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NMR Studies of Picolyl-type Carbanions. V.[1,2] ^{7}Li and ^{13}C Spectra of Picolyl-type Anions with Lithium as a Counter Ion

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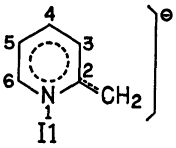
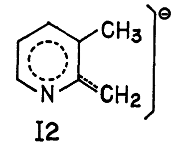
The ^{7}Li and ^{13}C NMR spectra have been observed for picolyl-type anions with lithium as a counter ion in polar solvents. With reference to the observed chemical shifts, it is concluded that these lithium salts are present in THF as tight ion pairs in which the anion-cation interaction takes place mainly at the ring nitrogen. Thus, the picolyl-type anions are characterized by their ion-pair structures.

In the previous reports on picolyl(pyridylmethyl)-type delocalized anions, the following points of interest were disclosed for I—IV (shown below) in polar solvents:[1,3] (1) The methylene carbon in I is virtually sp^2-hybridized; (2) for I1, the observed ^{13}C chemical shifts are linearly related to the calculated π-electron densities; and (3) II—IV can be regarded as delocalized anions with the same significance as I. In order to delineate the nature of interaction between the picolyl-type anions under discussion and the lithium ion, the ^{7}Li, ^{13}C, and ^{1}H resonances of these ionic species have been investigated in polar solvents. The anions prepared are numbered as follows:


I1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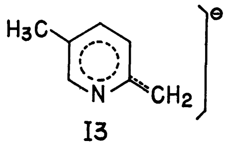
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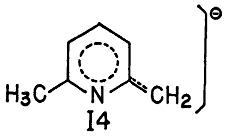
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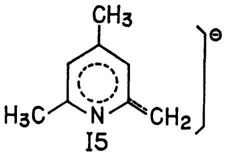
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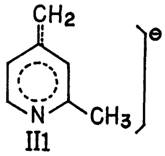
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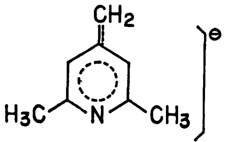
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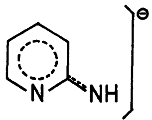
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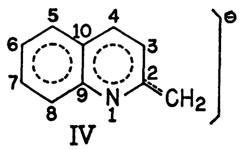
IV

Experimental

The procedures used in this study are similar to those described in previous reports.[1,3] All the anions were produced by reacting methyl-substituted pyridines, 2-methylquinoline, and 2-aminopyridine with butyllithium.

The ^{7}Li and ^{13}C NMR spectra were measured on a Varian FT 80A spectrometer installed at the Institute for Molecular Science, operating in the FT mode at 30.913 and 20.000 MHz respectively. The measuring temperatures and sample concentrations were 36—37 °C and 0.8—1.3 mol dm^{-3}. The lithium chemical shifts were expressed relative to that for aqueous LiCl (0.5 mol dm^{-3}), used as an external reference. The carbon chemical shifts were evaluated with the solvent peaks used as an internal reference. The more shielded peaks of diethyl ether (DEE), tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), the most shielded peak of tetraglyme (TG), and the peak of hexamethylphosphoric triamide (HMPA) were taken to be 17.1, 26.4, 58.8, 58.6, and 37.0 ppm from TMS respectively.

The PPP and CNDO/2 MO calculations for the 2- and 4-pyridylmethyl (picolyl) anions[4] were carried out using the Okitac-4300C and Hitac-8450 computer systems installed at The Industrial Technology Center of Mie Prefecture and at the Nagoya Institute of Technology respectively, using the same procedure as that described in the preceding paper.[1] The bond lengths between the methylene and 2-carbons and between the methylene and 4-carbons were set at 1.39 Å in the calculations.

Results and Discussion

Some typical spectra of the anions with lithium as a counter ion are shown in Figs. 1 and 2. The ^{7}Li and ^{13}C chemical-shift data are given in Tables 1 and 2 respectively.

TABLE 1. THE LITHIUM CHEMICAL SHIFTS FOR THE ANIONS, IN ppm[a)]

Anion	Solvent	
I1	DEE	−0.52
	THF	−0.29
	DME	−0.62
	TG	−0.26
	HMPA	−0.05
I1′[b)]	THF	−0.01
I1″[b)]	THF	−0.26
I1‴[b)]	THF	−0.40
I2	THF	−0.24
I3	THF	−0.34
I4	THF	−0.30
I5[c)]	DEE	−0.10
II1	THF	−0.22
II2	THF	−0.03
	HMPA	−0.08
III	THF	1.08
	HMPA	0.78
IV	THF	−0.08
	HMPA	−0.10

a) Errors are estimated to be within ±0.05 ppm. b) In proportions of starting materials, 2-methylpyridine : butyllithium=1.77 : 1, 1.31 : 1, and 0.58 : 1 for I1′, I1″, and I1‴ respectively. c) Contaminated with a small amount of II2.

Table 2. The carbon chemical shifts of the anions, in ppm[a)]

Anion	Solvent	Assignment										
		2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C	CH_2	CH_3
I1	DEE	165.5	118.8	134.7	102.0	149.8					57.5	
	THF	164.2	116.1	131.6	97.3	148.7					57.0	
	DME	163.5	115.7	131.3	96.2	148.8					58.0	
	TG	161.9	114.8	130.5	94.1	149.0					61.5	
	HMPA	161.3	113.6	129.8	92.2	149.8					62.6[b)]	
I2	THF	163.2	119.4	130.7	97.2	146.7					56.2	21.0
I3	THF	164.1	116.6	134.2	104.6	147.1					54.2	18.1
I4	THF	166.0	112.7	132.6	97.3	155.7					54.1	24.6
I5	DEE	169.1	114.2	144.7	104.7	156.8					52.9	22.6 25.5
II1	THF	149.7	107.9	150.0	107.9	143.7					64.9	24.4
II2	THF	150.2	106.4	151.9	106.4	150.2					62.2	24.3
	HMPA	150.1	105.2	150.5	105.2	150.1					62.2	24.8
III	THF	174.2	113.3	136.3	104.7	148.1						
	HMPA	173.2	112.2	134.4	101.0	148.6						
IV	THF	159.0	126.0	128.6	126.3	111.8	128.2	117.7	155.8	122.7	70.2	
	HMPA	159.0	125.0	127.9	125.5	108.7	127.7	119.0	156.5	121.9	70.7	

a) Errors are estimated to be within ±0.3 ppm. b) This value should be adopted, though it is somewhat different from the corresponding CH_2 value in Table 2 of Ref. 1.

NMR Spectra of the Anions with Lithium as a Counter Ion.[5)] *^{7}Li Spectra*: A typical spectrum is shown in Fig. 1. With changes in the anion, the solvent, the concentration, and the temperature, the chemical shifts and/or linewidths varied. In the case of 2-pyridylmethyllithium (I1),[6)] the variation in the chemical shift was 0.24 ppm, and the linewidth increased about 6.5 times (*i.e.*, from about 14 to 90 Hz), with a change in solvent from THF to HMPA.

^{13}C Spectra: The signals were assigned by comparison with the ^{1}H spectra and by confirmation of a quarternary carbon by means of the off-resonance decoupling method. The 2- and 4-pyridylmethyl anions with lithium as a counter ion, produced from methyl-substituted pyridines by the action of butyllithium, were distinguishable by a difference in spectral pattern, as is shown in Fig. 2.

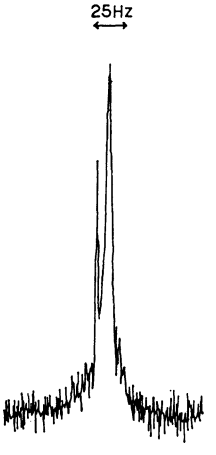

Fig. 1. ^{7}Li spectrum for I1 in THF. The less shielded peak is due to the signal of aqueous LiCl used as an external reference.

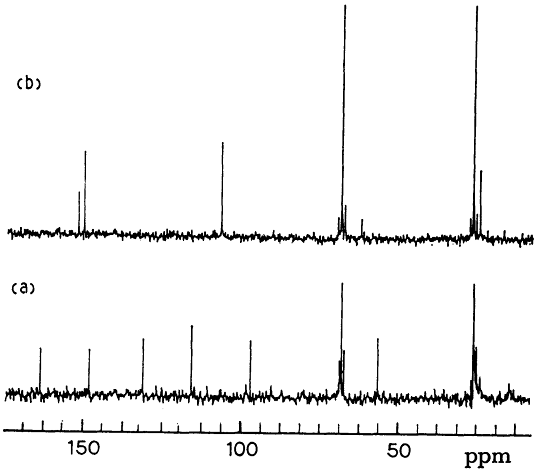

Fig. 2. ^{13}C spectra of pyridylmethyl anions in THF; (a) I1 and (b) II2.

Types and Structures of Ion Pairs Formed. In the ^{7}Li NMR spectra for I—IV, the signals appear at higher fields than those of typical alkyllithium compounds (*i.e.*, 1—2 ppm in ether, triethylamine, and cyclopentane)[7)] and at lower fields than those of typical aromatic lithium salts present in THF as primarily loose (or solvent-separated) ion pairs, such as fluorenyl-, 1,3-diphenylallyl-, triphenylmethyl-, and cyclononatetraenyllithium (*i.e.*, −1——2 ppm in THF).[8)] These ^{7}Li spectra may indicate that the ionic natures of lithium salts of I—IV are different from those of the alkyllithiums and the loose ion pairs. As has already been reported,[9)] phenylmethyl-(benzyl-), 1-phenylallyl-, cyclopentadienyl-, and indenyllithium exist as tight (or contact) ion pairs in THF. The signals of phenylmethyl- (*i.e.*, −0.12 ppm in THF) and 1-phenylallyllithium (*i.e.*, −0.71) are found within a range (−1—1 ppm) similar to those for I—IV, but those of cyclopentadienyl-(*i.e.*, −8.37) and indenyllithium (*i.e.*, −6.12) show an upfield shift of more than 6 ppm from I—IV.[8,10] This large difference reflects the specific location of the counter ion in relation to the anion in a tight ion pair. Consequently, if I—IV form tight ion pairs with lithium cations, the cations are not situated so as to be strongly subject to the diamagnetic shielding of the induced ring current.[11]

The dependence of the lithium chemical shift with a solvent for the I1, II2, III, and IV given in Table 1 is relatively small. The lithium shift for I1 in DME is 0.33 ppm upfield from the THF value. This variation is similar to those for typical tight ion pairs, but is not large enough to indicate primarily loose ion pairs in THF and DME. An 1 ppm or greater difference between THF and DME should be observed for primarily loose ion pairs.[8]

The carbon chemical shifts of I1, II2, III, and IV in various solvents are given in Table 2. As can be seen from the table, the effect of a change in solvent is large on the carbon shifts of I1. The 5-carbon shift, being a well-defined index of electron delocalization,[1] appears in a higher field with the change to a more polar solvent in this order: DEE, THF, DME, TG, and HMPA; it is about 5 and 10 ppm upfield in HMPA from the THF and DEE values respectively. The same tendency is observed with the proton chemical shifts.[1,3,12] This upfield shift is induced by a change in the ion-pair equilibrium toward loose ion pairs or an increase in the external solvation of tight ion pairs.[13] Generally, the same overall trends for the carbon and proton shifts are observed on a lowering of the temperature as on an increase in the solvating ability of the solvent. The 5-proton shifts of I1 in THF and DME show a relatively large temperature dependence, but the magnitude of the upfield shift induced by changing the temperature from 40 °C to −30 °C in DME is slightly larger than that in THF.[1,3] The temperature dependence of the 5-proton shifts of I1 and I2 in DME is shown in Fig. 3. The shift of I1 at −60 °C is about 0.25 ppm upfield from the 40 °C value, but it is still about 0.2 ppm downfield from that at room temperature in HMPA, favoring loose ion pairs in comparison with DME. In addition, the two curves depicted in this figure cannot be claimed to be the remarkable sigmoid curves, which imply a change in the ion-pair equilibrium toward loose ion pairs in this temperature range.[13] Consequently, in THF and DEE, which favor tight ion pairs in comparison with DME at room temperature, the significant upfield shift induced by the change in solvent from DEE to THF can be accounted for by an increase in the external solvation of tight ion pairs. These results on the lithium and carbon shifts in various solvents and the proton shifts at various temperatures lead to the conclusion that I1 forms a tight ion pair with a lithium cation in THF, and that, therefore, so do I2—IV.

At concentrations in the range of 0.5—2.0 mol dm^{-3}, the variation in the lithium shifts for I1 in THF is negligibly small, but the linewidth at the half-peak height varies from 21 to 8 Hz. At 0.8—1.2 mol dm^{-3}, the variations for I1 in DME, and for I4 and II1 in THF are less than 0.05 ppm. Thus, no meaningful difference in lithium shift for I1 is observed on a change in the concentration in discrete solvents. Consequently, it is reasonable to assume that either the state of association does not change in this concentration range or that the effect of association is not important in determining the lithium shifts.[8]

The lithium shifts for I1′—I1‴ contaminated with an excess of the starting materials in THF are given in Table 1. With an increase in the proportion of 2-methylpyridine relative to butyllithium, the lithium signal is shifted to a lower field, and the linewidth becomes broader. In view of these shifts, the effect of contamination is negligibly small for the lithium salts prepared in this study. Further, when lowered to −76 °C, the peak for I1′ and I1″ is split into two, but not so for I1‴, as is shown in Fig. 4. The ratio of the two peak areas for I1′ is roughly 1.8 : 1, while that for I1″ is 0.22 : 1. One of the two peaks for I1′ and I1″ appears at about 1.35ppm, and the other, at −0.1— −0.2 ppm. It seems that the less and more shielded peaks with respect to inorganic lithium are attributable to

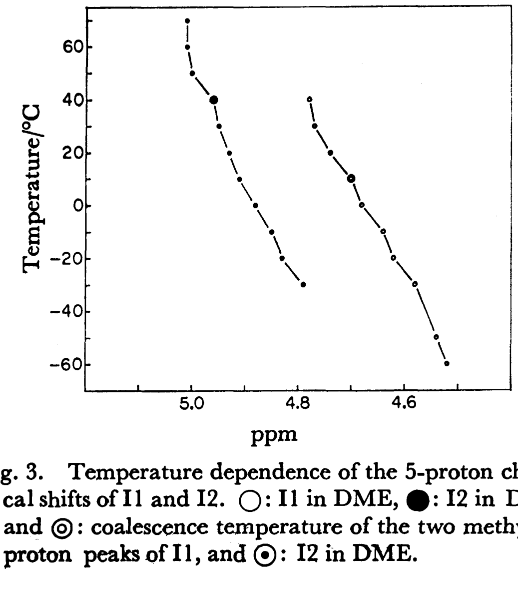

Fig. 3. Temperature dependence of the 5-proton chemical shifts of I1 and I2. ○: I1 in DME, ●: I2 in DME, and ◎: coalescence temperature of the two methylene proton peaks of I1, and ⊙: I2 in DME.

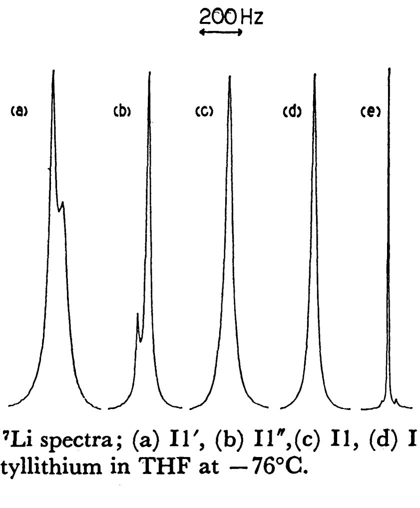

Fig. 4. ^{7}Li spectra; (a) I1′, (b) I1″, (c) I1, (d) I1‴, and (e) butyllithium in THF at −76°C.

the 2-pyridylmethyllithium–2-methylpyridine complex formed and to 2-pyridylmethyllithium respectively.

Turning now to the comparison of 2-pyridylmethyllithium (I1) with phenylmethyl alkali compounds, especially with phenylmethyllithium in THF, we note first that the preparation of I1 is indeed easy, and that I1 is thermodynamically very stable in THF and DME.[3] Secondly, it is apparent that phenylmethylpotassium is much more ionic than phenylmethyllithium in THF.[10,14,15] The ^{1}H and ^{13}C spectra of phenylmethylpotassium in THF are similar to those of I1 in DME, except for the positions bonded to the ring nitrogen, *i.e.*, the 2- and 6-positions. With the procedure reported for naphthylmethyl alkalis present as tight ion pairs in THF at room temperature,[16] the proton chemical shifts, calculated on the basis of the assumption that the cation radius for the phenylmethyl anion can be infinitely large (that is, that the phenylmethyl anion may form a loose ion pair or free ions with the cation), would be about 5.2, 5.7, and 4.2 ppm for the *o*-(3-), *m*-(4-), and *p*-(5-)protons respectively. These values are comparable to values of 5.16, 5.68, and 4.33 ppm for I1 in HMPA.[1] The π-electron densities, calculated using the PPP MO method, at the 3-, 4-, and 5-positions in the phenylmethyl anion are also comparable to those in I1. These suggest that I1 may be present as a loose ion pair in HMPA. Thirdly, we recall that the methylene carbon in I1 is virtually sp^2-hybridized.[3] Fourthly, an *o*-position in I1 is a nitrogen atom. The excess charge density, calculated using the PPP and CNDO/2 MO methods, at the *o*-nitrogen (ring nitrogen) is comparable to that at the methylene carbon. Thus, I1 has some different features as compared with phenylmethyllithium, apparently caused by the effect of *o*-nitrogen, but it seems to be monomeric in polar solvents, much like to phenylmethyl and naphthylmethyl alkalis.[16,17] Therefore, when I1 is present as a tight ion pair in THF, either the methylene carbon or the ring nitrogen can be regarded as the site where the anion-cation interaction mainly takes place.

A good correlation has been obtained between the carbon chemical shifts and the π-electron densities calculated using the PPP and CNDO/2 MO methods for the 2-pyridylmethyl anions I and 4-anions II. The relationship given in Fig. 5 shows that the π-electron densities at the carbons in both 2-anion I1 and 4-anion II2 can be evaluated from the carbon chemical shifts using an identical scale. In addition, as is shown in Table 1, the lithium-shift difference between lithium salts of the 2-anions I and the 4-anions II is less than 0.31 ppm in THF; especially, that between I2 and II1 is negligibly small. These imply that both have essentially the same ion-pair structure in THF. However, it was previously reported that 2,4-dimethylpyridine and 2,4,6-trimethylpyridine underwent deprotonation to give 2-anions such as I, and that isomerization took place from the 2- to the thermodynamically more stable 4-anions II.[3] The lithium salts of the 4-anions II are indeed surprisingly stable, for about 30—40% of these lithium salts in TG could still be detected in the ^{1}H spectra after the samples had stood for 1 h at 100 °C, while the lithium salts of the 2-anions I completely changed to the corresponding methyl-substituted pyridines in TG. In view of these experimental facts, it is not reasonable to assume that the anion-cation interaction takes place mainly at the methylene carbon in lithium salts of the 2-anions I and the 4-anions II present as tight ion pairs in THF, for this assumption would predict a primarily loose ion-pair structure for both lithium salts I—II. Therefore, in both lithium salts I and II and, furthermore, in III—IV, the ring nitrogen can be regarded as the site where the anion-cation interaction mainly takes place.

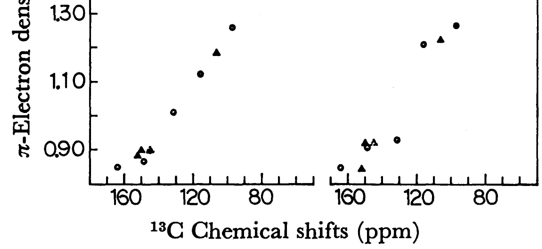

Fig. 5. π-Electron densities *vs.* ^{13}C chemical shifts.
○:I1, △: II2 in THF, and ⚠: 2- and 6-C corrected for effect of methyl group by reducing 5 ppm in II2.

It is concluded that I—IV are present in THF as tight ion pairs in which the anion-cation interaction takes place mainly at the ring nitrogen. Thus, the picolyl-type anions with lithium as a counter ion are characterized by their ion-pair structures.

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4) On the basis of the assumption that lithium salts of these anions exist as completely free ions, the π-electron densities have been calculated using the PPP and CNDO/2 MO methods.

5) ^{14}N Spectra: The spectra of the starting materials could be easily observed, but it was difficult to observe those of the anions. At present, the signals can not be confirmed. ^{15}N Spectra: Further studies are now in progres.

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