January, 1990] © 1990 The Chemical Society of Japan **N O T E S** Bull. Chem. Soc. Jpn., 63, 241—243 (1990) 241

Carbon-13 NMR Study of Naphthylmethanide Ions in Polar Solvents

Yukihiro Yokoyama† and Kensuke Takahashi*
Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466
†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

(Received April 5, 1989)

Synopsis. The ^{13}C NMR parameters for 1- and 2-naphthylmethanide ions were obtained in two polar solvents, THF and HMPA. Excess charge distributions in the ions are discussed in connection with the nature of the solvents.

A number of NMR studies have been carried out concerning carbanions which have phenyl rings that have stabilizing and delocalizing effects regarding excess charge in the anionic species.[1] The naphthyl ring is considered to have a larger delocalizable field of excess charge than does the phenyl ring, since the resonance energy of naphthalene is larger by ca. 110 kJ mol^{-1} than that of benzene.[2] Therefore, delocalization of the excess charge is considered to be more effective in the naphthyl ring than in the phenyl ring. Naphtylmethanide ions were previously reported by Kronzer and Sandel who made investigations using the proton NMR technique.[3] In their study, however, the estimation of the excess charge distribution in the molecule was not sufficiently described.

In the present work we examined the hitherto unreported ^{13}C NMR parameters of the 1- and 2-naphthylmethanide ions (**1** and **2**) in polar solvents. Here, we discuss the excess charge distributions in the naphthyl ring and their form around the anionic center, while comparing it with the phenylmethanide ion (**3**). Both phenyl- and naphthylmethanide ions are fundamental and typical carbanions, with charge distributions in the molecules worth knowing and investigating from a theoretical point of view.

Experimental

The starting materials, 1- and 2-bromomethylnaphthalenes, were commercially available. The solvent used for the preparation of anionic sample solutions, tetrahydrofuran (THF), was refluxed upon sodium metal, distilled, degassed, and finally kept on a sodium–potassium alloy. Hexamethylphosphoric triamide (HMPA) was dried and distilled over calcium hydride, and then degassed and stored in sealed vessels with a breakable seal.

Naphthylmethyl alkali metal salts were generated from the corresponding bromides by means of halogen–metal exchange reaction. The starting material was in contact with lithium or sodium metal flakes in a solvent at room temperature in a handmade reaction vessel under vacuum. The solution was kept in the vessel with stirring for three or four hours until the reaction solution became rust-colored. Then, the resulting solution was filtered into an NMR tube attached to the reaction vessel, and the sample was sealed under vacuum. All of the NMR samples were prepared as approximately 0.5 mol dm^{-3} solutions sealed in 5- or 10-mm o.d. tubes.

It is well-known that the reactions of aryl halide with organolithium often give better yields than does the reactions of halides with lithium metal, due to less side reaction.[4] In this work, however, we obtained pure sample solutions of naphthylmethanide ions NMR-spectroscopically, employing a direct reaction of bromomethylnaphthalene with metal lithium. Typical ^{13}C NMR spectra are shown in Fig. 1.

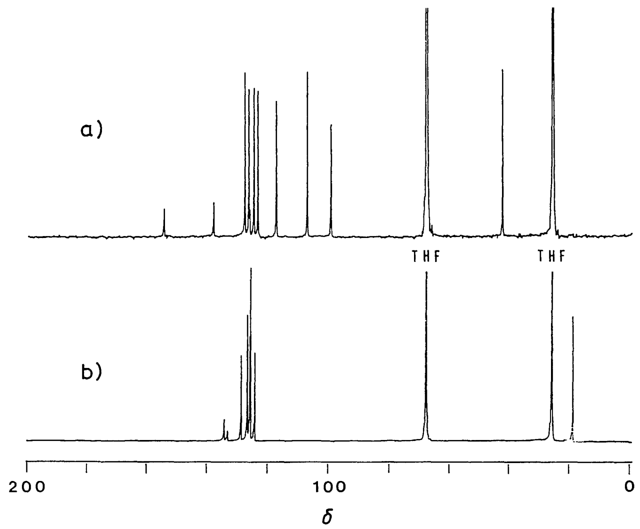

Fig. 1. ^{13}C NMR spectra at ambient temperature (ca. 25 °C) in THF. (a) 1-Naphthylmethyllithium and (b) 1-methylnaphthalene.

All of the NMR spectra were measured on a Varian XL-200 Fourier transform spectrometer at ca. 25 °C. The ^{1}H and ^{13}C chemical shifts were evaluated from the solvent peak used as an internal reference and then converted to δ_H and δ_C values from TMS, by taking δ_H 1.79 and δ_C 26.4 for THF, and δ_C 37.0 for HMPA. Spectral assignments were ascertained by ^{1}H{^{1}H} decoupling, ^{13}C{^{1}H} selective decoupling, or the HETCOR method.

Results and Discussion

Chemical Shifts and Excess Charge Distributions. The carbon chemical shifts of 1- and 2-naphthylmethanide ions (**1** and **2**) and the corresponding neutral molecules, 1- and 2-methylnaphthalenes (**1a** and **2a**) are collected in Table 1. For comparison's sake, the values for the phenylmethanide ion (**3**) and toluene (**3a**) are also included in the table. The large shift changes of the carbons caused by the conversion of hydrocarbons into anions are transpired from the data given in Table 1 and the spectra given in Fig. 1. The C_1 of **1**, or the C_2 of **2** which attaches to the active center, and the α-carbons are significantly deshielded. This tendency of the downfield shift changes is similar to the trend observed in phenylmethanide ions.[9] The C_3, C_8 (in THF), and C_{10} of **1** and the C_9 of **2** are also slightly deshielded. All other ring carbons, on the other hand, are shielded. The largest variations of the ring carbons

Table 1. ^{13}C Chemical Shifts of the Alkali Metal Naphthylmethanides and the Corresponding Neutral Molecules at 25 °C

Compd.	Counter cation	Solvent	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_α
1	Li	THF	154.80	107.68	128.17	99.89	126.90	123.95	117.77	125.27	126.59	138.44	43.27
1	Li	HMPA	148.13	105.16	127.58	89.72	124.09	122.90	112.90	123.92	125.73	140.46	60.46
1	Na	THF	150.27	103.44	128.39	95.31	125.88	124.04	116.94	124.17	124.62	138.74	49.66
1a	—	THF	134.89	127.33	126.30	127.23	129.30	126.30	126.50	124.81	133.67	134.71	19.52
1a	—	HMPA	134.21	127[a]	126[a]	127[a]	129.16	126[a]	126[a]	124.44	133.11	134.11	19.50
2	Li	THF	101.91	156.62	121.18	126.57	127.30	112.19	125.20	125.98	139.52	123.84	44.31
2	Li	HMPA	95.62	149.75	121.69	126.20	126.43	104.70	124.96	125.47	140.92	122.79	61.64
2a	—	THF	127.60	136.03	128.71	128.45	128.32	125.64	126.54	127.98	132.92	134.85	21.78
2a	—	HMPA	127.38	135.39	128[a]	128[a]	128[a]	125.50	126.40	127.87	132.48	134.36	21.79
3[b]	Li	THF	161.5	117.0	128.6	104.7	128.6	117.0	—	—	—	—	36.9
3[b]	K	THF	153.2	111.0	130.8	95.6	130.8	111.0	—	—	—	—	52.8
3a[b]	—	THF	138.5	129.7	129.0	126.1	129.0	129.7	—	—	—	—	21.5

a) With large uncertainty due to overlapping. b) The values are cited from Ref. 9.

in the anions are −27.34 and −25.69 ppm at the C_4 of **1** and the C_1 of **2**, respectively in THF. It is pointed out that the C_{10} of **2** also shows a relatively large upfield shift (−11.01 ppm).

In the π-systems the ^{13}C chemical shift can be used to evaluate the π-electron density (ρ^π) in a molecule using the following empirical equation:

$$\delta = a + k\rho^\pi$$

where a and k are constants of 290 ppm and 160 ppm/electron, respectively.[1,10] Thus, the electron densities on the carbon atoms can be estimated by using the above equation. Then, the total π-electron densities for anions **1** and **2** are experimentally evaluated to be 11.78—11.93, which are consistent with the theoretical value of 12. The relatively large increase of π-electron densities caused by the conversion of the neutral molecules into the anions were recognized on the C_2, C_4, C_7, and C_9 of **1**, and the C_1, C_3, C_6, and C_{10} of **2**. The positions of the carbon atoms where the electron density increases, are consistent with those expected from a consideration of the possible resonance structures. These facts suggest that in naphthylmethanide ions the dominative factor of the charge distribution in the naphthyl rings is a probable pπ–pπ interaction, and that the excess charge of the anions is delocalized into the whole naphthyl ring. The extent of the delocalization, therefore, can be known from the chemical shift changes from the C_4 of **1a** to that of **1**, and from the C_6 of **2a** to that of **2**, taking into consideration that there is no steric inhibition of resonance interactions at these positions. Thus, the ^{13}C NMR shift changes in these carbon atoms are quantitatively reliable indicators of excess charge distribution as well as the para-carbon shift change in the phenylmethanide ions.[11]

The excess charge distributions in the anionic species are considerably affected by the counter cations and solvents. For example, the π-electron densities estimated for the lithium salts of the naphthylmethanide ions in HMPA are quite different from those evaluated in THF.

$^1J_{CH}$ of the Anionic Centers and Rehybridization Effect. The one-bond C–H coupling constants of the anionic centers and the corresponding methyl groups are summarized in Table 2. It is pointed out that the values of $^1J_{CH}$ of the C_α of **1** and **2** (139—152 Hz) are significantly larger than those of **1a** and **2a** (126—127 Hz), and even those of the phenylmethanide ions[12] (116—135 Hz). It has been well-known that $^1J_{CH}$ are very sensitive to hybridization of the carbon atom. The changes in the $^1J_{CH}$ of the naphthylmethanide ions, therefore, can be mainly attributed to the rehybridization of the carbon atoms from sp^3 in **1a** or **2a** to sp^2-hybridized character in the anions. It should be noted that the $^1J_{CH}$ in HMPA solutions (152 and 152 Hz) are consistent with those of typically sp^2-hybridized carbons.[13] These facts demonstrate that naphthylmethanide ions in HMPA can be assumed to be complete π-systems, while the anions in THF have a somewhat sp^3-hybridized character at the active center,

Table 2. One-Bond ^{13}C–^{1}H Coupling Constants for the Anionic Centers of the Carbanions and Their Corresponding Neutral Hydrocarbons under Several Conditions

Compd.	Counter cation	Solvent	$^{1}J_{CH}$[a]
1	Li	THF	142
1	Li	HMPA	152
1	Na	THF	149
1a	—	THF	126
1a	—	HMPA	126
2	Li	THF	139
2	Li	HMPA	152
2a	—	THF	127
2a	—	HMPA	126
3	Li	THF	132[b]
3	Li	Et_2O	135[b]
3a	—	THF	126[b]

a) In Hz with accuracy of ±1 Hz. b) The values are cited from Ref. 12.

since their $^{1}J_{CH}$ values in THF are somewhat smaller than those in HMPA. This is analogous to the situation that the π-electron density of the ring in an HMPA solution is larger than that in THF (as described above). Thus, the phenomena are associated with an equilibrium established between contact ion pairs (CIP) and solvent-separated ion pairs (SSIP), which is generally considered in anionic solutions. The lithium salts are in the SSIP or the free ions in HMPA, but not in THF. The anionic centers in a THF solution interact strongly with the counter cations so that any excess charge is more localized on the center atom than that in HMPA.

The Origin of the Charge Delocalization. In solutions of the anions, it must generally be considered that the anionic species interact with the counter cations as an equilibrium between CIP and SSIP. The situation of the ion pairs varies with solvent and kind of counter cation. It seems that the hybridization of C_α atoms of the naphthylmethanide ions is determined by the manner of interaction with a counter cation. Thus, in the case of a free ion or a SSIP whose counter cation is highly solvated, the anionic center is assumed to be in a complete sp^2-hybridization and forms a π-system on the whole molecule. The charge transmission into the aromatic ring, therefore, is mainly governed by an exact $p\pi$–$p\pi$ interaction between the anionic center and its adjacent carbon. On the other hand, in the case of CIP, whose covalency of the carbon–lithium bond increases somewhat, any excess charge tends to locate on the α-carbon atom. Therefore, the polarization between the C_α and the aromatic ring increases. The extent of polarization can be known from the ^{13}C-shift difference between the active carbon and the substituted carbon, C_1 of **1** or C_2 of **2**. The present data of Table 1 show that the polarization is larger in THF than in HMPA for both **1** and **2**.

Generally, there are two major mechanisms in the transmission of the electronic effect from the anionic center to the aromatic ring, namely resonance and polarization effects.[14] The charge distribution on the anionic molecules is presumed to be made up of a superposition of resonance and polarization effects. It should be pointed out that the dominating factor, either the resonance or the polarization, depends on the hybridization of the active center of the anion.

The authors wish to thank Messrs. Katsuhiko Kushida and Hajime Katoh (Varian Instruments Ltd.) for their kindness in measuring several HETCOR spectra at 300 MHz. This work was partly supported by a Grant-in-Aid for Scientific Research (1988), No. 63540336, from the Ministry of Education, Science and Culture.

References

1) E. H. O'Brien, "Comprehensive Carbanion Chemistry," ed. by E. Buncel and T. Durst, Elsevier, New York (1980), Vol. 5A, p. 271.

2) L. Pauling, "The Nature of The Chemical bond," 3rd ed., Cornell Univ. Press, New York (1960).

3) F. J. Kronzer and V. R. Sandel, *J. Am. Chem. Soc.*, **94**, 5750 (1972).

4) J. C. Stowell, "Carbanions in Organic Synthesis," John Wiley & Sons, New York (1979).

5) J. W. Emsley, S. R. Salman, and R. A. Storey, *J. Chem. Soc. B*, **1513**, (1970).

6) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

7) K. Takahashi, M. Takaki, and R. Asami, *Org. Magn. Reson.*, **3**, 539 (1971).

8) W. Brügel, "Handbook of NMR Spectral Parameters," Heyden & Son Ltd., London (1979), Vol. 1, p. 33.

9) K. Takahashi, Y. Kondo, R. Asami, and Y. Inoue, *Org. Magn. Reson.*, **6**, 580 (1974).

10) a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960). b) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, **1961**, 468.

11) G. A. Olah and R. J. Hunadi, *J. Am. Chem. Soc.*, **102**, 6989 (1980).

12) R. Waack, L. D. McKeever, and M. A. Doran, *Chem. Commun.*, **1969**, 117.

13) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972).

14) E. Buncel, T. K. Venkatachalam, B. Eliasson, and U. Edlund, *J. Am. Chem. Soc.*, **107**, 303 (1985).