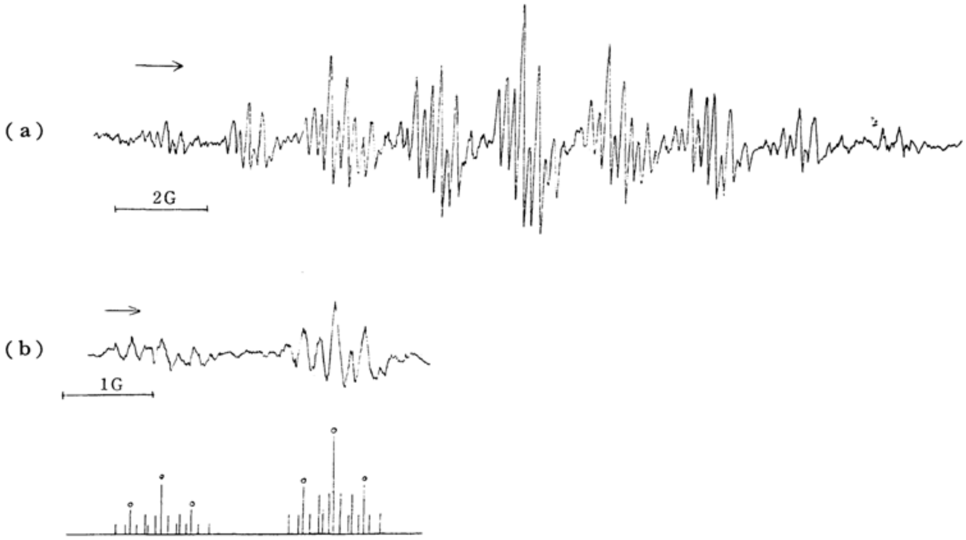

Fig. 8. (a) The ESR spectrum of the phthalonitrile-sodium ion pair in THP at −5°C.
(b) An enlargement of the left-end two groups in (a), and its reconstruction.
○ : Lines from spectrum III. Other lines represent those from spectrum II.

I). Although the effect on the other cyano group tends to produce a positive spin density at the same atom, there is a possibility that the superposition of the effects of the two cyano groups leaves a negative spin density at the 2′′-carbon atom. Thus, in the scope of the superposition model, it will be reasonable to conclude that the sign of 0.66 gauss is positive; this is assigned to 2′′-carbon atom. On the other hand, the Mclachlan treatment of the phthalonitrile anion by Rieger and Fraenkel showed the spin densities at 2-carbon atoms to be negative.[4] Therefore, some uncertainty remains as to the above conclusion.

The comparision between spectra I and II offered additional evidence for an inversion of the sign between the 2′- and 2′′-proton coupling constants. When the spectrum varied from spectrum I to II, of the quartet with equal intensities arising from the 2′- and 2′′-protons in spectrum I, the outer two lines disappeared, but the inner two remained unchanged to compose the side lines of the triplet arising from two 2-protons in spectrum II. The same sign of the two proton coupling constants will lead the to disappearance of the inner two lines (see Fig. 9).

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[4] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1963).

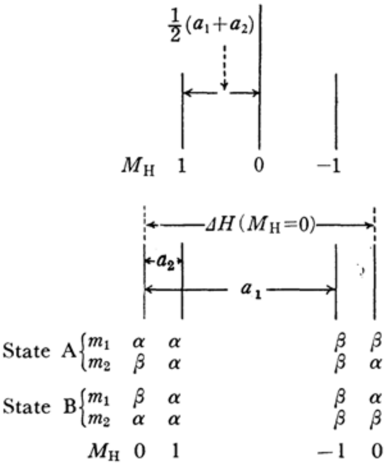

Fig. 9. Schematic spectra for two protons with opposite signs, where a system jumps between two states A and B. The upper spectrum is applied to the limit of short life-time at each state, and the lower spectrum to the limit of long life-time. In state A, proton 1 has hyperfine coupling constant a_1 (negative) and proton 2 has a_2 (positive). In state B, the hyperfine coupling constants are interchanged.

The Variation in the 2-Proton Coupling Constant. As is listed in Table 1, the coupling constants of the protons and the nitrogens varied with the counter cation, and sometimes with the solvent and the temperature.

Among these variations, the observation of the 2-proton coupling constant a_2 was of interest. The a_2 obtained from the sodium ion pair was the same as that spectra II and III, independent of the solvent, and the temperature.

As to the lithium ion pair, however, $|a_2|$ markedly decreased from spectrum III to II. Eurthermore, the $|a_2|$ obtained from spectrum II itself varied with the solvent and the temperature, as is shown in Table 3. At 20°C, the $|a_2|$ obtained from spectrum II decreased in the order, DME>THF>THP, and the value in the THP was equal to the $|(a_{2\cdot}+a_{2\,\cdot})/2|$ from spectrum I. When, with lowering of the temperature, the transfer rate of the lithium ion in DME or THF decreased, approaching that in THP at 20°C, a similar approach of $|a_2|$ was observed. Thus, there will be a close relation between the value of $|a_2|$ and the transfer rate.

TABLE 3. SOLVENT AND TEMPERATURE DEPENDENCES OF THE 2-PROTON COUPLING CONSTANT (a_2) IN SPECTRUM II OF THE LITHIUM ION-PAIR

Solvent	Coupling constant (in gauss)			
	20°C	−25°C	−60°C	−80°C
DME	0.265	0.245	0.220	0.210
THF	0.245	0.220	0.210	0.210
THP	0.210			

When, in the process of the transfer of the lithium ion between the two cyano groups, the staying time at a transition state is comparable in order to that at a cyano group, such a variation of a_2 will take place. However, the fact that the present alternating line width could be well explained by the two-jump model seemed to negate this mechanism. Another possible mechanism is to assume that the equilibrium location of the lithium ion in the proximity of a cyano group varied wtih the temperature and the solvent. The solvent and the temperature effects on the alkali metal splittings seemed to support this mechanism. The equilibrium location of the lithium ion for spectrum I or II will not be the same as that of the sodium ion.

The Lithium and the Sodium Coupling Constants. The temperature and the solvent effects on the lithium and the sodium coupling constants were unusual, as is illustrated in Fig. 10.

The sodium and the lithium coupling constants obtained from spectrum II decreased in the order: DME>THF>THP or MeTHF at the same temperature. This order of solvents is contrary to the observation in most cases. As the temperature was lowered, the sodium coupling constant decreased, but the lithium constant was increased. Such solvent and temperature dependences have

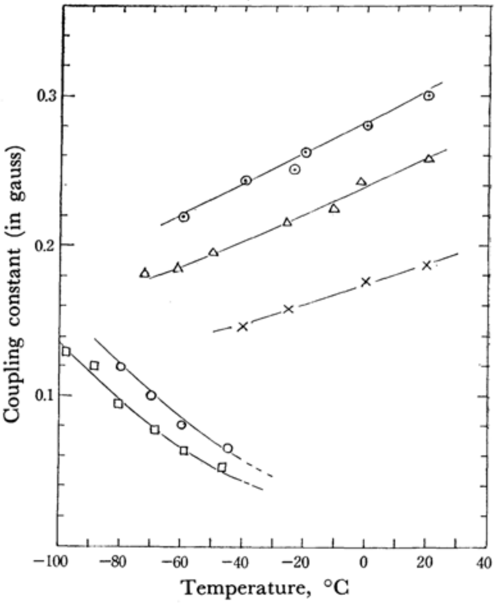

Fig. 10. Temperature and solvent dependences of the sodium and the lithium coupling constants in spectrum II.
○: lithium in DME □: lithium in THF
⊙: sodium in DME △: sodium in THF
×: sodium in THP

TABLE 4. ΔH FOR EACH NUCLEAR SPIN STATE

Line	$\lvert M_1 \rvert$	$\lvert M_N \rvert$	$\lvert M_2 \rvert$	ΔH	$(\Delta H)^2$	Number of state
1	1	2	1	0	0	1
2	1	2	0	Δa_2	3.03	2
3	1	1	1	Δa_N	0.19	2
4	1	1	0	$\Delta a_2+\Delta a_N$	1.72	2
				$\Delta a_2-\Delta a_N$	4.71	2
5	1	0	1	0	0	1
				$2\Delta a_N$	0.74	2
6	1	0	0	$\Delta a_2+2\Delta a_N$	0.77	2
				Δa_2	3.03	2
				$\Delta a_2-2\Delta a_N$	6.76	2
7	0	2	1	Δa_1	8.12	2
8	0	2	0	$\Delta a_1-\Delta a_2$	1.23	2
				$\Delta a_1+\Delta a_2$	21.1	2
9	0	1	1	$\Delta a_1+\Delta a_N$	5.86	2
				$\Delta a_1-\Delta a_N$	10.8	2
10	0	1	0	$\Delta a_1-\Delta a_2+\Delta a_N$	0.46	2
				$\Delta a_1-\Delta a_2-\Delta a_N$	2.37	2
				$\Delta a_1+\Delta a_2+\Delta a_N$	17.3	2
				$\Delta a_1+\Delta a_2-\Delta a_N$	25.2	2
11	0	0	1	$\Delta a_1+2\Delta a_N$	3.96	2
				Δa_1	8.12	2
				$\Delta a_1-2\Delta a_N$	13.8	2
12	0	0	0	$\Delta a_1-\Delta a_2+2\Delta a_N$	0.06	2
				$\Delta a_1-\Delta a_2$	1.23	2
				$\Delta a_1-\Delta a_2-2\Delta a_N$	3.88	2
				$\Delta a_1+\Delta a_2+2\Delta a_N$	13.9	2
				$\Delta a_1+\Delta a_2$	21.0	2
				$\Delta a_1+\Delta a_2-2\Delta a_N$	29.7	2

M_1, M_2 and M_N: the sum of nuclear magnetic quantum numbers of two 1-protons and so on.
$\Delta a_1=a_{1'}-a_{1''}=-2.85$ gauss. $\Delta a_2=a_{2'}-a_{2''}=-1.74$ gauss. $\Delta a_N=a_{N1}-a_{N2}=+0.43$ gauss.

been found only in the mononitrobenzene derivative-alkali metal system.[5]

Spectra I and III did not exhibit any alkali metal hyperfine lines, except for spectrum III in the ethyl ether solution of the lithium ion pair lower than −70°C, a phenomenon which has not yet been completely interpreted.

The Relative Location of the Cation. Recently the existence of two species of the ion pairs, the contacting and the solvent-separated pairs, in the solution of the carbanion has been established by means of electronic spectroscopy and conductmetry.[6] This conception is not applicable to the present case, because one usually observes by ESR spectroscopy an averaged state of the contact and the solvent-separated ion pairs on account of a rapid exchange rate (probably greater than 10^{10} sec^{-1}) between these species.[6,7] (The present two species will essentially belong to the contacting ion pair.) Thus, in this case, we should be able to distinguish the species by means of the location of the cation relative to the anion, and the exchange rate of the cation between two locations will be small (less than 10^5 sec^{-1} from the line width).

As to the location of the cation for spectrum III, since the absence of spectrum III in the terephthalonitrile ion pair excludes the possibility of the cation existing above the benzene ring, it may be reasonable to assign the location of the cation to the spacing between the in-plane p-orbitals of the two nitrogen atoms. This assignment is supported by the fact, shown in Table 2, that spectrum III was observed in the solvents with less solvating ability for the cation.

Although the location of the cation for spectrum I or II has been approximately determined to be somewhere in the proximity of a cyano group, a more precise assignment needs a definite interpretation of the following experimental results: (1) the other temperature dependences between the lithium and sodium splittings; (2) the anomaly of the solvent effect on alkali metal splittings; (3) only the lithium ion pair exhibited a difference in the proton and the nitrogen coupling constants between spectra II and III, the solvent- and temperature-variations of the 2-proton coupling constant for spectrum II, and the alternating line width.

These results suggest that the interaction of the lithium ion with the cyano group is markedly different in nature from that of the sodium ion,

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[5] K. Nakamura, This Bulletin, **40**, 1 (1967).
[6] T. E. Hogen-Esch and S. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966).
[7] N. Hirota and R. Kreilick, *ibid.*, **88**, 614 (1966).

TABLE 5. A/S ON LINE-WIDTH ALTERNATION IN THE LITHIUM ION-PAIR

Line	In DME						In THF			
	20°C		−15°C		−50°C		20°C		−70°C	
	Ob.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1	1	1	1	1	1	1	1	1	1	1
2	(0.55)	(0.55)	(0.32)	(0.32)	*	0.07	*	0.07	*	0.01
3	1	0.96	1	0.92	(0.68)	(0.68)	(0.73)	(0.73)	(0.47)	(0.47)
4	0.55	0.56	0.36	0·35	*	0.07	*	0.09	*	0.02
5	0.96	0.89	0.91	0.83	0.56	0.53	0.51	0.57	0.38	0.42
6	0.58	0.57	0.41	0.39	*	0.12	0.06	0.15	*	0.04
7	0.17	0.27	*	0.11	*	<0.01	*	0.01	*	<0.01
8	0.35	0.42	0.26	0.30	*	0.09	0.06	0.11	*	0.03
9	0.17	0.29	*	0.12	*	0.01	*	0.02	*	<0.01
10	0.41	0.42	0.34	0.31	0.06	0.13	0.13	0.18	*	0.06
11	0.20	0.29	0.08	0.13	*	0.02	*	0.02	*	<0.01
12	0.41	0.44	0.37	0.32	0.15	0.18	0.18	0.20	0.08	0.14
W_{max} of line 1(in gauss)	0.09		0.10		0.26		0.09		0.28	

* Unobserved.

w_{max}: a peak-to-peak line width. An increase of w_{max} is due to the lithium hyperfine interaction.

Figures represent the value of A/S, where A is an amplitude relative to line 1, and S a statistical weight.

The figure in the parentheses of each column corresponds to X_s in Eq. (4).

and that the equilibrium location of the cation in the proximity of a cyano group will shift with the temperature, the solvent, and the species of the cation. No complete interpretation, however, has not been formulated.

The Alternating Line Width. The details of the alternating line width of the present system are expressed by the A/S value for each line, as is given in Table 5, where A is the amplitude relative to line 1 in the same table, and S a statistical weight. These data indicate that the present alternating line width is much more complex than those published so far.[8-13] It will be necessary to deal with this system from a quantitative point of view.

As has been described in Paper I, an increase in a line width paprameter due to the transfer of the cation between two sites is given by:

$$\Delta T_2^{-1} = \frac{1}{8}\gamma t(\Delta H)^2, \qquad \text{(in gauss)} \quad (1)$$

where ΔH is a shift of the resonance field for a particular spin state due to the transfer of the cation. The ΔH for the phthalonitrile anion is equal to:

$$\Delta H = \{(M_{1'} - M_{1''})\Delta a_1 + (M_{2'} - M_{2''})\Delta a_2 + (M_{\mathrm{N}1} - M_{\mathrm{N}2})\Delta a_{\mathrm{N}}\}, \quad (2)$$

where $M_{1'}$ is the nuclear magnetic quantum number of the 1′-proton, and so on. $\Delta a_1 = a_{1'} - a_{1''} = -2.85$ gauss, $\Delta a_2 = a_{2'} - a_{2''} = -1.74$ gauss, and $\Delta a_{\mathrm{N}} = a_{\mathrm{N}1} - a_{\mathrm{N}2} = 0.43$ gauss. ΔH in terms of Δa_1, Δa_2 and Δa_{N} and the numerical values of $(\Delta H)^2$ are given for each nuclear spin state in Table 4. The use of these values led to the present alternating line-width according to the following procedure:

When a line shape is assumed to be Lorentzian and the r and s lines to be composed of spin states of which the ΔH values are the same for the respective lines, the X_r of line r is expressed by:

$$X_r = \frac{1}{\left\{1 + \frac{1}{8}\gamma t T_2 (\Delta H_r)^2\right\}^2} \quad (3)$$

using Eq. (1) and the relations, $(\text{intensity})_1 \propto (T_2^{-1})^{-1}$ and $(\text{intensity})_r \propto (T_2^{-1} + \Delta T_2^{-1})^{-2}$, where X denotes A/S, the undersuffix 1 denotes line 1 in Table 4, and T_2^{-1} is the line-width parameter of the line 1. If the value of X_s for line s is known, Eq. (3) becomes:

$$X_r = \frac{1}{\left\{1 + \left(\frac{1}{\sqrt{X_s}} - 1\right)\left(\frac{\Delta H_r}{\Delta H_s}\right)^2\right\}^2} \quad (4)$$

on eliminating $\gamma t T_2$ from Eq. (3) and the similar expression for X_s.

When line r is composed of spin states with different ΔH values ($\Delta H_{r'}$, $\Delta H_{r''}$ and so on), the use of these values for ΔH_r in Eq. (4) leads

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to X_r, $X_{r''}$ and so on. The approximate X_r value for line r is given by:

$$X_r = \frac{S_{r'}X_{'} + S_{r''}X_{r''} + \cdots}{S_r}, \tag{5}$$

where $S_{r'}$ is a degeneracy of spin states with $\Delta H_{r'}$ and so on, and where S_r is equal to $S_{r'}+S_{r''}+\cdots$. As is shown in Table 5, the calculation using Eqs. (4) and (5) essentially accords with the observation, in spite of a rather rough approximation. Thus, the present alternating linewidth can be explained by the two-jump model.

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