

[CONTRIBUTION FROM THE KONINKLIJKE/SHELL-LABORATORIUM AMSTERDAM (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.)]

## Line Width Alternation in the Electron Spin Resonance Spectrum of the Alkali Radical-Ion Complex of Pyracene

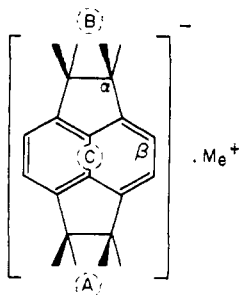
BY E. DE BOER AND E. L. MACKOR

RECEIVED APRIL 1, 1963

The e.s.r. spectra of the ion pair of the negative ion of pyracene and the positive alkali ion taken in solvents of various ion associating power reveal changes in the spin density distribution caused by electric fields and an alternating line broadening, caused by an intramolecular exchange reaction. This alternating effect arises from relaxation processes, set off by the movement of the cation, which introduces time-dependent modulations in the isotropic coupling constants.

### I. Introduction

Maki and Geske<sup>1</sup> investigated the e.s.r. spectrum of the *p*-nitrobenzaldehyde anion. They observed that the isotropic coupling constants of the two protons *ortho* to the nitro group were different and attributed this effect to a restricted rotation of the aldehyde group about the C-C bond. Maki<sup>2</sup> obtained additional evidence for this interpretation by studying the terephthalic aldehyde anion. An e.s.r. spectrum was found corresponding to an equilibrium mixture of the *cis* and *trans* modifications of the ion. Bolton, Carrington, and Todd<sup>3</sup> found that the hindered rotation of the OH groups in the durosemiquinone cation and in the naphthazarin semiquinone cation causes a marked line-width alternation in the hyperfine pattern. Recently, similar observations were reported by Fraenkel, *et al.*,<sup>4</sup> for the negative ions of dinitrodurene and *m*-dinitrobenzene. We have observed a similar line-width alternation effect in the e.s.r. spectrum of the alkali-pyracene radical ion.<sup>5</sup>



The interpretation of the line width alternation in the spectrum of this ion differs from the explanation given for the hitherto published findings. In the present case the alternation is not caused by rotating groups, covalently bonded to the radical ion, but by the movement of the associated counter ions. The motion of the cation between two positions in the negative ion introduces time-dependent modulations in the isotropic coupling constants, giving rise to additional relaxation mechanisms. The experiments will show that the kinetic process responsible for the line-width alternation is intramolecular, rather than intermolecular.

### II. Experimental

The solvents were purified and the solutions prepared in the usual way.<sup>6,7</sup> Li, Na, and K were the alkali metals used. Below

- (1) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).
- (2) A. H. Maki, *J. Chem. Phys.*, **35**, 761 (1961).
- (3) J. R. Bolton and A. Carrington, *Mol. Phys.*, **5**, 161 (1962); A. Carrington, *ibid.*, **5**, 425 (1962); J. R. Bolton, A. Carrington, and P. F. Todd, *ibid.*, **6**, 169 (1963).
- (4) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1156 (1962); J. H. Freed, Ph. H. Rieger, and G. K. Fraenkel, *ibid.*, **37**, 1879 (1962); J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962).
- (5) E. de Boer and E. L. Mackor, *Proc. Chem. Soc.*, 23 (1963).
- (6) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).
- (7) P. Balk, G. J. Hoijsink, and J. W. H. Schreurs, *Rec. trav. chim.*, **76**, 813 (1957).

a temperature of  $-30^{\circ}$  stable paramagnetic yellow solutions were formed. Raising the temperature of the solutions from  $-30$  to  $0^{\circ}$  caused decay of the e.s.r. signal and a simultaneous color change to yellow-brown. The transformation occurred rapidly above  $0^{\circ}$ . Decomposition was most rapid for the potassium complex.

E.s.r. spectra were recorded on the Varian V-4501 spectrometer, operating at 9500 Mc./sec. and using high-frequency modulation (100 kc./sec.). A Varian high-resolution 12-in. magnet was used. Samples were kept at low temperatures with the aid of the Varian V-4547 variable temperature accessory.

### III. Results and Discussion

The phenomena described in the first section are dependent on the properties of the solvent and on the alkali metals used. Therefore it seems useful to summarize briefly the factors governing the behavior of alkali-hydrocarbon complexes in solutions. Aten, Dieleman, and Hoijsink<sup>8</sup> have discussed ion pair formation in relation to solvation, radius of the counter ion, and temperature in connection with a study of electron-transfer reactions. From their observations they conclude that the absolute value of the free enthalpy of solvation increases with increasing dielectric constant and with decreasing radii of the ions. Owing to the negative temperature coefficient of the dielectric constant, the solvation becomes stronger at lower temperatures. The formation of ion pairs increases with increasing radius of metal ion, with decreasing dielectric constant, and, consequently, with increasing temperature.

The solvents used in our experiments were 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (2-MeTHF). Ion pair formation was strongest in 2-MeTHF, which has the lowest dielectric constant ( $D = 4.63^9$ ). The dielectric constants of DME and THF are almost equal ( $\sim 6.0^9$ ). It appeared that in DME, sodium-pyracene is completely dissociated into ions, whereas in THF ion pairing occurred. The geometrical structure of DME is probably more favorable for solvation of ions than that of THF. In accordance with the above rules the formation of ion pairs in the alkali-pyracene systems depends on the counter ions; it increases in the order  $\text{Li} < \text{Na} < \text{K}$ .

**The Hyperfine Pattern of Pyracene in 1,2-Dimethoxyethane (DME).**—No association with Li, Na, and K has been observed in DME. Figure 1 shows the hyperfine pattern of the "free" ion in DME at  $-70^{\circ}$  with K as gegenion. The splitting pattern arises from interaction with two sets of equivalent protons, *viz.*, the eight aliphatic protons ( $\alpha$ -protons) and the four aromatic protons ( $\beta$ -protons). The magnitudes and signs of the coupling constants are given in Table I.

The small peaks between the main proton lines are caused by  $\text{C}^{13}$  present in natural abundance.

**The Spectrum of the Sodium Complex in 2-Methyltetrahydrofuran (2MeTHF).**—In 2MeTHF strong ion

(8) A. C. Aten, J. Dieleman, and G. J. Hoijsink, *Discussions Faraday Soc.*, **29**, 182 (1960).

(9) J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 4767 (1959).

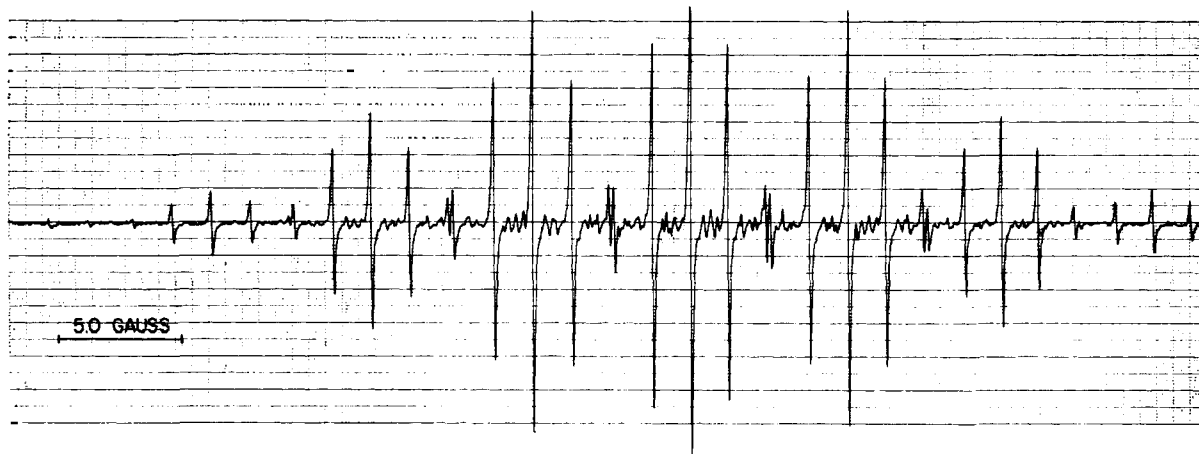


Fig. 1.— $-d\chi''/dH$  vs.  $H$  for pyracene<sup>-</sup> in dimethoxyethane, at  $-70^\circ$ , K as cation.

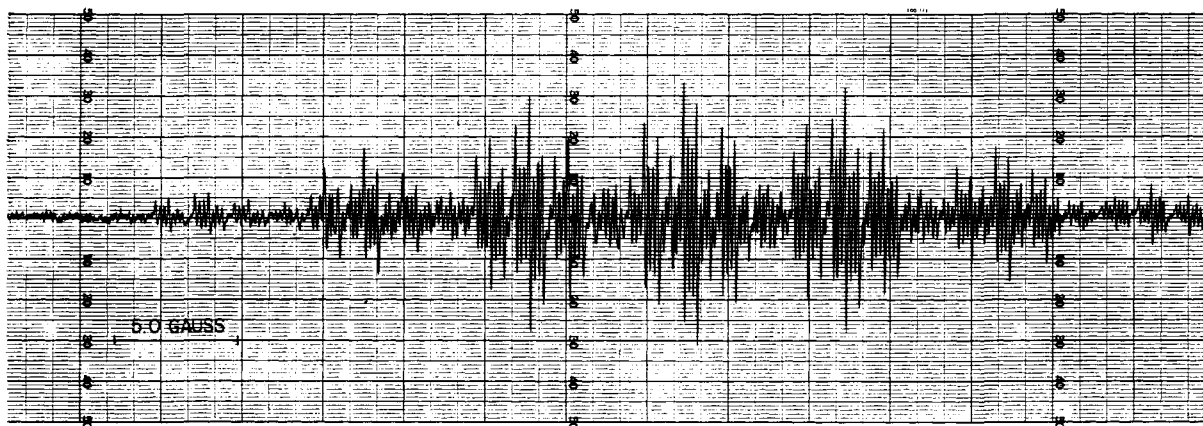


Fig. 2.— $-d\chi''/dH$  vs.  $H$  for the ion pair formed by the sodium ion and the pyracene ion in 2-methyltetrahydrofuran at  $-83^\circ$ .

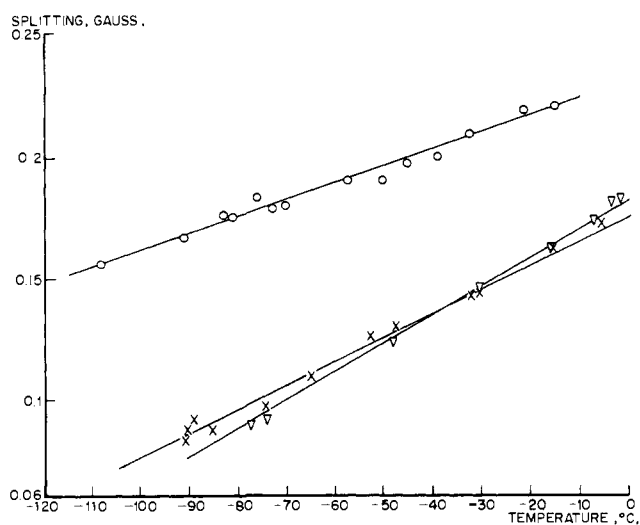


Fig. 3.—Alkali hyperfine splittings ( $a$ ) vs. temperature:  $\Delta$ ,  $a_{Na}$  in tetrahydrofuran;  $\times$ ,  $a_K$  in tetrahydrofuran;  $O$ ,  $a_{Na}$  in 2-methyltetrahydrofuran.

association occurs<sup>10</sup> and accordingly the observed spectrum is quite different in shape from that of the free ion in DME. Besides the sodium splitting ( $I = 3/2$ ) the spectrum (Fig. 2) shows another interesting feature: the eight aliphatic protons are no longer equivalent. Owing to the close vicinity of the counter ion two distinct aliphatic coupling constants appear ( $a_{\alpha,1}$  and  $a_{\alpha,2}$ ). With the set of splitting constants

(10) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961).

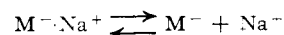
given in Table I the experimental spectrum is closely matched.

	Pyracene			Naphthalene	
	DME, $-70^\circ$	2MeTHF, $-80^\circ$	THF, $-30^\circ$	2MeTHF, $+27^\circ$	THF, $+27^\circ$
$a_\alpha$	+6.58	+6.93	+6.65 (+6.37)		
$a_\beta$	-1.58	-1.63	-1.63	-1.865 <sup>b</sup>	-1.865 <sup>b</sup>
$ a_{Na} $	...	0.176	0.146	1.115 <sup>b</sup>	1.05 <sup>b</sup>

<sup>a</sup> Signs of splitting constants are determined from the anomalous line-width broadening, occurring at temperatures lower than  $-70^\circ$  (cf. E. de Boer and E. L. Mackor, *Mol. Phys.*, **5**, 493 (1962)). <sup>b</sup> Taken from ref. 10.

Comparison of these values with those of the "free" ion shows that the electric field of the counter ion brings about changes in the spin density distribution. In particular, the effect on the  $\alpha$ -proton coupling constant is large, the difference between  $a_{\alpha,1}$  and  $a_{\alpha,2}$  amounting to 0.56 gauss. Marked changes in the values of proton coupling constants have also been observed by others for different radical systems.<sup>11</sup>

Since no traces of splittings due to the free anion are noticeable, the formation of ion pairs must be strongly favored. Assuming a simple dissociation equilibrium



one can derive from the known concentration of  $M^{\cdot-} \cdot Na^+$  an upper limit for the dissociation constant  $K$  at  $-83^\circ$ :  $K \leq 5 \times 10^{-8}$  mole/l.

(11) (a) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962); (b) P. B. Ayscough and R. Wilson, *Proc. Chem. Soc.*, 229 (1962); (c) F. W. Heineken, M. Bruin, and F. Bruin, *J. Chem. Phys.*, **37**, 452 (1962).

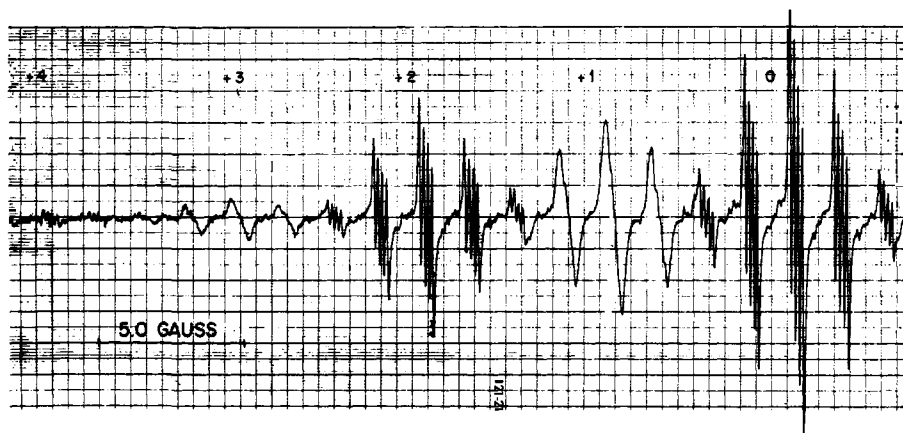


Fig. 4.— $-d\chi''/dH$  vs.  $H$  for the potassium-pyracene complex in tetrahydrofuran at  $-30^\circ$ .

**Structure of the Ion Pair.**—Some observations throw light on the nature of the ion complex. The first of these is the fact that the alkali splitting decreases at lower temperature (Fig. 3). The same behavior was found for the sodium splitting in the sodium-naphthalene system, studied by Atherton and Weissman.<sup>10</sup> To account for it they assume that the alkali nucleus remains close to the nodal plane of the  $\pi_{n+1}$  molecular orbital, and this also holds for the pyracene negative ion.

Secondly, the observed hyperfine pattern in 2MeTHF furnishes information. It requires that the location of the counter ion is such that two sets of four equivalent aliphatic protons arise. Positions A, B, and C in the diagram given in the Introduction meet this condition. Furthermore, the position of the alkali ion should account for the fact that the value of the sodium splitting is much smaller in the pyracene complex than in the naphthalene complex. This makes A and B the most likely equilibrium positions of the cation.

**Spectra in Other Solvents.**—Figure 4 shows half of the spectrum of the potassium derivative in THF at  $-30^\circ$ . The values of  $M_\alpha$ , the magnetic quantum number for the total  $z$  component of the nuclear spin angular momentum of the eight aliphatic proton nuclei, are indicated in the figure. Note that the quintuplets with even  $M_\alpha$  exhibit a well-resolved quartet structure, whereas in the other quintuplets the alkali quartet structure is not resolved. This alternating effect arises from the dynamical equilibrium existing between the two possible conformations of the ion pair, with the cation in position A and in position B. The migration from A to B and *vice versa* causes time-dependent modulations in the isotropic coupling constants, particularly in the aliphatic proton couplings. If the lifetime  $\tau$  of a distinct conformation (A or B) is short compared to  $\{\gamma(a_{\alpha,1} - a_{\alpha,2})\}^{-1}$ , in which  $\gamma$  is the gyromagnetic ratio of the electron, an average splitting constant for the  $\alpha$ -protons will be observed:  $\bar{a}_\alpha = \frac{1}{2}(a_{\alpha,1} + a_{\alpha,2})$ . In intermediate cases, when  $\tau \times \gamma(a_{\alpha,1} - a_{\alpha,2}) \approx 1$ , complex spectra are obtained, since some lines will broaden and others remain narrow as the cation moves. If  $\tau > \{\gamma(a_{\alpha,1} - a_{\alpha,2})\}^{-1}$  a spectrum is observed corresponding to one particular conformation of the ion pair and all hyperfine lines will be sharp. Experiments at various temperatures and in different solvents (mixed solvents if necessary) yield spectra corresponding to each of these situations.

The spectrum in 2MeTHF corresponds to  $\tau > \{\gamma(a_{\alpha,1} - a_{\alpha,2})\}^{-1}$ , since all lines are sharp. The average measured line width  $\Delta H$  is 65 mG. (between points of extreme slope). This value sets a lower limit on the lifetime  $\tau$  of the ion pair. Taking into account other mechanisms contributing to  $\Delta H$ , it is likely that  $\tau > 10^{-5}$  sec.

The temperature dependence of the alkali splittings in THF and in the mixed solvents was analogous to the behavior in 2MeTHF (Fig. 3). On cooling the solution in THF, the features of the spectrum due to the "free" ion became observable at  $-90^\circ$  for the potassium-reduced pyracene anion and at  $-80^\circ$  for the sodium-reduced anion. The hyperfine pattern of the ion pair disappeared completely on lowering the temperature by a further  $20^\circ$ . The experimental spectrum at these temperatures was identical with that shown in Fig. 1: the "free" ion in DME. In the transition range the spectrum is a superposition of two spectra, arising from the two radical species in the solution that are present in comparable amounts.

No association occurred in THF when Li was used as the reducing agent.

**The Line-Width Alternation.**—In nuclear magnetic resonance the effect of chemical exchange on line shape and on resonance frequency is well known.<sup>12</sup> The phenomenon described in this communication is closely related to this and can be described in a similar fashion. Owing to the spin density fluctuations induced by the migration of the counter ion, the isotropic hyperfine interaction constants become time-dependent. From Table I it may be noticed that mainly the aliphatic isotropic splitting constants are affected. Considering only the interaction with the aliphatic proton nuclei, the electron spin resonance transition frequencies,  $\omega/2\pi$ , in the high-field approximation are given (in the standard notation) by

$$\omega_i(t) \equiv \gamma H_0 + \gamma [a_1(t)M_1 + a_2(t)M_2]$$

$a_1$  and  $a_2$  (the subscript  $\alpha$  has been dropped) depend on time and  $M_1$  and  $M_2$  are the magnetic quantum numbers for the total  $z$  components of the nuclear angular momenta of the two sets of four equivalent aliphatic nuclei. If  $M_1 = M_2$  the transition frequencies are not influenced by the exchange process, since at any instant the sum of the last two terms is equal to the average value  $2\gamma M_1 \bar{a}(t)$ . Therefore hyperfine components characterized by equal values of  $M_1$  and  $M_2$  should remain sharp during the exchange process. Only if the sum of the last two terms deviates from the average value—which will be the case for all nuclear spin arrangements for which  $M_1 \neq M_2$ —will the transition frequencies fluctuate and line broadening occur.

This special dependence of the transition frequencies on the nuclear spin arrangements causes the marked line width alternation in the electron spin resonance spectra, as is clearly demonstrated by the spectrum

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 218.

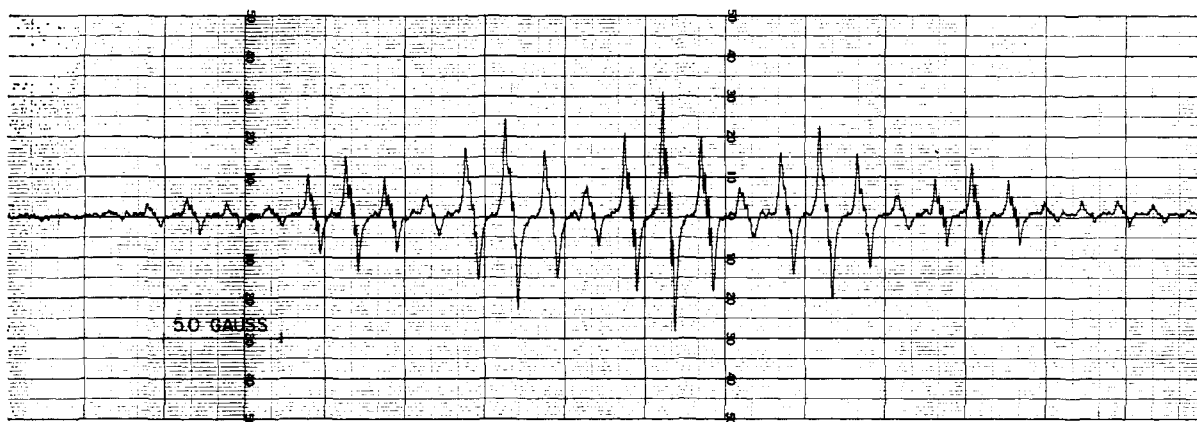


Fig. 5.  $-d\chi''/dH$  vs.  $H$  for the sodium-pyracene complex in a mixture of equal parts of tetrahydrofuran and dimethoxyethane at  $-20^\circ$ ;  $|a_{Na}| = 138$  mG.

shown in Fig. 4. Since this spectrum corresponds to the situation of rapid exchange, the contributions to the line width ( $T_2^{-1}$ ) due to the modulation of the isotropic hyperfine interaction can then easily be calculated with the aid of the formula valid for rapid exchange between two equivalent sites<sup>12</sup>

$$\Delta(T_2^{-1}) = \frac{1}{2}\tau[\omega_j(0) - \bar{\omega}]^2$$

where  $\omega_j(0)$  is the resonance frequency for the nuclear arrangement  $j$  in the absence of exchange and  $\bar{\omega}$  the resonance frequency for fast exchange ( $\bar{\omega} = \gamma\bar{a}(M_1 + M_2)$  for  $1/\tau \rightarrow \infty$ ). Substituting the expressions for  $\omega_j(0)$  and  $\bar{\omega}$  in this equation gives

$$\Delta(T_2^{-1}) = \frac{1}{8}\tau\gamma^2(a_1 - a_2)^2(M_1 - M_2)^2$$

In Table II the various contributions to  $T_2^{-1}$  are indicated, expressed in the parameter  $J(0)$ , the secular spectral density function [ $\Delta(T_2^{-1}) = J(0)(M_1 - M_2)^2$ ]. If  $J(0)$  is large, lines with  $M_\alpha = \pm 3, \pm 1$  will be broadened, whereas lines with  $M_\alpha = \pm 4$  and the intense ones with  $M_\alpha = \pm 2$  and 0 will be sharp. The remaining lines are too broad to be observed. The table illustrates the alternation in line width, which follows from the model proposed.

TABLE II

$M_\alpha =$ $M_1 + M_2$	$M_1$	$M_2$	$n^a$	Contribution to $(T_2)^{-1}$
+4	+2	+2	1	0
+3	+2	+1	4	$J(0)$
	+1	+2	4	$J(0)$
+2	+2	0	6	$4J(0)$
	+1	+1	16	0
	0	+2	6	$4J(0)$
+1	+2	-1	4	$9J(0)$
	+1	0	24	$J(0)$
	0	+1	24	$J(0)$
	-1	+2	4	$9J(0)$
0	2	-2	1	$16J(0)$
	1	-1	16	$4J(0)$
	0	0	36	0
	-1	+1	16	$4J(0)$
	-2	+2	1	$16J(0)$

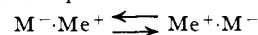
<sup>a</sup>  $n$  indicates the degeneracy of the spin state level ( $M_1, M_2$ ). Exchange contributions to the line width of the hyperfine components determined by the magnetic quantum numbers  $M_1$  and  $M_2$  of the aliphatic proton nuclei only.

If the reasonable assumption is made that the value of  $a_1 - a_2$  in THF is equal to that in 2MeTHF, the lifetime  $\tau$  of a distinct conformation (A or B) at  $-30^\circ$  in THF should be shorter than  $10^{-7}$  sec.

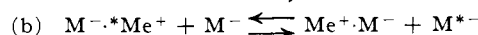
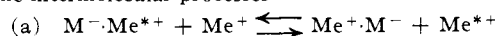
**Intramolecular and Intermolecular Exchange Reactions.**—No attention has been paid to the nature of

the exchange processes involved. Two types of reactions deserve consideration

(1) the intramolecular process



(2) the intermolecular processes



Me stands for the alkali metal, M for the neutral molecule.

A conclusion as to the nature of the exchange process is arrived at by the following reasoning. The lines in the sharp quintuplets (Fig. 4) have a width of 90 mG., corresponding to a value of  $T_2$  of  $0.7 \times 10^{-6}$  sec. The mean lifetime of a particular conformation in THF at  $-30^\circ$ , however, is shorter than  $10^{-7}$  sec. These facts can be reconciled only if during the exchange process the spin state of the alkali nucleus is preserved, so that it does not affect the line width of the lines in the sharp quintuplets. Such a preservation of spin can be rationalized only by an intramolecular process. Thus reaction 1 must be responsible for the line-width alternation. Since for a zero-order reaction  $1/\tau$  is equal to the rate constant,  $k$  line-width alternation occurs within the range  $10^{+5} \text{ sec.}^{-1} < k < 10^{+7} \text{ sec.}^{-1}$ . If  $k$  is smaller than  $10^5 \text{ sec.}^{-1}$  the e.s.r. spectrum corresponds to one distinct conformation (Fig. 2); if  $k > 10^7 \text{ sec.}^{-1}$  a sharp averaged spectrum is obtained with  $\bar{a}_\alpha = \frac{1}{2}(a_{\alpha,1} + a_{\alpha,2}) = 6.65$  gauss.

Preliminary experiments were performed in order to assess the effect of reactions 2a and 2b. One experiment was carried out in a mixture of equal volumes of THF and DME. The spectrum of the ion pair is shown in Fig. 5. On every hyperfine component alkali splitting is observed, but even in the quintuplets  $M_\alpha = \pm 4, \pm 2, 0$  the quartet structure is not quite resolved. When the temperature was lowered, the dissociation of the ion pair increased, and simultaneously the quartet structure vanished. Addition of a small amount of a sodium halide to a solution of sodium-pyracene in THF also resulted in a complete loss of alkali splitting. Lack of knowledge of the exact concentrations of the cations and the possible existence of more complicated complexes in the solutions prevent precise evaluation of the rate constants of reactions 2a and 2b. However, rate constants of the order of  $10^9$ – $10^{10}$  l. mole<sup>-1</sup> sec.<sup>-1</sup> are in agreement with the very low value  $\{K(-83^\circ) \leq 5 \times 10^{-8} \text{ mole/l.}\}$  estimated for the dissociation constant.

**Acknowledgment.**—The authors are grateful for valuable assistance given by Mr. A. P. Praat and Mr. A. R. Korswagen.