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THE ^{1}H AND ^{7}Li MAGNETIC RESONANCE SPECTRA OF SOME ARYLLITHIUMS

J. PARKER AND J. A. LADD
Department of Chemistry and Applied Chemistry, University of Salford, Salford (Great Britain)

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SUMMARY

The ^{1}H magnetic resonance spectra of phenyllithium, *meta*- and *para*-tolyllithium and the corresponding chloro derivatives have been analysed and, where possible, the results have been compared with previous work. Serious errors have been found in the work of Fraenkel *et al.* The ^{7}Li magnetic resonance spectra of these compounds have also been obtained and an observed correlation of the ^{1}H and ^{7}Li chemical shifts has been interpreted in terms of the ionic character of the carbon–lithium bond.

INTRODUCTION

The PMR spectrum of phenyllithium in diethyl ether solution has previously been analysed by an iterative method[1] and also using the sub-spectral approach[2]. Both of these investigations were based on a 100 MHz spectrum obtained by the courtesy of Varian Associates, Palo Alto, California. The present availability of a HA 100 spectrometer in this department prompted a reinvestigation of the proton spectrum of this compound together with those of some substituted phenyllithiums in an effort to gain some insight regarding the ionic character of the carbon–lithium bond and the influence of substituents upon this factor. As model compounds, *meta*- and *para*-tolyllithium and the corresponding chloro compounds have been prepared, some for the first time, and their ^{1}H spectra analysed. Their ^{7}Li spectra have also been obtained and the relative shifts are discussed.

While this work was in progress, analyses of the 60 MHz PMR spectra of phenyllithium, *p*-tolyllithium and *p*-chlorophenyllithium were published by Fraenkel *et al.*[3,4]. The discrepancies between Fraenkel's results concerning phenyllithium and our previous results[1,2] were disconcerting and emphasized the need for a reinvestigation of the spectrum of this compound. We report here the results of our studies.

EXPERIMENTAL

All the preparations, working up of solutions and loading of NMR tubes were carried out in a Vacuum Atmospheres dry-box under an inert atmosphere of argon. The atmosphere of this box was circulated through large columns of molecular sieve (Linde 4A) and a lower oxide of manganese[5] in order to remove traces of water and oxygen, respectively.

Phenyllithium was prepared by the reaction of freshly cut bulk lithium metal (B.D.H.) with a solution of diphenylmercury (Eastman) in anhydrous diethyl ether and the product was recrystallised from this solvent. The other aryllithiums were prepared from n-butyllithium (Pfizer) and the appropriately substituted phenyl halide in anhydrous hexane. The *meta*- and *para*-substituted phenyllithiums were precipitated over a period of 2–6 h, filtered off, thoroughly washed with hexane and subsequently dissolved in diethyl ether. (*Caution*: *m*-chlorophenyllithium was found to be violently explosive when dried on a sintered glass filter in the inert atmosphere of the dry-box. It could be handled safely only when in solution or under hexane.)

^1H and ^7Li magnetic resonance spectra of ~1 *M* ethereal solutions of these aryllithiums were obtained using a Varian HA 100 spectrometer. The ^7Li spectra were obtained at 38.9 MHz using HR mode and referenced to a capillary containing 70% methanolic lithium bromide solution. Chemical shifts were then measured by the audio-sideband technique.

In all cases concentrations were estimated by spectral integration of the solute and solvent resonances.

Spectral analysis

The ^1H spectra were analysed using an English Electric KDF9 computer and computer programmes NMRIT and NMREN1[6]. Initially values of the chemical shifts and coupling constants were estimated from previous work and from examination of the spectra in the symmetric cases. The spectra were calculated using the programme NMRIT and the constants adjusted to give a reasonable correlation

TABLE 1

PMR PARAMETERS FOR ARYLLITHIUMS

Coupling constants[a] (Hz)										Chemical shifts (τ values)					Ref.
J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}	τ_2	τ_3	τ_4	τ_5	τ_6	
Phenyllithium															
6.90	1.62	0.52	0.82	7.55	1.66	0.52	7.55	1.62	6.90	1.994	2.956	3.041	2.956	1.994	[b]
6.52	1.62	0.84	0.65	7.20	1.17	0.84	7.20	1.62	6.52	1.976	2.975	3.042	2.975	1.976	3
6.85	1.53	0.51	0.73	7.26	1.65	0.51	7.26	1.53	6.85	1.989	2.950	3.030	2.950	1.989	1
	1.65			7.14			7.14	1.65							2
m-Chlorophenyllithium															
6.50	1.14		0.16	6.51		0.84		1.84		2.095	3.032	3.064		2.187	[b]
p-Chlorophenyllithium															
7.40		0.40	0.94		1.74	0.40			7.40	2.112	2.983		2.983	2.112	[b]
8.10		0.73	2.20		2.20	0.73			8.10	2.545	2.744		2.744	2.545	4
m-Tolyllithium															
7.78	1.40		0.29	7.33		0.77		1.83		2.145	3.037	3.200		2.197	[b]
p-Tolyllithium															
6.98		0.34	0.82		1.57	0.34			6.98	2.170	3.081		3.081	2.170	[b]
7.04		0.57	0.63		1.68	0.57			7.04	2.090	3.080		3.080	2.090	4

[a] Errors in *J* values range from 0.05 to 0.10 Hz, the average error being 0.07 Hz. [b] This work.

between the observed and calculated spectra. The observed lines were then assigned to the various allowed transitions on the basis of both frequency and intensity, checked by applying the frequency sum rule[6], and finally the spectral constants were refined using NMREN1 and NMRIT. The results are in Table 1.

The possibility of other sign combinations of the coupling constants were investigated but were found to be untenable, in agreement with the results of Fraenkel *et al.*

RESULTS

Phenyllithium

The spectral parameters obtained here for phenyllithium do not differ markedly from those of our previous investigations[1,2] except perhaps for J_{34} which has gone from 7.26 to 7.55 Hz. The agreement between calculated and observed spectra is shown in Fig. 1 and, as an additional check, a similar comparison has been made (Fig. 2) between the calculated and observed AB_2 spectrum obtained when the *ortho* protons (H_2, H_6) were strongly irradiated at their resonant frequency. Also shown

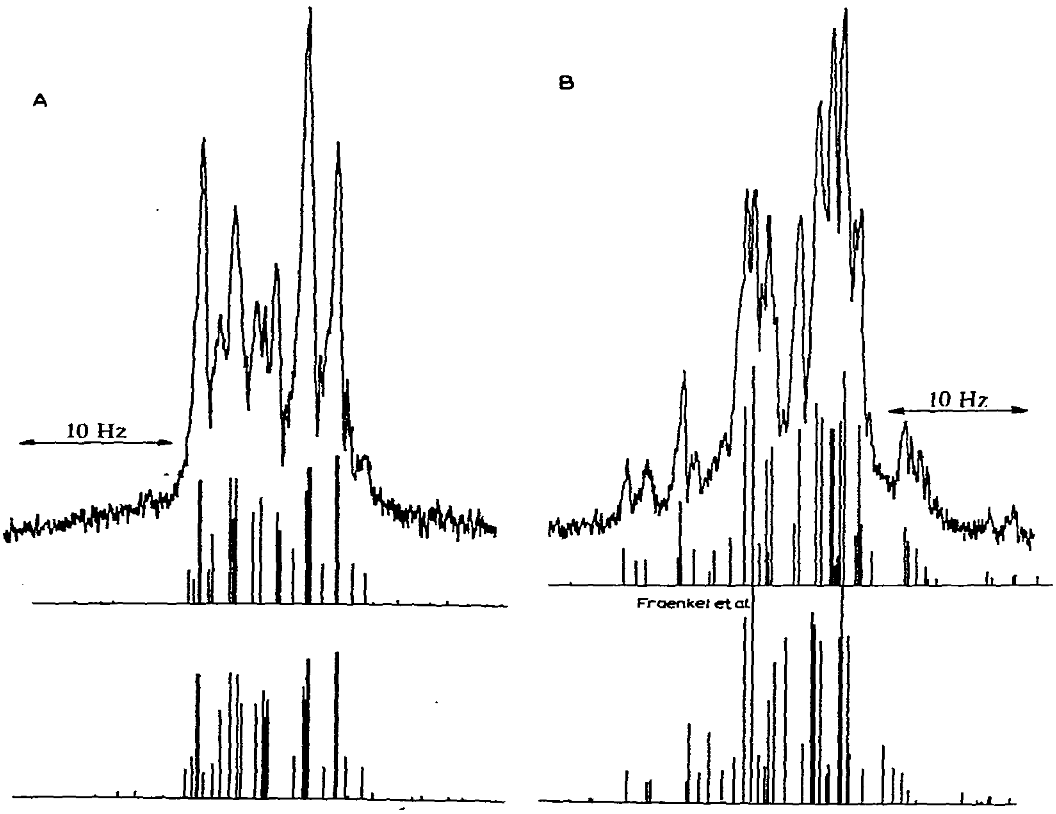

Fig. 1. Comparison of calculated and observed ^1H spectra of phenyllithium in ethereal solution: (A) low field multiplet, (B) high field multiplet.

in these Figures are the spectra calculated using Fraenkel's parameters. It is evident that the latter do not provide as good a fit to the observed 100 MHz spectra.

The discrepancy in Fraenkel's work could have arisen from a concentration dependence of the spectrum. Although both investigations appear to have involved ~1 *M* ethereal solutions, Fraenkel's published 60 MHz spectra exhibit a poor signal to noise ratio compared to ours. While this in itself makes the spectral analysis more difficult, it is not inconceivable that some contamination with lithium phenoxide had occurred and this led to an overestimate of the phenyllithium concentration in the subsequent analysis. Our method of determining the concentration also does not distinguish phenyllithium from impurities but the considerably better signal to noise ratio is reassuring in this respect. However, we have not been able to detect a significant effect on dilution so that the discrepancy lies elsewhere.

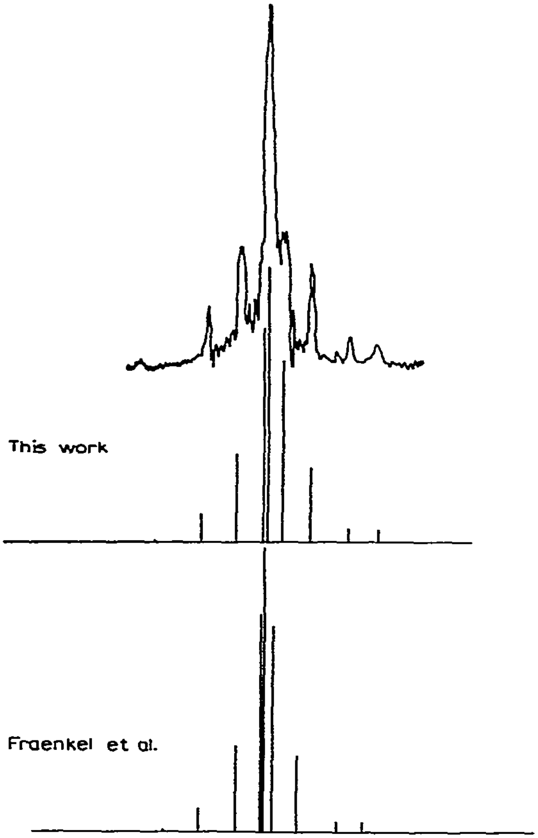

Fig. 2. Comparison of calculated and observed AB_2 spectra obtained by decoupling the *ortho* (H_2, H_6) protons.

p-Chlorophenyllithium and p-tolyllithium

The ^1H spectra of these compounds in ethereal solution are of the AA'BB' type. Starting parameters for the analyses were obtained by the treatment given by

Pople *et al.*[7] and Fraenkel's values were also employed. It was immediately apparent that the chemical shifts reported for *p*-chlorophenyllithium in the latter work were seriously in error and the values $J_{26}=J_{35}=2.20$ Hz seemed quite unreasonable in comparison with the other lithium aryls.

There is no reason to suppose that the coupling constants J_{26} and J_{35} should be equal but, if this assumption is made in the choice of starting parameters, it will be maintained throughout the analysis. A completely artificial set of coupling constants then results although the associated errors may be reasonably small. To demonstrate this, Fraenkel's coupling constants for *p*-chlorophenyllithium together with the correct chemical shifts were used in an analysis of this spectrum and the sum of the squares of the residual errors converged to 0.337. The resulting value of J_{26} and J_{35} was 1.47 Hz. However, taking $J_{26} < J_{35}$ initially, the sum of the squares of the residual errors converged to 0.016 and the values of the coupling constants so obtained (Table 1) are seen to be much more in conformity with those for the related compounds.

m-Chlorophenyllithium and m-tolyllithium

The ^{1}H spectra of these asymmetrically substituted compounds are of the ABCD type, the protons *ortho* to lithium being expected to be observed at lower field strengths than the remaining two. In each it was found that the proton *ortho* to both lithium and the substituent resonated at the lowest field strength.

The spectral constants determined for the other compounds were used to estimate starting values for the coupling constants, and chemical shifts were estimated by inspection. The results of the analyses are in Table 1.

^{7}Li spectra

The ^{7}Li spectrum of each of the aryllithiums consisted of a single resonance line downfield from the lithium bromide reference. The linewidths ranged from 2 to 3 Hz. Significantly different chemical shifts for the various compounds were measured and, in order to make these meaningful, account must be taken of bulk susceptibility corrections. However, since we were interested only in the relative shifts of the different compounds, it was sufficient to obtain all the spectra under identical conditions. Thus each was examined at the same concentration in ethereal solution and referenced to the same lithium bromide solution. Dilution resulted in very slight shifts to higher field strength in each case.

DISCUSSION

Examination of the ^{7}Li chemical shifts shows that the introduction of a methyl or chloro substituent at either a *meta* or *para* position results in a downfield shift relative to phenyllithium itself. This might be interpreted to mean that the carbon–lithium bond becomes more ionic leading to decreased shielding of the ^{7}Li nucleus or, alternatively, that the ring-current effect[7] is enhanced on substitution.

The latter possibility is immediately ruled out, however, by the observation that all the proton resonances experience an upfield shift on substitution. A more detailed consideration of the former suggestion is therefore required.

It has been proposed previously[1] that the chemical shifts of the protons in phenyllithium itself are governed mainly by the magnetic anisotropy of the carbon atom involved in the carbon–lithium bond and that this is of particular importance in the case of the protons *ortho* to the metal (H_2, H_6). The origins of the anisotropy were considered to arise from a mixing of the ground and low-lying excited states of the molecule under the influence of the applied field and it was reasonable to suppose that the major contribution arose from the lowest-lying excited state. By analogy with the isoelectronic pyridine molecule, the lowest energy electronic transition was expected to be $\sigma \rightarrow \pi^*$ where an electron from the carbon–lithium bond was promoted to an anti-bonding π-type molecular orbital of the phenyl ring. Consequently any change in the ionic character of the carbon–lithium bond brought about by substitution on the phenyl ring would be expected to lead to marked changes in the chemical shifts of the *ortho* protons: an increase in ionic character would lead to downfield shifts whereas a decrease in ionic character would lead to upfield shifts. Clearly then, the proton and ^{7}Li shifts on substitution seem to be incompatible.

This difficulty is resolved however if one assumes that the lithium atom lies on the principal axis of the phenyl group and the secondary magnetic fields induced at the anisotropic carbon atom are reconsidered (Fig. 3). A paramagnetic effect arising at the carbon atom in question is seen to produce a deshielding of the *ortho* protons while at the same time shielding the ^{7}Li nucleus. Since this effect predominates at the *ortho* protons[1], then it is reasonable to suppose that the ^{7}Li chemical shifts are also governed in the same way. Thus the upfield shift of the proton resonances and the downfield shift of the ^{7}Li resonances on substitution are both a direct result of a decrease in the ionic character of the carbon–lithium bond.

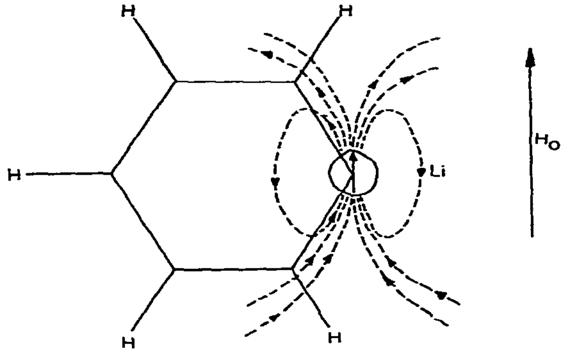

Fig. 3. Secondary magnetic field induced at the carbon atom involved in the carbon–lithium bond.

The correlation between the ^{7}Li chemical shifts and the chemical shifts of the H_2 proton is plotted in Fig. 4. There is not a 1/1 correspondence, probably because electron density changes in the ring have not been taken into account. In this connection, the fact that both methyl and chloro substitution lead to shifts in the same direction is noteworthy. From an inductive point of view, the methyl group is electron-releasing while chlorine is electron-withdrawing. However, it is possible for the lone-pair electrons of the chloro substituent to be donated into the ring system[8] and this π-donor contribution might override the expected effect due to the electron withdrawing property of chlorine. It would appear from the observed shifts that this is indeed the case whether chlorine is a *meta* or *para* substituent in these compounds.

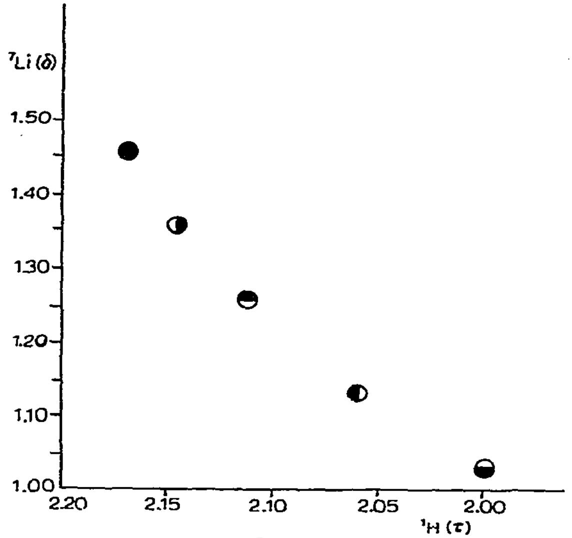

Fig. 4. Correlation of the ^7Li chemical shifts (ppm) with those of the H_2 proton (τ). Key: ● *p*-tolyllithium; ◑ *m*-tolyllithium; ◓ *p*-chlorophenyllithium; ◐ *m*-chlorophenyllithium; ◒ phenyllithium.

Phenyllithium is dimeric in ether solution[9,10] and it is therefore necessary to consider our results in the light of this fact. It is a characteristic feature of bridge bonding in electron deficient organometallic compounds that the bridging group forms an acute angle with the two metals (Li–C–Li angle[11] approximately equal to 70°). Assuming that this sharp angle obtains in phenyllithium dimer, the lithium atoms do not lie far from the principal axis of the phenyl ring, and our conclusions are therefore not inconsistent with a dimeric structure in solution.

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