An NMR Study on Ion-Pair Structures of Pyridine–Butyllithium Adducts

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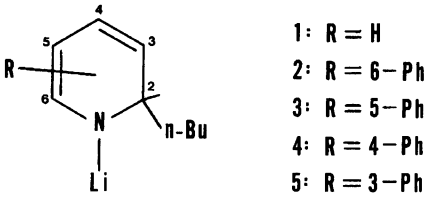
The ^{13}C and ^{7}Li NMR spectra of the title adducts were observed in THF. In a temperature range from 20 to −80 °C the adducts existed as contact ion pairs in THF. Below −70 °C, the adduct derived from pyridine or 4-phenylpyridine showed three ^{7}Li signals related to three different associated species in solutions. On the other hand, the adduct derived from 2- or 3-phenylpyridine did not give such multiplet signals at −70 °C. The results are related to the interaction between nitrogen and lithium, and the extent of negative-charge migration into the substituent (phenyl ring) in the adduct.

Studies concerning the behavior of ionic species in polar solvents are important and have attracted the attention of many researchers. The equilibria between contact ion pairs (CIP) and solvent-separated ion pairs (SSIP) in various carbanions were studied extensively using UV,[1—4] ^{1}H NMR,[5—9] and ^{13}C NMR[10,11] techniques. Although there have been many reports concerning the ion pairs between carbon and lithium atoms, only a few articles have been reported concerning the ion pairs between nitrogen and lithium atoms. Konishi et al. reported that the lithium salts of the 2-pyridylmethyl anions are present in THF as tight ion pairs.[12] On the other hand, Ide et al. reported that the lithium salt of aniline is present in DMSO as loose ion pairs.[13] Accordingly, the ion-pair structures between nitrogen and lithium atoms are strongly dependent on the surrounding circumstances, such as the solvent, temperature, or concentration. In the present work, interactions between nitrogen and lithium atoms and the phenyl-substituent effects in the title adducts were studied using ^{13}C and ^{7}Li NMR techniques. The prepared adducts are given in Scheme 1 along with the reference numbers from **1** to **5**. The structures of similar adducts and their N–Li covalent bond characters were previously studied by means of ^{1}H NMR techniques.[14]

Experimental

The pyridine and phenylpyridines used as starting materials were commercially available. These starting materials were dried over calcium hydride and degassed by a freeze-pump-thaw procedure, and then stored in sealed ampules with a break seal. Tetrahydrofuran (THF) and 2-methyltetrahydrofuran (MTHF) were dried over sodium, and then stored over a sodium–potassium alloy. The preparation of the adducts was carried out in vacuo. A starting material (0.25—0.75 mmol) was reacted with an equimolar amount of butyllithium in hexane (Hx) or Hx mixed with THF at −78 °C. After the solvent had been distilled off until almost dry, the residue was dissolved in a solvent such as THF or MTHF. The solution was then introduced into an NMR sample tube, which was sealed under a vacuum. The concentration of the solution was approximately 1 mol dm^{-3}. The reaction proceeded almost quantitatively, except for the case of 3-phenylpyridine; 3-phenylpyridine formed two products, **3** and **5**. The yields were 73 and 27% for **3** and **5**, respectively. The ^{13}C chemical shifts are referred relative to the more shielded peak of THF as the solvent (26.40 ppm from TMS). ^{7}Li chemical shifts are referred relative to an external LiCl/D$_2$O standard. The ^{7}Li spin-lattice relaxation times were measured using a 180°–τ–90° pulse sequence (inversion recovery) with a 90° pulse of 14.1 μs, a spectral width of 2000 Hz, and 20000 data points. A delay of at least 15 times of T_1 was applied between acquisitions. The NMR probe temperature was controlled to ±0.1 °C.



Scheme 1.

Results and Discussion

Temperature Dependence of the ^{13}C Chemical Shifts. The ^{13}C chemical shifts are known as an empirical guide to the distributions of the electron densities in charged molecules.[15] Therefore, the temperature dependence of the ^{13}C chemical shifts in **2**, **3**, or **4** was measured within a temperature range from 20 to −80 °C. The results of the measurements are given in Fig. 1. Although that for **3** was measured in a mixed solution of **3** and **5**, that for **5** could not be obtained because of the small amount of **5** in the mixed solution. All ring carbon signals, except for C$_3$ and C$_5$ of **4**, moved toward the higher field upon lowering the temperature. The chemical shift changes, however, were small for all of the carbons of either **2**, **3**, or **4** within a change of 1.6 ppm. On the other hand, the signals of C$_3$ and C$_5$ of **4** (at about 95 and 90 ppm) moved toward a lower field upon lowering the temperature from −40 to −70 °C, and then moved toward the higher field within a temperature range from −70 to −80 °C. Further, their line widths became broader than the other ones within a temperature range from −40 to −60 °C, as shown in Fig. 2. The signals then became sharp again at −80 °C. This specific behavior of the C$_3$ and C$_5$ signals of **4** is interpreted as being caused by an inversion at C$_2$ of **4**, whose rate would be comparable with the NMR

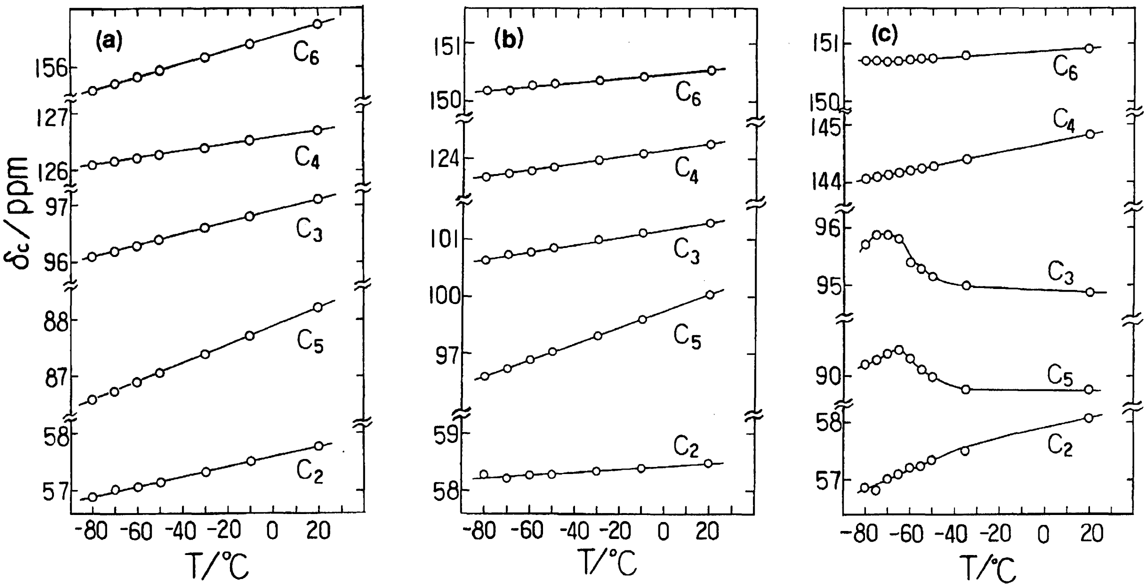


Fig. 1. Temperature dependence of the ^{13}C NMR chemical shifts of (a) **2**, (b) **3**, and (c) **4** in THF and at 50.3 MHz.

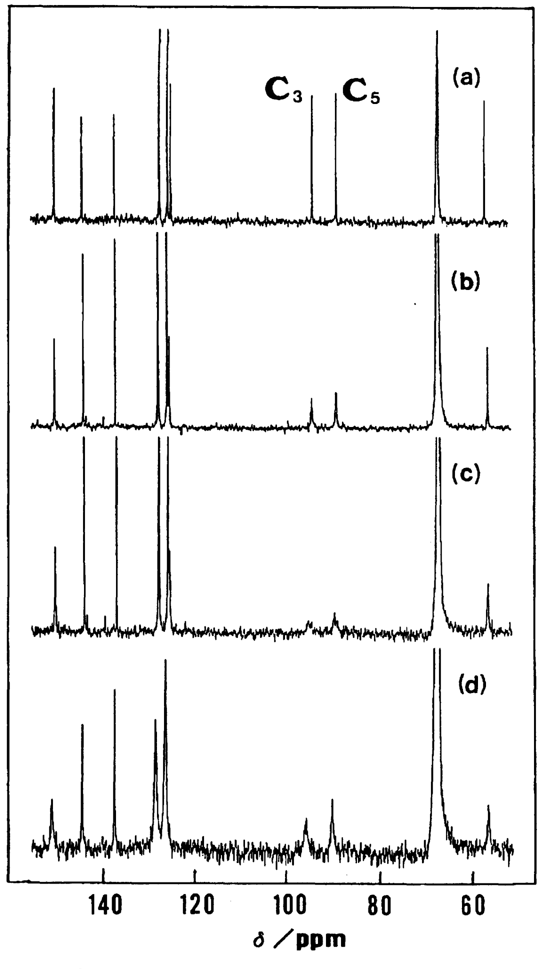


Fig. 2. ^{13}C NMR spectra of **4** in THF at 50.3 MHz, and at (a) 22, (b) −35, (c) −55, and (d) −80 °C.

time scale related to the C_3 or C_5 chemical shifts of the two inverted forms of **4**. O'Brien et al. reported that the ion-pair equilibrium between CIP and SSIP can be differentiated based on the behavior of the ^{13}C chemical shifts to the temperature change.(10) In the temperature range from 20 to −80 °C, the ^{13}C chemical shifts are not constant for the carbons in **2**, **3**, and **4**. From these observations, it is concluded that the adducts are mainly present as CIP, and not as SSIP.

^{7}Li NMR Spectra. ^{7}Li NMR is more useful than ^{13}C NMR for studying exchange systems. This is because the former is usually available with a faster time scale and a higher digital resolution than the latter. The ^{7}Li NMR signals in **1**—**4** are observed within a narrow range of approximately −0.20 to 1.16 ppm, as given in Table 1.(16) They are shielded similarly to those of 2-pyridylmethyllithium(12) (0—−0.6) and typical alkyllithiums (2—0.4 ppm),(17) and are less shielded than

Table 1. ^{7}Li NMR Chemical Shifts of the Adducts at 77.7 MHz$^{a)}$

No.	Solv.	Concn	δ			
		mol dm^{-3}	ppm			
1	THF-d_8	1.0	1.06	0.46	−0.05	
1	THF/Hx=2$^{b)}$	1.0	1.16	0.55	0.04	
1	MTHF	1.0	0.91	0.31	0.10	−0.20
1	THF	0.5	1.10	0.49	−0.01	
1	THF	1.5	1.05	0.44	0.23	−0.06
2	THF	1.0	0.01			
3, **5**$^{c)}$	THF	1.0	−0.04			
4	THF	1.0	1.10	0.48	−0.03	

a) Measurements were carried out at −80 °C for **1** and **4**, and at −70 °C for **2**, **3** and **5**. LiCl/D$_2$O was used as an external reference. b) Volume ratio. c) A 7 : 3 mixture of **3** and **5**.

Table 2. ^{7}Li NMR Spin-Lattice Relaxation Times for **1** at −80 °C

Solv.	Concn	T_1/s			
	mol dm^{-3}	A[a)]	B	C	D
THF-d_8	1.0	0.116±0.010 (1.00)[c)]	—[b)]	0.088±0.010 (0.76)	0.093±0.009 (0.80)
MTHF	1.0	0.055±0.004 (1.00)	0.052±0.004 (0.95)	0.049±0.004 (0.89)	0.048±0.003 (0.87)
THF	1.5	0.058±0.009 (1.00)	0.040±0.006 (0.69)	0.034±0.002 (0.59)	0.029±0.002 (0.50)

a) Signals are named as A, B, C, and D from upfield. b) Not observed. c) Values in parentheses are the ratios of T_1 referred to that of the most upfield signal.

those of typical aryllithiums (−0.38—−8.99 ppm).[18)] They are more deshielded than those present as SSIP in THF. The half widths of the ^{7}Li signals are dependent on the temperature, as shown in Fig. 3. The widths, except for that of **1**, decrease linearly upon lowering the temperature. Since ^{7}Li nuclei have I=3/2 and a quadrupole moment, their relaxation is mainly controlled by quadrupole relaxation, which is effectively affected at lower temperature. If this mechanism is operative, the half widths of the signals of the adducts should increase at lower temperature. However, as shown in Fig. 3, they decreased with lowering temperature, except for that of **1**. This fact shows that in the present system the quadrupole relaxation mechanism is not so effective within the temperature range from 20 to −60 °C. Another relaxation mechanism seems to be operative. On the other hand, for **1**, a small maximum value of the half width was observed at about 240 K. This line broadening may be interpreted in terms of an exchange among several species in **1**. The ^{7}Li nucleus of **1** is in the fast motional region above −30 °C and in the slow motional region in the temperature range from −30 to −50 °C. The ^{7}Li NMR signals in **1** are shown in Fig. 4 with a temperature range from −50 to −80 °C. Three signals below −65 °C can be related to three different species. The structures of such aggregates were previously confirmed by ^{15}N NMR[19)] or X-ray structural data.[20)] For example, the lithium atom can possess two coordinate bonds and the aggregates have a planer four-membered $(LiN)_2$ ring and an eight-membered $(LiN)_4$ ring for the dimer and the tetramer, respectively.[20)]

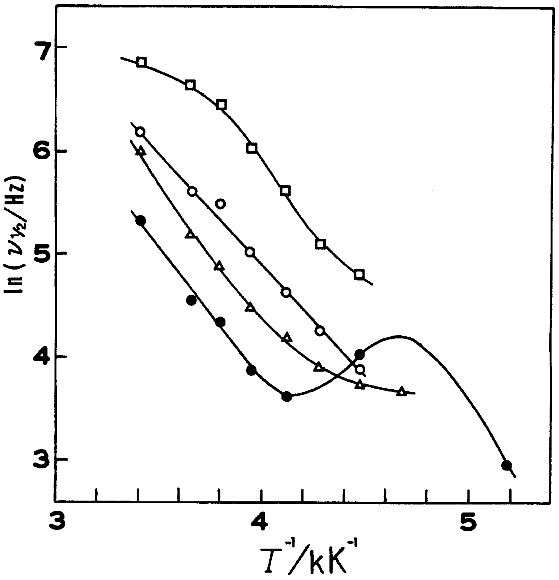


Fig. 3. Temperature dependence of the line widths of the ^{7}Li signals of **1** (●), **2** (○), **3** (△), and **4** (□).

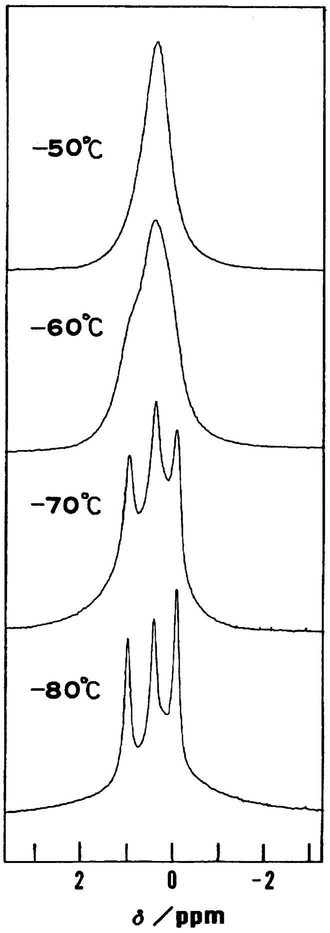


Fig. 4. ^{7}Li NMR spectra of **1** in THF at different temperatures and at 77.7 MHz.

To ascertain the origin of the three signals, the samples were prepared with different ratios of pyridine to

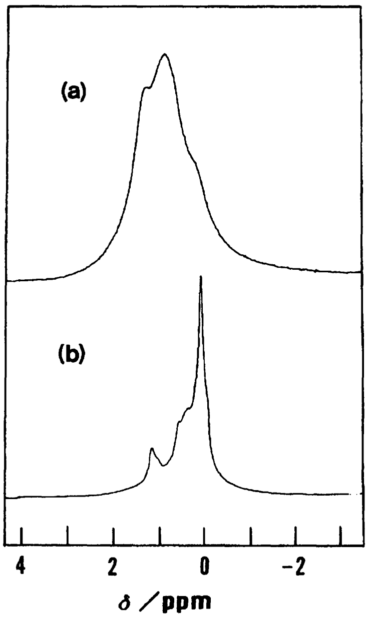


Fig. 5. ^{7}Li NMR spectra of the adducts in THF at −80 °C prepared with the ratios of pyridine to butyllithium of (a) 2 : 1, and (b) 1 : 2, respectively.

butyllithium. As can been seen in Fig. 5a, the ^{7}Li spectrum measured in the presence of an excess amount of pyridine and an absence of free butyllithium[21] showed three signals, although they are poorly resolved. Another spectrum (Fig. 5b), which was measured in the presence of an excess amount of butyllithium, appeared as a new signal at a slightly lower field from the most upfield signal. This signal is almost 0 ppm, which seems to be ascribed to a symmetrically solvated species.[22] The signal may be assigned to unreacted butyllithium. Further, separated signals showed that the exchange between different Li species is slow compared with the related NMR time scale. On the other hand, in cases in which the concentration of butyllithium is larger than 1.5 mol dm^{-3}, or when MTHF was used as a solvent, a new signal appeared near 0.23 or 0.10 ppm. Under these conditions, therefore, four different species were observed in the solutions. To investigate the substituent effects on the ion-pair structures, the ^{7}Li NMR spectra of **2**, **3** (in a mixture with **5**), and **4** were measured at −70 °C, as shown in Fig. 6. The ^{7}Li signal of **2** or **3** (with **5**) did not split into two or three, but that of **4** split into three, as observed for **1**. It corresponds to the fact that the phenyl ring of **4** has the smallest negative charge increase at the para position in the adduct formation among those of **2**—**5**.[23] Therefore, the result shows that the substituted position of the phenyl group strongly affects the bonding between the nitrogen and lithium atoms.

The relaxation times of the ^{7}Li signals were measured in order to obtain information about the circumstances around the lithium in the adducts. It seems to be difficult to compare the relaxation times of different samples directly. Accordingly, a comparison was made within several signals in the same sample, as given in Table 2 for **1**. The larger value was always observed for the upfield signal than that for the deshielded one. The T_1 values are not sensitive to the kind of solvent, such as THF or MTHF. However, when the concentration increased to above 1.5 mol dm^{-3}, two signals of the uppermost and lowermost signals showed a big difference in their T_1s. This means that the signals are related to association equilibrium in the adducts. It is assumed that three different aggregates of **1** will consist of the monomer, dimer, and tetramer or hexamer. Generally, δ_{Li} increases with the extent of association, and the uppermost signal is ascribed to the smallest aggregate and the signals of the aggregates are deshielded with an increase in their association.

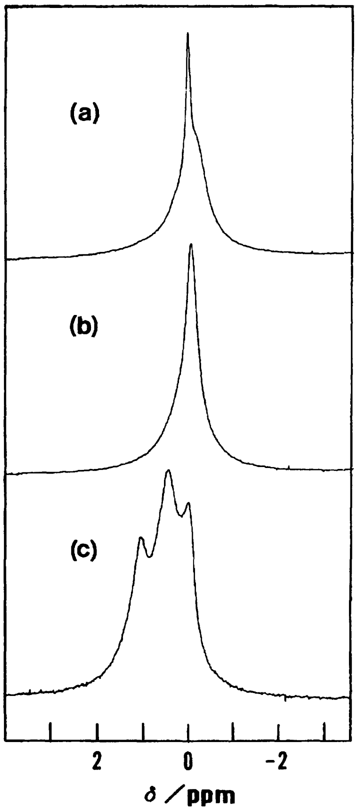


Fig. 6. ^{7}Li NMR spectra of (a) **2**, (b) a mixture of **3** and **5**, and (c) **4** observed in THF at 77.7 MHz and −70 °C.

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