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A DNMR Study of Restricted Methylene Rotation in 2-Pyridylmethyl- and 3-Methyl-2-pyridylmethyllithium

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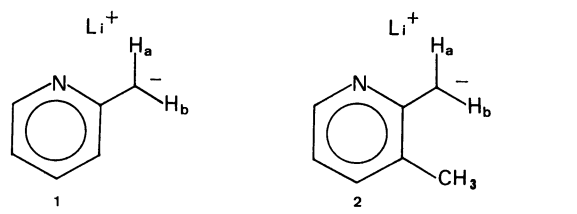
Thermodynamical parameters for the restricted rotation of the title carbanions have been obtained by means of the DNMR techniques. The activation energies and entropies thus obtained are about 93 kJ mol^{-1} and 95 J K^{-1} mol^{-1} for the two carbanions studied; these values are larger than those of the similar rotations observed in arylmethanide ions. The methylene rotation is thus extremely hindered in these carbanions.

Rotational barriers about bonds with partial double-bond character have been studied extensively by means of the DNMR techniques. Especially, a lot of interesting information on rotation about the N-C bonds in amides has been obtained so far.[1] These techniques have also been applied to the hindered rotations in cations and anions with large conjugated π-systems. The barriers and the mechanism of rotation of phenyl groups in the arylmethanide-ion systems have been reported.[2-5] 2-Pyridylmethanide ions discussed in this study are one of the systems similar to the phenylmethanide ion, which is the simplest one among the arylmethanide ions. A hindered rotation about the bond between the methylene group and the pyridine ring has been previously noted.[6] The aim of this study is to obtain temperature-dependent NMR spectra of the two title carbanions (hereafter referred as **1** and **2**, as shown in Fig. 1) and to evaluate the barriers for the rotation about the bond between the pyridine ring and the α-carbon by means of the DNMR techniques.

Experimental

All reagents used were commercially available. Precursors (2-picoline and 2,3-lutidine) were dried with calcium hydride and distilled in a vacuum and then divided to a suitable amount in several Pyrex ampoules with breakable seals. Butyllithium in hexane was also ampouled with the same manner in a vacuum after filtering to remove small suspended solid particles. Precursors were reacted in vacuum with butyllithium in a small reaction vessel with a 5-mm o.d. NMR tube. About two hours after the reaction started, hexane was distilled off and *ca.* 0.35 ml of dried THF-d_8 was introduced into the system. The prepared THF-d_8 solution of the carbanion was transferred into an NMR tube, a small amount of TMS was added, and the tube was sealed off. The concentration of the sample was about 1.3 mol dm^{-3}, on the basis of the precursor used. The ^{1}H NMR spectra were recorded at a sweep time of 200 s and with a sweep width of 120 or 300 Hz, with a Hitachi R-20B spectrometer at 60 MHz equipped with a R-202VTC temperature controller. The temperature was calibrated with temperature-dependent chemical shifts of methanol (low-temperature range) or ethylene glycol (high-temperature range) using the standard equation. Theoretical DNMR spectra were calculated by a modified Quabex program[7] with a Hitachi M-170 computer and plotted with an on-line XY-plotter.



2-Pyridylmethyllithium 3-Methyl-2-Pyridylmethyllithium

Fig. 1. Numberings of the carbanions studied.

Results and Discussion

A typical ^{1}H NMR spectrum of the carbanion studied is given in Fig. 2. The first-order NMR parameters thus determined are given in Table 1. The parameters are almost consistent with those previously re-

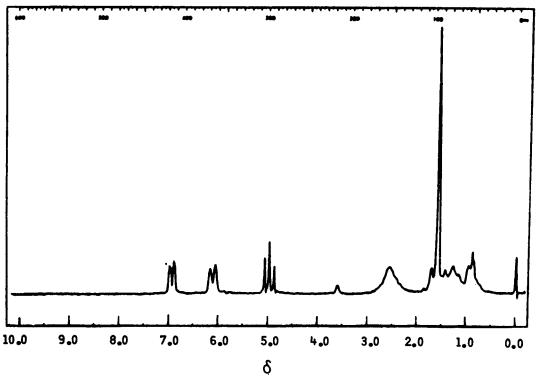


Fig. 2. ^{1}H NMR spectrum of 3-methyl-2-pyridylmethyllithium (**2**) dissolved in THF-d_8 at 60 MHz and 304.8 K. The peaks at 0.5—1.7 ppm may be due to residual butyllithium.

TABLE 1. ^{1}H NMR DATA OF 2-PYRIDYLMETHYL-(**1**) AND 3-METHYL-2-PYRIDYLMETHYLLITHIUM (**2**) IN THF-d_8 AT 304.7 K AND 60 MHz[a]

Compound	1	2
δ(2)	2.49(2.39 and 2.54 at 243.2 K)	2.59 (2.22 and 2.77 at 253.2 K)
δ(3)	5.62	1.58 (CH_3)
δ(4)	6.04	6.11
δ(5)	4.82	4.99
δ(6)	6.86	6.95
J(ab)	2.20	1.40
J(34)	9.09	—
J(35)	1.35	—
J(36)	0.96	—
J(45)	6.20	6.16
J(46)	1.97	1.60
J(56)	5.44	5.48

a) The δ values are given in ppm, referred to the internal TMS, and the J values are in Hz.

ported.[6] The DNMR analyses were carried out to the spectra of the methylene proton signals. The analyses were performed as an AB system although there is a small coupling between a methylene proton and a ring proton, as stated before.[6] The analyses need a parameter concerned with the line widths. This is determined by visual fittings of the calculated and observed spectra at both the slow- and fast-exchange limits. Two limiting T_2^* values thus determined were the same for **1** but were different for **2**. For the latter case, the T_2^* value was linearly correlated with the temperature studied. The parameters used for the DNMR analyses are given in Table 2. The chemical shift between two methylene protons of **1** was also linearly correlated with the temperature. But the value for **2** was kept constant because of the line-shape-fitting consideration. The kinetic parameters have been determined by visual fittings of the calculated lineshapes with the experimental ones. Several typical DNMR spectra are given in Fig. 3. The rate constants thus determined are given in Table 3. The thermodynamic parameters were obtained by the Eyring and Arrhenius plottings of the rate constants with inverse temperatures, one of which is shown in Fig. 4. The parameters thus determined are given in Table 4.

The hindered rotations of several substituted phenylmethanide ions have rates within the NMR-time scale and have been studied many researchers.[2,3,8-12] As compared with the values previously studied, the values obtained in this study are characteristic from

Table 2. Parameters used for the DNMR analyses of the methylene protons of 2-pyridylmethyl- (**1**) and 3-methyl-2-pyridylmethyllithium (**2**)

Compound	**1**	**2**
δ(ab)/Hz	9.50+0.040t[a)]	33.2
J(ab)/Hz	2.2	1.4
T_2^*/s	0.25	0.202+0.00012t

a) The values are dependent upon the temperatures studied, which are expressed as t given in °C.

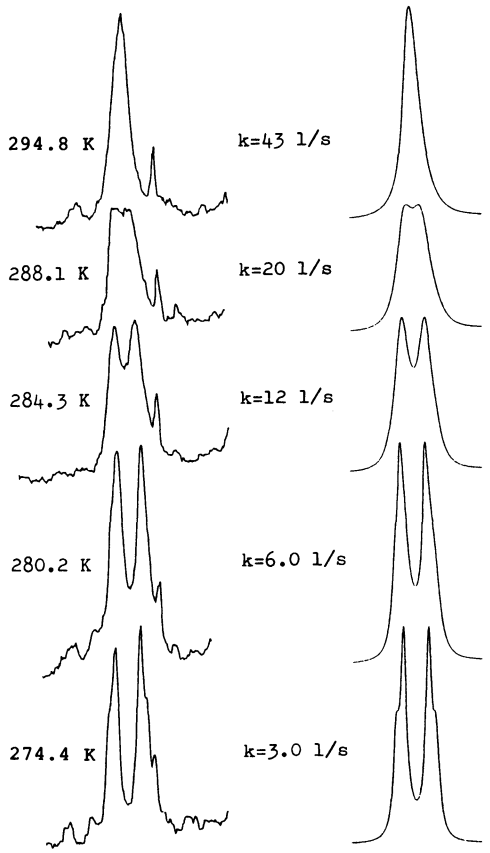


Fig. 3. Observed (left) and calculated (right) ^{1}H NMR spectra of the methylene hydrogens of 2-pyridylmethyllithium (**1**) in THF-d_8 at different temperatures and 60 MHz. An unknown peak is appeared in each oberved spectra.

Table 3. Rate constants (k) of the hindered rotation of the methylene groups in 2-pyridylmethyl- (**1**) and 3-methyl-2-pyridylmethyllithium (**2**)

1		**2**	
Temp/K	k/s^{-1}	Temp/K	k/s^{-1}
294.8	43±1.0	325.9	1500±100
288.1	20±1.0	314.4	470±10
284.3	12±1.0	304.8	150±10
280.2	6.0±0.1	302.8	69±1.0
274.4	3.0±0.1	298.5	37±1.0
269.4	1.1±0.1	294.8	25±1.0
263.3	0.5±0.1	288.1	12±1.0
		284.3	6.9±0.1
		274.4	1.8±0.1
		263.3	0.5±0.1

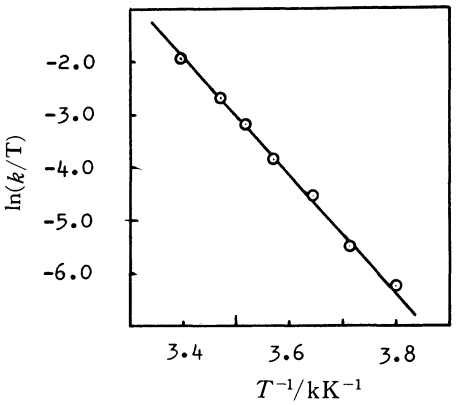


Fig. 4. An Eyring plot for the methylene rotation of 2-pyridylmethyllithium (**1**) in THF-d_8.

Table 4. Thermodynamic parameters for the hindered rotation of the methylene groups of 2-pyridylmethyl- (**1**) and 3-methyl-2-pyridylmethyllithium (**2**) in THF-d_8

Carbanion	E_a / kJ mol^{-1}	ln A	$\Delta H^{\#}$ / kJ mol^{-1}	$\Delta S^{\#}$ / J K^{-1} mol^{-1}
1	93.4±2.3	41.9±1.0	91.0±2.3	95.8±8.4
2	93.5±3.7	41.6±1.5	91.1±3.6	93.1±12.4

TABLE 5. ^{13}C NMR DATA OF 2-PYRIDYLMETHYL- (**1**) AND 3-METHYL-2-PYRIDYLMETHYLLITHIUM (**2**) IN THF-d_8 AT 298 K AND 50.3 MHz[a)]

Compound	1	2
δ(2)	164.07	163.13
δ(3)	115.80(157.5)[b)]	119.23
δ(4)	131.27(149.5)	130.49(150)
δ(5)	96.69(162)	97.22(161)
δ(6)	148.55(163.5)	146.34(163.5)
$\delta(CH_2)$	57.20(150)	55.63(150)
$\delta(CH_3)$	—	20.73(124.5)

a) The δ values are given in ppm, referred to the internal TMS. b) The values in parentheses are the one-bond coupling constants between carbon and proton given in Hz.

two view points, as follows. (1) The activation energies of the 2-pyridylmethanide ions observed are larger than those observed in the similar systems. This means that the methylene rotation is extremely hindered in the carbanions studied. (2) The activation entropies are large and positive.

Generally speaking, the barrier of the hindered rotation of the aryl group in various arylmethanide ions is related to both the extent of delocalization of the electronic charge from the α-carbon to the aryl ring and the ionic nature of the carbon-metal bond.

The hindered rotations of the lithium salts have rates within the NMR-time scale for several arylmethanide ions. But for the other salts, such as the potassium and cesium ones, the barriers are too high to be studied by the DNMR techniques.[2,9,11] The reason may be the covalent nature of the carbon-metal bond. The nature of the carbon-metal bond is related to the hybridization of the α-carbon, which is reflected by the one-bond carbon-proton coupling constants. The observed ^{13}C NMR data are given in Table 5. The $^1J(CH)$ values of **1** and **2** are about 150 Hz, which are much larger than that of phenylmethyllithium (133 Hz).[13] The observed $^1J(CH)$ of the α-carbons are almost the same with those of the C_4. This shows that the α-carbons have the high sp^2-hybridized nature which is in favor with the delocalization of the extra-electronic charge from the α-carbon to the ring. And this results in a high barrier in the carbanions. This tendency is also strengthened by the nitrogen atom in the ring, whose electron-attracting nature is profitable for the charge migration from the α-carbon to the ring.

The coalescene temperatures of the two carbanions (**1** and **2**) are about 288 and 303 K. Although they are different for the two, the activation parameters are almost the same. Therefore, the introduction of the methyl group is apparently not effective for the rotation of the methylene group. This is a peculiar and unexpected result. Because some appreciable effects of the alkyl qroups were reported by Fraenkel *et al.* and Bushweller *et al.*,[2,4] it might be expected that the introduction of a methyl group at the 3-position would cause a decrease of the rotation barrier of the bond in both the electronic and steric senses. Our experimental results are thus unexpected. Therefore, it must be noted that the 3-positioned methyl group does not interfere the methylene rotation of the carbanions studied.

The observed activation entropies of the 2-pyridylmethanide ions are large and positive. This large entropy increase would be caused by the different solvations around the lithium atom accompanied with the change of the carbanions from the ground planar structure to an excited twisted one. This explanation needs more knowledge about the solvation change of the counter cation. Therefore, it is not clear at present.

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