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LITHIUM-7 NMR STUDIES OF ALKYLARENELITHIUM SALTS

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Summary

Solutions of alkylarenelithium salts chelated by a diamine (TMEDA) or a tetraamine (HMTTA) were studied by ^{7}Li NMR. Good correlations between the chemical shift and the pK of the parent hydrocarbon are obtained in each case. Shielding is higher when tetraamine is used. Steric hindrance to solvation reduces the chemical shifts of the ethylnaphthalene and 2-methylnaphthalene salts.

Introduction

This investigation forms part of a more general study on the reactivity of the lithium salts of alkylaromatic hydrocarbons in the proton exchange reaction (metalation), and in the alkylation of olefins. In general, the reactivity of these salts is linked to their basicity, i.e. inversely proportional to the acidity of the corresponding hydrocarbon, and it is possible to define a pK_a scale based on the metalation [1,2]. Yet the steric effects, on one hand, and the nature of the ion pairs on the other (contact ion pairs or ion pairs separated by the chelating agent) complicate this simple picture.

Additional information about the structure of these salts can be obtained by ^{7}Li NMR spectroscopy, since the ^{7}Li chemical shift is a function of its first solvation layer [3]. The shift is thus expected to depend predominantly on the nature of (a) the anion; (b) the solvent or chelating agent; and (c) the pair of ions formed. Our objective was to check this.

Results and discussion

In order to reveal the effect of the complexing agent, which acts on both cation solvation and the nature of the ion pairs, we used two amines with very different chelating powers, viz. tetramethylethylenediamine (TMEDA) and hexamethyltriethylenetetraamine (HMTTA). The chemical shifts obtained using these two amines are shown in Table 1 for a series of salts of hydrocarbons of increasing

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TABLE 1

LITHIUM-7 NMR CHEMICAL SHIFTS FOR LITHIUM SALTS OF ALKYLARENES CHELATED WITH TMEDA AND HMTTA

Hydrocarbons used for lithium salt formation	Symbol	^{7}Li (ppm) [a]		ΔpK [d]
		TMEDA [b]	HMTTA [c]	
p-Xylene	pX	0.66	0.75	0.96
p-t-Butyltoluene	ptBT	0.45	0.63	0.72
Mesitylene	Mes	0.48	0.60	0.43
Toluene	Tol	0.76	1.05	0
1,4-Dimethylnaphthalene	1,4 DMN	1.11	1.70	−0.88
2,6-Dimethylnaphthalene	2,6 DMN	0.45	1.20	−1.05
2-Methylnaphthalene	2 MN	0.98	1.60	−1.66
2-Ethylnaphthalene	2 EN	0.78	1.50	−1.76
1-Methylnaphthalene	1 MN	1.71	2.45	−1.91
1-Ethylnaphthalene	1 EN	0.79	0.70	−2.01
Diphenylmethane	DPM	2.68	insoluble	−3.75

[a] Relative to n-butyllithium [b] *N,N,N′,N′*-Tetramethylethylenediamine. [c] Hexamethyltriethylenetetraamine. [d] Derived from metalation equilibrium constants [2].

acidity. Except for the diphenylmethyllithium-tetraamine complex, which does not give homogeneous solution, it can be seen that the lithium is more shielded by the tetraamine than by the diamine.

It is also evident from Table 1 that the shielding generally increases with the acidity of the hydrocarbon used to form the salt. Table 1 also shows the pK_a's of these hydrocarbons as defined by the proton–lithium exchange reaction [1,2].

$$R^1H + R^2Li \overset{K_{12}}{\rightleftarrows} R^1Li + R^2H$$

$$\Delta pK_{12} = -\log K_{12}$$

The pK_a values for the two ethylnaphthalenes were derived from values obtained by Streitwieser et al. [4] with caesium salts in cyclohexylamine. (Significant pK_a values cannot be obtained from lithium salts in the case of two sterically hindered compounds [5]). Use of this pK scale leads to the plots shown in Fig. 1 and 2, which show that there is a fairly good correlation between the ^{7}Li chemical shift and the pK_a of the corresponding hydrocarbon, at least when the salts from the ethyl- and 2-methylnaphthalenes are excluded.

The increase in the shielding of the cation (involving shifts to higher fields) with the acidity of the corresponding hydrocarbon can be attributed to the fact that higher acidities are associated with greater delocalization of the charge in the anions. We assume that the greater the delocalization the stronger are the ring currents and the larger the increase in the shielding of the cation, which is probably located above the π cloud of the aromatic rings [6].

The effect of the number of amine coordination sites (greater shielding for the more chelating amine) is at first surprising. However, Cox et al. have shown that shielding generally decreases as the base strength of the solvent increases [3]; this is due to overlap between the solvent donor atoms and the Li orbitals [7–9].

Melchior et al. have also observed that the lithium bromide shielding decreases when diamine (TMEDA) is replaced by tetraamine (HMTTA) [10]. In our case, the problem is more complex since the more chelating polyamine favours the formation of ion pairs separated by chelation [1,2] and this leads to greater delocalization of the charge over the aromatic nucleus and on increase in the ring current. In our

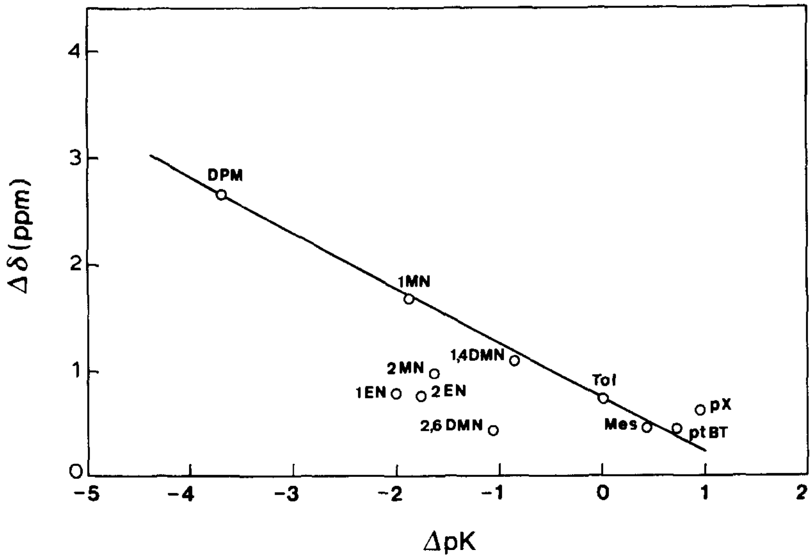


Fig. 1. Correlation between ^{7}Li NMR chemical shifts of the lithium salts TMEDA · complex and the ΔpK of the parent hydrocarbons. pX = p-xylene. ptBT = p-t-butyltoluene. Mes = mesitylene. mX = m-xylene. Tol = toluene. 1,4DMN = 1,4-dimethylnaphthalene. 2,6DMN = 2,6-dimethylnaphthalene. 2MN = 2-methylnaphthalene. 2EN = 2-ethylnaphthalene. 1MN = 1-methylnaphthalene. 1EN = 1-ethylnaphthalene. DPM = diphenylmethane.

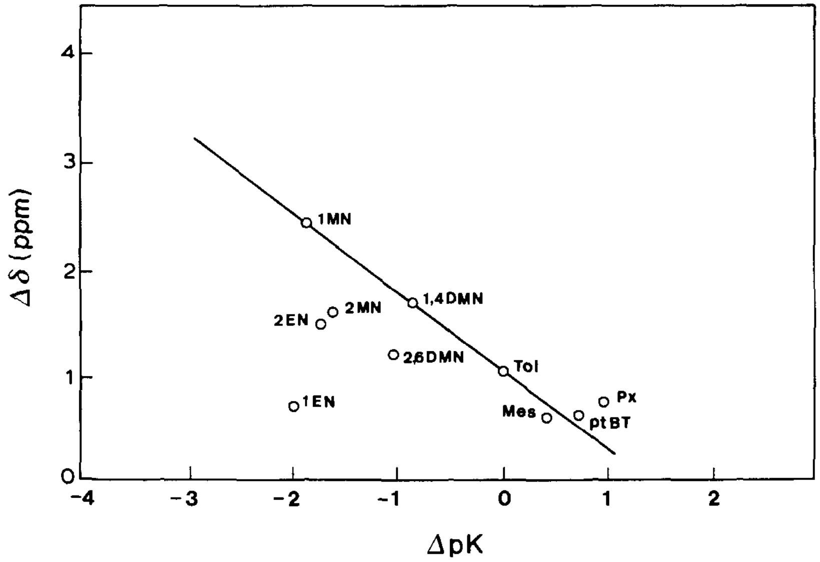
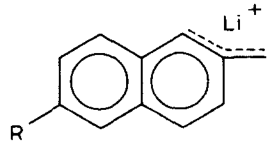


Fig. 2. Correlation between ^{7}Li NMR chemical shifts of the lithium salts HMTTA · complex and the ΔpK of the parent hydrocarbons.

system it seems that of these two opposed effects the second prevails, increased shielding being observed in all cases when diamine is replaced by tetraamine.

The steric effect of the methyl group in an α position with respect to the carbanion interferes with solvation, and so reduces the delocalization. This explains why the chemical shifts for the lithium salts of the ethylnaphthalenes deviate markedly from the lines drawn in Fig. 1 and 2. Figure 2 also reveals that the lithium salt of 1-ethylnaphthalene in the presence the more bulky tetraamine is doubly hindered, not only by the α-effect just mentioned but also by a peri type interaction with the second aromatic nucleus.

Another feature of the lithium salts of 2-methylnaphthalene and 2,6-dimethylnaphthalene should be mentioned, viz. that these compounds can form allylic complexes, the cation being located preferably in the plane defined by the three carbons of the allylic system [6,11], i.e. in the naphthalene plane defined by the aromatic rings and thus outside the ring currents:



(R = H or CH_3)

More information about the structure of these complexes can be obtained from the ^{13}C chemical shifts for the carbon atom bearing the anionic charge. The influences of the polyamines on these chemical shifts are shown in Table 2 along with those for the ethers [12].

Waack et al. have explained the effect of deshielding of the α carbon relative to the neutral molecule in terms of the rehybridization $sp^3 \rightarrow sp^2$ brought about by solvation [12,13]. The data in Table 2 thus provide a measure of the relative base strength in these systems of the amines and the ethers.

The effect of an increase in sp^2 character on the ^{13}C shift is also evident when toluene is compared with 1-methylnaphthalene, which has a more readily delocalized anion. Table 3 shows the deshielding is larger for the latter.

The effect of the allylic nature of the lithium salt of 2-methylnaphthalene is again evident. The salt from 2-methylnaphthalene, which is a less acidic hydrocarbon would be expected to have less sp^2 character, but the ^{13}C data show that this is not the case with either diamine (TMEDA) or tetraamine (HMTTA), in keeping with the ^7Li data.

TABLE 2

LITHIUM-7 NMR CHEMICAL SHIFTS RELATIVE TO THE NEUTRAL MOLECULE IN DIFFERENT MEDIA

Solvent or complexing agent	Δ (ppm)[a]
Diethyl ether	3.5[b]
Tetrahydrofuran	9.0[b]
N,N,N′,N′-Tetramethylethylenediamine	13.7[c]
Hexamethyltriethylenetetraamine	16.5[c]

[a] Difference of chemical shift between the anion and the neutral carbon. [b] From ref. 12. [c] Results obtained in our laboratory.

TABLE 3

CARBON-13 NMR CHEMICAL SHIFTS FOR ALKYLARENE HYDROCARBONS AND THEIR LITHIUM SALTS

Hydrocarbons and their lithium salts	$\delta(^{13}C_\alpha)$ (ppm) [a]	Δ (ppm) [b]
Toluene	21.53	
Benzyllithium·TMEDA	35.27	13.74
Benzyllithium·HMTTA	38.06	16.53
1-Methylnaphthalene	19.30	
1-Lithiomethylnaphthalene·TMEDA	44.25	24.95
1-Lithiomethylnaphthalene·HMTTA	46.48	27.18
2-Methylnaphthalene	21.50	
2-Lithiomethylnaphthalene·TMEDA	46.64	25.14
2-Lithiomethylnaphthalene·HMTTA	52.62	31.12

[a] ^{13}C chemical shift relative to TMS. [b] Difference of chemical shift between the anion and the neutral carbon.

Conclusion

The ^7Li chemical shifts of the lithium salts derived from some aromatic hydrocarbons correlate with the pK_a's of the hydrocarbons, indicating that the variations in the chemical shifts are mainly due to the influence of the ring currents of the aromatic rings on the lithium atom. The proportion of the carbanionic charge delocalized over the aromatic nucleus depends on the nature of the chelating amine and of the hydrocarbon. Such a correlation with pK_a values has the advantage of revealing anomalies due to steric effects or to special structural features.

Experimental

The lithium salt solutions of the alkylaromatic hydrocarbons were prepared from 1.6 *M* n-butyllithium in hexane.

A mixture of 0.01 mol of n-butyllithium, 2 ml of the alkylaromatic hydrocarbon, and 0.01 mol of the chelating polyamine in a nitrogen-filled vessel was diluted with 5 ml of benzene. The lithium salt of the alkylaromatic hydrocarbon was formed in approximately 2 h in a concentration of ca. 0.7 mol/l.

A 1 ml portion of this solution was transferred to an NMR tube which was then tightly sealed, and placed inside a larger sealed tube containing 0.5 ml of 1.6 *M* n-butyllithium in n-hexane + 0.5 ml hexadeuterated benzene as external standard. The ^7Li NMR spectra were recorded with an accuracy of ± 0.05 ppm, at 30°C on a Varian FT-80-A spectrometer at 30.913 MHz. Details of the recording procedure are as follows: spectral width, 3000 Hz; acquisition time, 1.3 s; pulse width, 10 μs; accumulation over 8192 points; number of transients, 1 to 100.

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