A DNMR Study of Restricted Methylene Rotations in Pyridyl-, Pyrimidyl-, and Quinolylmethyllithium

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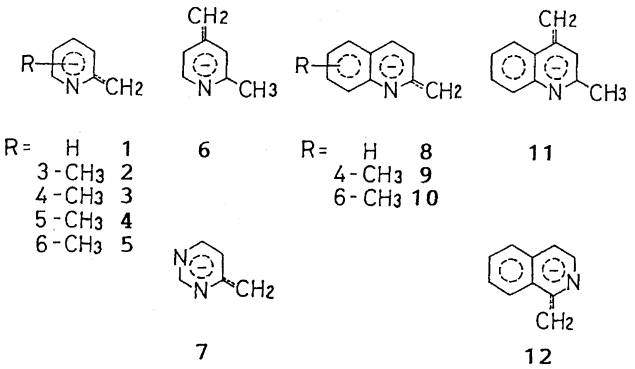
The thermodynamical parameters for the title rotations were obtained by means of the DNMR technique. The parameters can be explained in terms of both steric and electronic effects of the substituents introduced. The largest activation energy and entropy were found to be about 122 kJ mol^{-1} and 153 J K^{-1} mol^{-1} for 6-methyl-2-quinolylmethyllithium.

Many bonds with a partial double-bond character have already been studied using the DNMR techniques.[1] The ^{1}H, ^{13}C, and ^{7}Li NMR parameters for the carbanions shown in Scheme 1 were reported in a previous paper,[2] in which the carbanions were present as tight ion-pairs in tetrahydrofuran (THF) and were characterized by the π-electron densities calculated using the PPP and CNDO/2 methods. All of the carbanions in Scheme 1 contain at least one nitrogen atom in the aromatic ring. These carbanions are interesting from the view point of a comparison with the benzyl carbanions. Among the 12 carbanions in Scheme 1, the restricted rotations of the methylene groups have far been reported only for **1** and **2**.[3] In the present paper the effects of the methyl substituent, hetero-atom, and conjugated pathway to the restricted rotations are discussed regarding ten carbanions, and are compared with the previous results. Further, the effect of the crown-ether is examined, because such complexing reagents are expected to strongly affect the interaction between the carbanions and counterions.

Experimental

The starting materials and reagents used were commercially available. Preparations of the pyridylmethyllithiums were the same as those reported previously.[2] Sample concentrations were about 1.2 mol dm^{-3} in THF or THF-d_8. ^{1}H NMR spectra were observed with a Hitachi R-20B spectrometer at 60 MHz equipped with a temperature controller (R-202 VTC). The spectra of **6** were recorded with a Varian XL-200 spectrometer. The temperature of the probe was calibrated using the temperature-dependent chemical shifts of methanol (low-temperature range) or ethylene glycol (high-temperature range) along with the standard equations.[4] Theoretical DNMR spectra were calculated with a Sharp MZ-80B personal computer using a modified Quabex program, as described before,[3] and plotted with an on-line dot printer.



Scheme 1.

Results and Discussion

DNMR analyses were carried out for the methylene signals of each sample. Although there were small couplings between the methylene and ring protons,[5,6] the spectra were analyzed as an AB-spin system. The static parameters used in the DNMR analyses are given in Table 1, in which some parameters are temperature-dependent. The kinetic parameters were determined by visual fittings of the calculated line-shapes with the experimental ones. Several typical spectra are shown in Fig. 1. The thus-obtained rate constants are summarized in Table 2 for 7 carbanions. The coalescence temperatures of the observed signals were about 281, 257, 249, 333, 330, 323, and 357 K for **3**, **4**, **5**, **8**, **9**, **10**, and **12**, respectively. Thermodynamical parameters are obtained by the Eyring and Arrhenius plots of the rate constants with inverse temperatures (Figs. 2 and 3), and are given in Table 3. In the figures the plotted lines are suitably distributed and are classified

Table 1. Parameters Used for the DNMR Analyses of Carbanions

Compound	$\Delta\delta$(ab)/Hz	J(ab)/Hz	T_2*/s
1[a]	9.50+0.040t[b]	2.2	0.25
2[a]	33.2	1.4	0.202+0.00012t[b]
3	10.0	2.2	0.22
4	7.5	1.5	0.175+0.00150t[b]
5	11.7	1.9	0.217+0.00164t[b]
8	13.2	1.7	0.22
9	13.1	1.8	0.38
10	14.3	1.9	0.19
12	22.5	1.0	0.26

a) Data from Ref. 3. b) The values are dependent upon the temperatures studied, which are expressed as t given in °C.

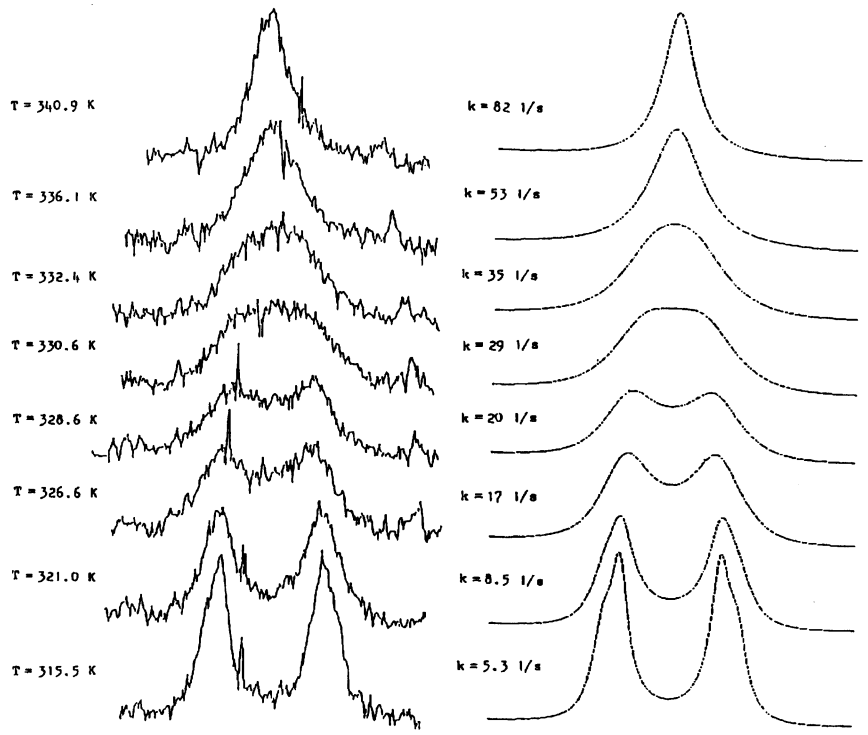


Fig. 1. Observed (left) and calculated (right) ^{1}H NMR spectra of the methylene protons of **9** in THF-d_8 at temperatures from 315.5 to 340.9 K and 60 MHz.

Table 2. Rate Constants (k)[a] of the Hindered Rotation of the Methylene Groups in Carbanions

3		**4**		**5**		**8**		**9**		**10**		**12**	
T/K[b]	k/s^{-1}	T/K	k/s^{-1}	T/K	k/s^{-1}	T/K	k/s^{-1}	T/K	k/s^{-1}	T/K	k/s^{-1}	T/K	k/s^{-1}
294.7	100	270.3	90	265.6	370	356.4	220	340.9	82	340.9	440	379.0	440
288.0	60	265.6	52	260.9	150	350.8	120	336.1	53	336.1	220	373.1	220
284.2	35	260.9	30	256.2	77	345.7	82	332.4	35	331.5	120	368.0	140
280.1	18	256.3	12	253.5	47	340.9	44	330.6	29	326.6	72	362.1	76
274.3	8.0	253.5	7.7	250.9	28	336.1	31	328.6	20	323.2	40	356.9	46
269.3	3.8	250.9	4.0	248.3	19	331.5	16	326.6	17	319.9	25	350.9	31
263.2	1.1			245.8	12	326.6	9.8	321.0	8.5	316.6	16	345.3	21
						321.0	6.5	315.5	5.3	313.6	10	340.9	12
						315.5	3.5					336.1	7.8
						310.7	1.2					331.5	4.2

a) Errors are estimated within ± 0.1 s^{-1}, ± 1.0 s^{-1}, and ± 10 s^{-1} for range of 1.0—9.9, 10—99, and 100—999, respectively. b) Errors are estimated within ± 0.5 K.

into two: One is from **1** to **5**, which has a pyridine ring; the other is from **8** to **12**, which has a quinoline or isoquinoline ring. The former plotted lines have slopes smaller than do the latter ones. The methylene groups of **6**, **7**, and **11** show no change in their line shapes over a temperature range of from -70 to 100°C. The signals of **7** and **11** appear as a quartet of an AB-spin system, even at 100°C. The signal of **6** has a singlet-like pattern at -70°C at 60 MHz; however, it splits into two at 90 °C and 200 MHz. This doublet seems to be two inner lines of the quartet of an AB-spin system. Therefore, the coalescence temperatures of the methylene signals of **6**, **7**, and **11** would be higher than 373 K. Several NMR data are given in Table 4.

Effect of Methyl Substituent. Among the anions from **1** to **5**, the activation energies are almost the same, except for that of **4**. The effect of the methyl group in **4** can be mainly explained by the mesomeric effect of the substituent, as compared with those in others. If it is correct, the mesomeric effect must also be expected for the substituent in **2**. However, the methyl group of **2** gives no effect for the activation energies, as compared with those of **1**, as pointed out previously.[3] This does not seem to be reasonable, compared with the substituent effect of **4**. It can thus be explained based on the assumption that the mesomeric effect of the methyl substituent of **2** doesn't result from a sterical point of view. Indeed, the ^{1}H chemical shifts given

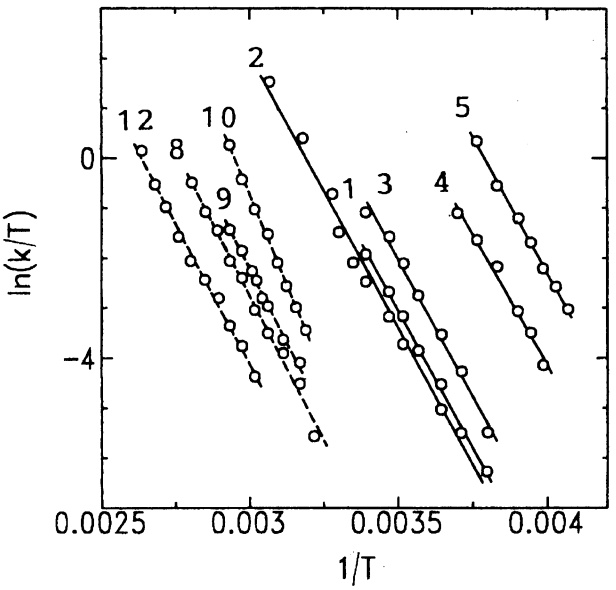


Fig. 2. Eyring plots for the restricted methylene rotations of nine carbanions.

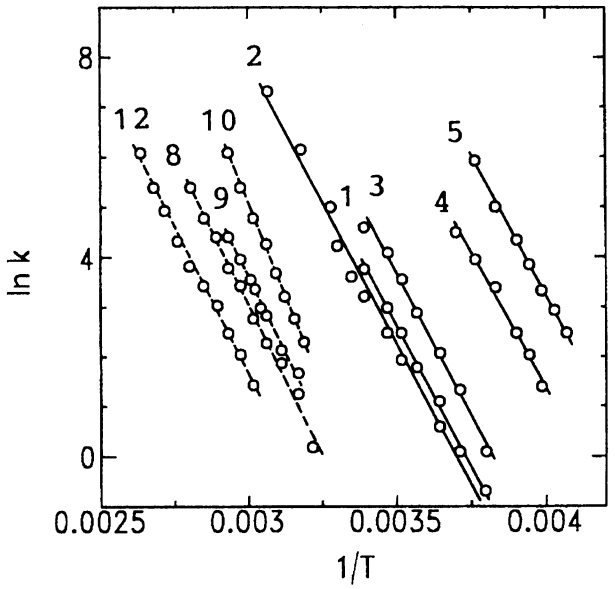


Fig. 3. Arrehnius plots for the restricted methylene rotations of nine carbanions.

in Table 4 show a large chemical shift difference between two methylene protons in **2** due to the steric effect. Another point of interest is that **10** has the largest activation energy and entropy. The 6-methyl group of **10** gives the largest increase compared with that of **8**. However, the direction of the increment is reversed to that of **4** to **1**, and the magnitude of the effect of **10** to **8** is very different from that of **4** to **1**. Therefore, the effect cannot be similarly explained in terms of the mesomeric effect of the substituent. Another different interpretation is necessary. The values for **8** and **9** are quite similar. Then, although the effect of the 4-methyl group of **9** is small in the quinolyl ring, that of the 6-methyl group of **10** is extremely large. The ^{13}C chemical shift of **10** given in Table 4 shows the most upfield shift among those in **8** to **11**. This suggests that the negative charge on the methylene carbon is rich, and that the carbon–lithium interaction must be large.

Table 3. Thermodynamic Parameters for the Hindered Rotations of the Methylene Groups of Carbanions

Compound	E_a / kJ mol^{-1}	log A	$\Delta H^{\neq}$ / kJ mol^{-1}	$\Delta S^{\neq}$ / J K^{-1} mol^{-1}
1[a]	93.4±2.3	18.2±0.4	91.0±2.3	95.8± 8.4
2[a]	93.5±3.7	18.1±0.7	91.1±3.6	93.1±12.4
3	93.6±4.0	18.7±0.7	91.3±4.0	106.0±14.5
4	89.8±5.1	19.4±1.0	87.7±5.1	118.8±19.7
5	93.0±1.7	20.8±0.3	90.8±1.7	146.6± 6.8
8	99.5±3.0	16.9±0.5	96.7±3.1	69.6± 9.2
9	100.2±3.2	17.3±0.5	97.5±3.2	76.6± 9.7
10	121.7±1.9	21.3±0.3	119.0±1.9	153.3± 5.7
12	97.0±2.6	15.9±0.4	94.1±2.6	50.4± 7.3

a) Data from Ref. 3.

Table 4. ^1H and ^{13}C NMR Data of Methylene Groups of Carbanions in THF-d_8 or THF[a]

Compound	^1H [b]	^{13}C [c]	$^1J_{CH}$ [d]
1[e]	2.49 (2.39 and 2.54 at 243.2 K)	57.20	150
2[e]	2.59 (2.22 and 2.77 at 253.2 K)	55.63	150
3	2.51 (2.59 and 2.76 at 243.2 K)	56.36	150
4	2.46 (2.33 and 2.46 at 243.2 K)	54.17	150
5	2.44 (2.38 and 2.58 at 223.2 K)	53.81	148
6	2.59	63.95	152
7	2.84 and 3.12	72.31	155
8	2.88 and 3.10	70.01	153.5
9	2.87 and 3.09	69.34	153
10	2.87 and 3.11	68.48	—[f]
11	3.40 and 3.56	72.25	154.5
12	3.24 and 3.61	67.42	153

a) The δ values are given in ppm, referred to the internal TMS, and the J values are in Hz. b) ^1H chemical shifts of the methylene protons at 304.7 K and 60 MHz. c) ^{13}C chemical shifts of the methylene carbon at 298.2 K and 50.31 MHz. d) $^1J_{CH}$ of the methylene carbon at 298.2 K and 50.31 MHz. e) Data from Ref. 3. f) The value is not available because of overlapping with large solvent peaks.

Effect of the Nitrogen Atom and Nature of the Active Methylene. The activation energies given in Table 3 are larger than about the 59 kJ mol^{-1} observed in phenylmethanide ions.[7] The effect of the nitrogen atom can therefore be evaluated to cause an increase of at least about 30 kJ mol^{-1} for the activation energy. Further, the methylene rotation of **7** seems to be extremely restricted, even at 100°C, due to two nitrogens in the aromatic ring. The electronic circumstances of the active methylene carbons in the anions can be known by measuring the one-bond carbon–proton coupling constants ($^1J_{CH}$), which are dependent upon the

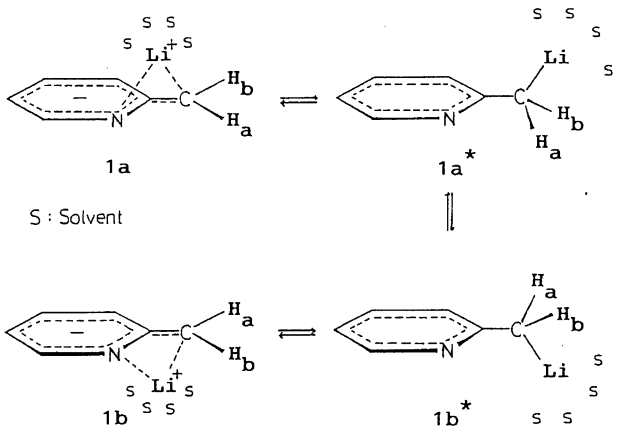
hydridization of the methylene carbons. These coupling constants fall into a narrow range of about 150 Hz, as given in Table 4. It is therefore concluded that the methylene carbons are nearly sp^2-hybridized. The $^1J_{CH}$ is larger in **7** than in **1**, while **5** has the smallest.

The activation energies of **8** and **9** are larger than those of **1** and **3**. This is ascribed to an extension of the conjugation pathway. This is also supported by their $^1J_{CH}$ values, which in **8** and **9** are 3 Hz larger than those of **1** and **3**, respectively. Moreover, this is further supported by the ^{13}C chemical shifts of the methylene carbons, which in **8** and **9** are about 13 ppm larger than those of **1** and **3**.

The methylene rotations of **6** and **11** (the γ-type anion) are more restricted than those of **3** and **9** (the α-type anion), respectively. These are also reflected by their $^1J_{CH}$ and ^{13}C chemical shifts.

Activation Entropies. The activation entropies obtained are large and positive, as was pointed out previously.[3] Regarding the carbanions of the first group, the values increase in the order **2**, **1**, **3**, **4**, and **5**. As described in previous papers, these carbanions form tight ion pairs.[2,6] If this is true, the lithium ion would situate above the center of a triangle plane formed by the N, C_2, and C_α atoms for the α-type carbanions, which is similar to that determined by a classical X-ray analysis of the benzyl anion.[8a] However, the structure seems to be strongly dependent upon its surroundings.[8b,8c] Then, one explanation of the positive activation entropy is considered as given in Scheme 2. If it has a η^3-type coordination, the lithium bonding with a nitrogen atom must be broken at the moment of the rotation of the methylene group. This change can be expressed as 1a→1a*, followed by a methylene rotation (1a*→1b*). The over-all rotation can be expressed as 1a→1b. In the process of this change, the lithium atom is loosely surrounded by several solvent molecules in 1a* or 1b*, but closely in 1a or 1b. The form of 1a* or 1b* has one lithium–carbon bonding in the carbanion. We considered another form which contains one lithium–nitrogen bonding. The former form was shown to have a heat of formation 49 kJ mol^{-1} lower than the latter, using the MNDO MO method.[9] The 1a→1a* change explains the positive activation entropy in the rotation of the methylene group in the picolyl carbanion.

In the second group, the activation entropies are smaller than those of the first group, except for that of **10**. The ^{13}C chemical shifts of the active methylene carbons in the second group are more deshielded than those of the first group, as given in Table 4. This is ascribed to the size of the delocalization network, causing a decrease in the interaction between the active carbon or nitrogen atom with lithium, which affects their bonding. Thus, the activation entropies decrease in the second group. In addition to the solvation of the ion-pair, an interaction between the lithium and nitrogen atoms seems to play an important role in these carbanions; **10** has the largest activation entropy and **8** has a rather small one in the second group. The values of 69.6 and 50.4 J K^{-1} mol^{-1} of **8** and **12** are still large as compared with the small values of 2- and 1-naphthylmethanide ions (1.3 and 6.3 J K^{-1} mol^{-1}).[10]



Scheme 2.

Effect of Crown Ethers. The behavior of the lithium ion would be perturbed by the presence of a complexing reagent, such as crown ether. For the rotation of the active methylene carbon of **1** the activation energy, enthalpy, and entropy of **1** decreased to 74.4, 72.0 kJ mol^{-1}, and 30.2 J K^{-1} mol^{-1}, respectively, with an equimolar addition of 15-crown-5. The use of 18-crown-6 did not have any effect on the THF solution. This is ascribed to the complexing ability of the crown ether to the lithium ion. The former crown is thus effective for solvation of the lithium ion, while the latter crown is not so effective, its effectiveness being as little as that of the solvent (THF).

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