

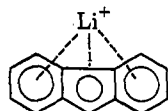
these intermediates might be trapped by other reagents than the starting ynamines.

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### A $^7\text{Li}$ Nuclear Magnetic Resonance Investigation of the Structure of Some Aromatic Ion Pairs

Sir:

In a previous investigation<sup>1</sup> of the proton and lithium-7 nmr spectra of fluorenyllithium in diethyl ether, a relatively large upfield shift<sup>2</sup> ( $\sim 6$  ppm) was observed for the lithium resonance as compared to an aqueous lithium chloride reference. This result was rationalized by suggesting that the lithium cation was located directly above the plane of the aromatic carbanion and in the shielding region of the diamagnetic ring current in the aromatic ion. Subsequently<sup>3</sup> it was shown that the effect of solvent itself on the  $^7\text{Li}$  chemical shifts of



$\text{LiBr}$  and  $\text{LiClO}_4$  can be of the same magnitude ( $\sim 6$  ppm). Since a change in the  $^7\text{Li}$  chemical shift of 3.2 ppm on changing the solvent from ether to benzene was observed for fluorenyllithium,<sup>1</sup> there remains the question of whether this change in chemical shift observed for fluorenyllithium is a result of a solvent effect or a change in the structure of the ion pair.

We wish to report some studies of the  $^7\text{Li}$  nmr spectra of aromatic carbanion systems which strongly suggest that the lithium cation is located above the  $\pi$  cloud of certain planar aromatic anions. The  $^7\text{Li}$  chemical shifts observed for these anions are determined largely by the distance separating the lithium cation and aromatic anion and to a lesser extent by the degree of delocalization of the negative charge in the anion.

The  $^7\text{Li}$  chemical shifts obtained from four aromatic carbanions<sup>4</sup> in various solvents are given in Table I. Changes in the  $^7\text{Li}$  shifts over the concentration range of 0.1–0.4  $M$  are less than 0.2 ppm. In all cases, the chemical shifts are upfield from that of the reference, external aqueous 1.0  $M$  lithium chloride. The  $^7\text{Li}$  chemical shifts for cyclopentadienyllithium (I) and indenylithium (II) are considerably upfield from those

(1) J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Amer. Chem. Soc.*, **87**, 1379 (1965).

(2) The  $^7\text{Li}$  chemical shifts of lithium alkyls are usually found from 1 to 2 ppm downfield from external aqueous lithium bromide reference: T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968).

(3) G. E. Maciel, J. K. Hancock, L. F. Lafferty, P. A. Mueller, and W. K. Musker, *Inorg. Chem.*, **5**, 554 (1966).

(4) All spectra were obtained on a Varian Associates HA-100 spectrometer operating at 38.8 MHz in the HR mode. Reported values of the chemical shifts are the average of either alternate upfield and downfield scans calibrated by the side-band technique. Samples were prepared either by using a glove bag with an argon atmosphere and/or high vacuum techniques using slightly modified nmr tubes.<sup>5</sup> Solvents were stored over sodium benzophenone ketyl and were distilled on the vacuum line directly into the sample tubes. The sample of cyclopentadienyllithium was of commercial origin (Alfa Inorganics). The remaining anions were prepared by treating the respective hydrocarbon with lithium metal in the appropriate solvent.

(5) R. H. Cox, E. G. Janzen, and J. L. Gerlock, *J. Amer. Chem. Soc.*, **90**, 5906 (1968).

Table I.  $^7\text{Li}$  Chemical Shifts for Some Aromatic Anion Systems

Anion <sup>a</sup> /solvent	$\delta$ , <sup>b</sup> ppm
Cyclopentadienyl/THF	8.37
Cyclopentadienyl/DME	8.66
Cyclopentadienyl/ <i>p</i> -dioxane	8.68
Indenyl/THF	6.17
Indenyl/DME	6.62
Phenylallyl/THF	0.61
Phenylallyl/DME	0.96
Fluorenyl/Et <sub>2</sub> O	6.95
Fluorenyl/DME	3.04
Fluorenyl/THF	2.07
Fluorenyl/HMPA	0.73

<sup>a</sup> Concentration is 0.4  $M$ . <sup>b</sup> In parts per million upfield relative to external, aqueous 1.0  $M$  LiCl.

of 1-phenylallyllithium (III). Since the relative chemical shifts of I–III are approximately the same for a given solvent (either THF or DME), the range of  $^7\text{Li}$  chemical shifts observed for I–III is most likely due to structural differences of the ion pairs.

Evidence from the effect of cation, solvent, and temperature on the proton chemical shifts of I, II,<sup>6</sup> and III<sup>7</sup> suggests that these systems exist in solution as contact or tight ion pairs. Furthermore, proton nmr data on III<sup>7</sup> and a substituted phenylallyl carbanion<sup>8</sup> suggest that the cation is coordinated with the allyl part of the molecule and not directly associated with the  $\pi$  cloud of the phenyl ring. Therefore, the differences in the  $^7\text{Li}$  chemical shifts of I, II, and III can be accounted for if the lithium cation is located above the  $\pi$  cloud of I and II in the shielding region of the induced diamagnetic ring current of these anions and coordinated with the allyl part of III. The smaller upfield shift of II compared to I with respect to the reference could possibly be due to a combination of two factors: (1) either the ring current in II is not as intense as in I or (2) the contact ion pair formed by II is not as tight an ion pair as that formed by I, resulting in smaller coulombic attractions between anion and cation. Either of these factors would result in a downfield shift of II compared to I with the lithium cation coordinated with the  $\pi$  cloud of these anions.

The data for fluorenyllithium IV (Table I) do not appear to support the above conclusions since the effect of solvent on the  $^7\text{Li}$  chemical shifts of IV is almost as large as the range of shifts observed for I–III. The suggestion<sup>1</sup> that the lithium cation is coordinated with the  $\pi$  cloud of the aromatic anion would account for the shift in diethyl ether but does not appear to account for the  $\sim 6$ -ppm variation in the  $^7\text{Li}$  shift with the other solvents. However, IV is a unique system compared to I–III in that IV forms<sup>9,10</sup> both contact and solvent-separated ion pairs in solution depending upon the solvent. In ether, only contact ion pairs are formed, whereas with THF, DME, and hexamethylphosphoric amide (HMPA), essentially all of the ions are in the

(6) J. B. Gruntzner, J. M. Lawlor, and L. M. Jackman, private communication.

(7) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 495 (1968).

(8) (a) H. H. Freedman, V. R. Sandel, and B. P. Thill, *ibid.*, **89**, 1762 (1967); (b) G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **86**, 1345 (1967).

(9) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

(10) L. L. Chan and J. Smid, *ibid.*, **90**, 4654 (1968).

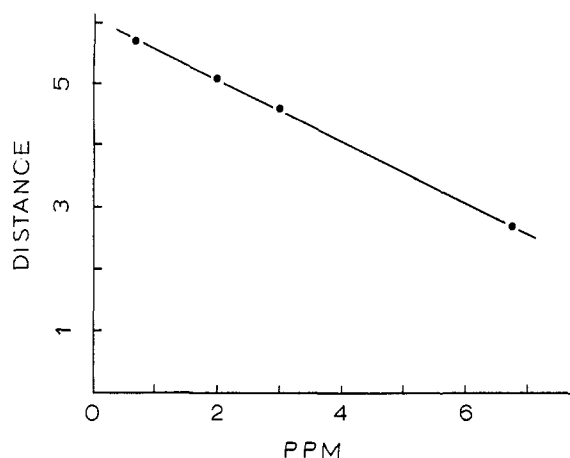


Figure 1. A plot of the  ${}^7\text{Li}$  chemical shift of fluorenyllithium in various solvents vs. the estimated distance (ångstroms) separating the two ions.

form of solvent-separated ion pairs. It occurred that the  ${}^7\text{Li}$  chemical shifts of IV could still be a result of the lithium cation being located above the  $\pi$  cloud of the fluorenyl anion if the distance between the two ions were changing with solvent.<sup>11</sup>

While the number of solvent layers separating the two ions in the solvent-separated ion pair is not known exactly, conductance studies of IV in THF<sup>12</sup> and DME<sup>13</sup> suggest an average of approximately one solvent layer. Furthermore, previous work<sup>1</sup> has shown that when fluorenyllithium is prepared in either THF or DME and the solvent removed by vacuum, at least three THF molecules or one DME molecule remain coordinated to IV. We have estimated the distance by assuming that there is an average of one solvent molecule separating the cation and anion in the solvent-separated ion pair. The distance separating the two ions in the contact ion pair (ether) was taken to be the sum of the ionic radius of the fluorenyl anion (2.1 Å)<sup>12</sup> and the ionic radius of the lithium cation (0.6 Å).<sup>14</sup> For the solvent-separated ion pairs the distance was taken to be that in the contact ion pair plus that of a solvent molecule as estimated from several measurements on Drieding models.<sup>15</sup> The  ${}^7\text{Li}$  shifts for fluorenyllithium are plotted vs. the distance separating the two ions in Figure 1. An excellent linear relationship is obtained.<sup>16</sup> Therefore, the large range of  ${}^7\text{Li}$  chemical shifts observed for IV with solvent is a direct result of solvent affecting the distance separating the fluorenyl and lithium ions. The suggestion that the lithium cation is located above the  $\pi$  cloud of certain planar aromatic anions is a valid description. Caution should be exercised, however, in using  ${}^7\text{Li}$  shifts for structural studies since the above data show that a

(11) The shielding experienced by the lithium ion as a result of its being located above the plane of the aromatic anion decreases as the distance separating the two ions increases: C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(12) J. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 318 (1966).

(13) T. Ellingsen and J. Smid, *J. Phys. Chem.*, **73**, 2712 (1969).

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 514.

(15) Measurements were made assuming the oxygen atoms of the solvent to be coordinated with the cation.

(16) Although the shielding of a nucleus located above the  $\pi$  cloud of a benzene ring is not strictly linear with distance,<sup>11</sup> it is linear to a first approximation from a distance of 2.8–4.0 Å.

large upfield shift is not a necessary requirement for lithium being located above the  $\pi$  cloud of an aromatic anion. The  ${}^7\text{Li}$  shift will also depend upon the type of ion pair formed and more specifically on the distance separating the two ions.

The results (Table I) for the effect of solvent on the  ${}^7\text{Li}$  shifts of I–III are somewhat surprising in view of the cation-solvating ability of these solvents. It is well known that the order of cation-solvating ability of these solvents is DME > THF > *p*-dioxane.<sup>17</sup> Since I–III form contact ion pairs<sup>6,7</sup> it might have been expected that their  ${}^7\text{Li}$  shifts in DME would have been downfield from that in THF. DME should solvate the ion pair better and, hence, disperse the cationic charge and weaken the coulombic interactions in the ion pair. The results indicate that we are probably observing a medium effect not related to the solvating ability of the solvents but due to some other bulk property of the solvent similar to the results reported<sup>3</sup> for LiBr and LiClO<sub>4</sub>.

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(17) J. F. Garst, R. A. Klein, D. Walmsley and E. R. Zabolotny, *J. Amer. Chem. Soc.*, **87**, 4080 (1965).

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## New Heteroaromatic Compounds. XXXIII.<sup>1</sup> 5,1,3,4-Boratriazoles<sup>2</sup>

Sir:

Previous papers of this series<sup>1,3</sup> have described numerous compounds derived from "normal" aromatic systems by replacing a pair of adjacent carbon atoms by the isoelectronic BN combination; the boron-nitrogen bonds in many of these show remarkable resistance to chemical attack, implying that they are aromatic, a conclusion supported by their other physical and chemical properties. On this basis it seems likely that medicinally valuable compounds might be obtained by analogous replacement of pairs of carbon atoms in the aromatic rings of biologically active materials. There is therefore an incentive to prepare analogs of "biological" aromatic rings such as benzene, pyrrole, and imidazole.

Unfortunately the benzene analog, borazarene (I), seems to be rather unstable, judging by the ease with which its derivatives resinify,<sup>4</sup> while the compounds so far prepared in which boron forms part of a five-membered ring undergo hydrolysis with great ease.<sup>3</sup> Recently it has been shown that derivatives of 3,2-

(1) Part XXXII: F. A. Davis, M. J. S. Dewar, R. Jones, and S. D. Worley, *J. Amer. Chem. Soc.*, **91**, 2094 (1969).

(2) This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121, the National Institutes of Health through Grant No. 1F02 GM-45321-01, and the Robert A. Welch Foundation.

(3) For reviews and nomenclature, see M. J. S. Dewar, *Progr. Boron Chem.*, **1**, 235 (1964); *Advan. Chem. Ser.*, No. 42, 227 (1964).

(4) K. M. Davies, M. J. S. Dewar, and P. Rona, *J. Amer. Chem. Soc.*, **89**, 6294 (1967).