Delocalized Carbanions. IV.[1] Structural Studies on the Alkali Metal Derivatives of 1- and 2-Methylnaphthalene

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Abstract: Carbon–metal bonding in 1- and 2-naphthylmethyllithium, -sodium, and -potassium was investigated using pmr spectroscopy. In tetrahydrofuran (THF), the chemical shifts of the ring protons of the carbanions relative to naphthalene (δ_N) increase in the upfield direction in the order Li < Na < K. They were found to follow the equation $\delta_N = \delta_{N\infty}(1 - 1/3.5R_{M^+})$, where R_{M^+} is the cation radius and $\delta_{N\infty}$ is the extrapolated chemical shift of the corresponding proton in the free anion. The term $(1 - 1/3.5R_{M^+})$ is interpreted as the amount of C–M bond delocalization in the contact ion pair. Appreciable barriers to rotation about the ring–methylene bonds in the anions show that the partial delocalization is not due to rapid equilibria between ionic and covalent forms. Lack of cation dependence of the spectra of the Li and Na compounds in hexamethlylphosphoramide (HMPA) indicated the presence of solvent separated ion pairs or free ions in this solvent. Comparison of the spectra of the Li compounds in ether and THF led to the conclusion that in ether the Li^+ ions may be allylically coordinated to the methylene carbon and a ring carbon.

There has been much speculation concerning carbon–metal bonding in delocalized organometallic compounds of the alkali metals, but very few investigations have been comprehensive enough to permit firm conclusions. The fluorenyl salts have undergone extensive investigation by a number of workers.[3–7] These are essentially ionic compounds with only weak interactions between cation and anion. Variations in the properties with solvent and cation are attributed largely to the effects of ion association.

Another delocalized carbanoid species which has received much attention recently is allyllithium and its derivatives. There is little agreement concerning the nature of bonding in this system. The nmr data on allyllithium[8] and the phenylallyl alkali metals[9] have been interpreted in terms of ionic structures. Alkyl-substituted allyllithiums have been described as σ-bonded[10] and either covalent or delocalized π-allylic[11] structures depending upon the solvent polarity. It is apparent that the structural implications of the spectral data in this system are to some extent subject to variable interpretation.

A third system of delocalized carbanions which is more pertinent to this paper is the arylmethyl type. Again the descriptions of carbon–metal bonding vary considerably from compound to compound and with the investigator. The polystyryl salts,[12] which are substituted benzyl anions, are usually treated as essentially ionic compounds. The benzyl, diphenylmethyl, and triphenylmethyl salts[13,14] have been similarly treated. In contrast, Waack,[15] *et al.*, have described the α carbon of benzyllithium as having substantial sp^3 character. Bonding is pictured as a dative bond between the α carbon and the metal ion, with the extent of charge localization being dependent upon the Lewis acidity of the solvated cation.

The most reliable structural information on benzyllithium comes from an X-ray diffraction study of its crystalline triethylenediamine complex by Patterman, *et al.*[16] They concluded that, although the carbon–metal bonding is largely ionic, the lithium atom's approach distance to the anion is short enough to imply some covalent character to the interaction as well. The lithium atom was found to lie nearest to the methylene carbon (2.21 Å), but it was also closer to one of the ortho ring carbons (2.59 Å) than to the other (3.38 Å), implying coordination with the π cloud of the anion. The authors suggest that the bonding between contact ion pairs in solution maintains the gross features of the solid-state structure, but they also report a large bathochromic shift in the electronic spectrum of the solid material relative to the solution spectrum. The existence of such a shift suggests that extrapolation of solid-state structures into solution may be dangerous. It also illustrates the need for the indirect structural examination of solutions themselves.

Thus the nature of carbon–metal bonds in delocalized organometallic compounds remains a fertile field for research. The present study is primarily an nmr investigation of the carbon–metal bonding in species commonly referred to as contact or intimate ion pairs.[17] The 1- and 2-naphthylmethyl system was chosen for

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(1) Preliminary communication: F. J. Kronzer and V. R. Sandel, *Chem. Ind.* (*London*), 210 (1972).

(2) (a) Taken in part from the Ph.D. Thesis of F. J. Kronzer, Michigan Technological University, 1971; (b) NASA Trainee 1967–1970.

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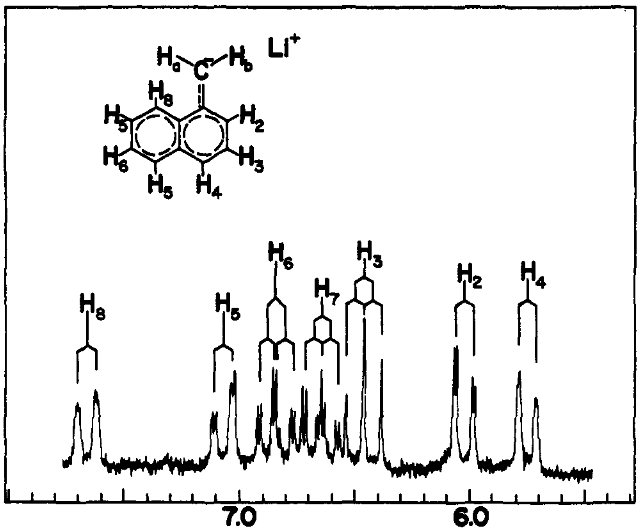


Figure 1. 100-MHz spectrum of 1-naphthylmethyllithium in THF-d_8.

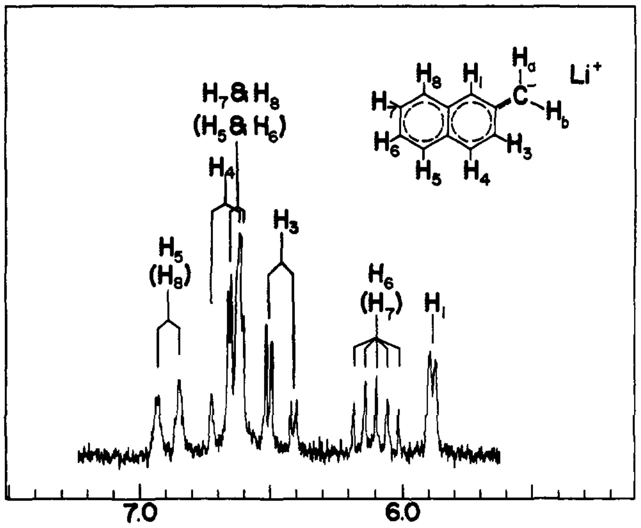
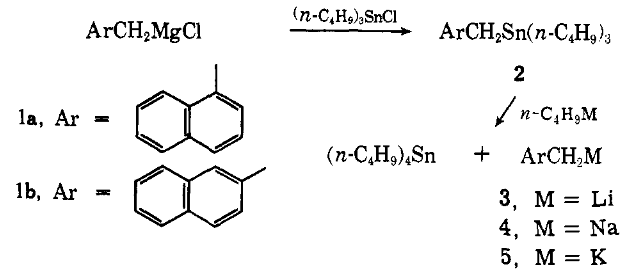


Figure 2. 100-MHz spectrum of 2-naphthylmethyllithium in THF-d_8.

this particular study because, in addition to the structural information, a number of interesting comparisons between the isomers may be examined and correlated with differences predicted by quantum theory. Many of these correlations will appear in a following paper of this series.

Preparation of the Naphthylmethyl Alkali Metals. The naphthylmethyl alkali metals were prepared by the method shown in Scheme I, which is a modification of the method of Seyferth and Weiner.[18] Butylsodium and butylpotassium for these syntheses were prepared from the corresponding metal *tert*-butoxides and *n*-butyllithium by the method of Lockmann, Popisil, and Lim.[19] Unfortunately, however, flame photometric analysis of a number of samples of **4a**, **4b**, and **5a** indicated a lithium content varying between 14 and 28 mol %. Although the presence of lithium in the sodium and potassium compounds was disturbing, it did not affect reproducibility of the nmr spectra. Several independent preparations of each of the sodium and potassium compounds yielded samples whose nmr spectra in THF were reproducible to within ±0.01 ppm. Lithium-free samples of 1-naphthylmethylsodium and -potassium were also prepared by the method of Pearson, Williams, and Levy,[20] which required the cleavage of 1,2-di(1-naphthyl)ethane with sodium and potassium metal in THF. The nmr chemical shifts measured from spectra of these samples were within 0.01 ppm of those from the contaminated samples.

Scheme I



Isopiestic molecular weight measurements in ether indicated both **3a** and **3b** are monomeric. Reliable molecular weights could not be obtained by this method for the sodium and potassium compounds because of decomposition.

Spectroscopic Results

Ultraviolet-Visible Spectra. Preliminary uv-visible spectra of approximately 10^{-2} and 10^{-3} M solutions of 1- and 2-naphthylmethyllithium in THF and diethyl ether were obtained at 21°. The data may be summarized as follows: 1-naphthylmethyllithium in ether, λ_{max} 306 nm (log ϵ 3.91), λ_{max} 472 (3.80); in THF, λ_{max} 498 nm, λ_{max} 306 nm; 2-naphthylmethyllithium in ether, λ_{max} 368 nm (3.70), λ_{max} 486 nm (2.77); in THF, λ_{max} 373 nm, λ_{max} 500 nm. Extinction coefficients in THF were not obtained because the dilute anions reacted rather rapidly with the solvent. In all cases the spectra of the dilute samples matched those of the more concentrated, indicating the absence of concentration dependent equilibria.

Nuclear Magnetic Resonance Spectra of the Aromatic Protons. Pmr spectra (100 MHz) of the lithium compounds (**3a** and **b**) were run at 0.2–0.3 M concentrations in diethyl ether, THF, and HMPA, and sodium and potassium compounds (**4a**, **4b**, **5a**, and **5b**) were run in THF. At least two samples of each compound were prepared independently, and all of the spectra were reproducible to less than 0.01 ppm.

The spectra of 1- and 2-naphthylmethyllithium in THF are shown in Figures 1 and 2, respectively. Proton assignments in the 1-naphthylmethyllithium spectrum were straightforward from the coupling patterns. The assignment of H_3 is obvious from its triplet pattern, being coupled nearly identically with H_2 and H_4. H_4 was distinguished from H_2 by its small coupling (identified by double resonance) to the low-field doublet assigned to H_8. The only well-documented inter-ring coupling found in substituted naphthalenes is between H_4 and H_8.[21] Inter-ring couplings between similarly

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Table I. Chemical Shifts (δ, ppm) from TMS in Various Solvents at 29°[a]

1-Naphthylmethyllithium				2-Naphthylmethyllithium			
Proton	Ether	THF	HMPA	Proton	Ether	THF	HMPA
2	5.958	6.036	5.386	1	5.799	5.902	4.997
3	6.635	6.464	5.912	3	6.495	6.438	5.88*
4	5.986	5.758	4.797	4	6.779	6.617	5.89*
5	7.182	7.062	6.481	5	6.946	6.820	6.134
6	6.973	6.849	6.431	6	6.316	6.100	5.250
7	6.827	6.662	6.070	7	6.71*	6.59*	6.051
8	7.773	7.645	7.193	8	6.75*	6.57*	5.827
α	2.506	2.426	THF-d_8	α	2.102	1.952	THF-d_8
α_a		2.595[b]		α_a		2.012[b]	
α_b		2.309[b]		α_b		1.932[b]	

[a] Chemical shifts marked with an asterisk are probably accurate to ±0.03 ppm. [b] In THF-d_8 at −40°.

disposed protons have been reported for indene and benzofuran as well.[22] H_8 is further identified by its low field position due to a steric interaction with a methylene proton. This interaction is similar to the peri interaction of the 4 and 5 protons of phenanthrene.[23] Further evidence for the downfield shift of H_8 in **3a** is presented later. H_7 was shown by double resonance to be coupled to H_8 by an ortho (8.3 Hz) coupling. The assignments of H_6 and H_5 now follow from their multiplicities.

The assignments made in the 2-naphthylmethyllithium spectrum (Figure 2) are not all unequivocal. H_1 is readily assigned because it experiences no ortho coupling. The 2.0-Hz meta coupling between H_1 and H_3 serves to identify H_3. Using double resonance, H_4 was identified by its coupling to H_3. In the B ring, two sets of assignments are possible, the alternate set being listed in parentheses. H_6 was assigned on the basis of charge density considerations. Resonance forms of the 1-naphthylmethyl anion can be drawn with charges on the methylene, 1, 3, 6, and 8 carbon atoms, and electron–electron repulsion would be expected to enhance the contribution of the structure with charge on the 6 carbon.[13] Recognizing the qualitative relationship between negative charge density and upfield chemical shifts,[24–26] H_6 is the logical choice of assignment to the upfield multiplet, rather than H_7. Once this choice is made, the other preferred assignments follow from the couplings. H_6 may be considered to be two overlapping triplets, being coupled virtually to H_7 and H_6 by about 4.0 Hz, and coupled to H_5 by 8.0 Hz. The virtual coupling to H_7 and H_8 requires these protons to have nearly the same chemical shift.

The spectra of **4a** and **4b** in diethyl ether and HMPA were similar enough to those in THF so that corresponding assignments were easily made. The spectra of the sodium and potassium compounds, **5** and **6**, were likewise similar to their lithium analogs. The spectra of all samples of 2-naphthylmethylpotassium were quite broad, but reasonable estimates for some of the chemical shifts were obtained.

Table II. Coupling Constants (Hz) for 1- and 2-Naphthylmethyllithium

	Protons	Ether	THF	HMPA
1-Naphthylmethyllithium	$J_{2,3}$	7.7 ± 0.2	7.8 ± 0.1	8.2 ± 0.1
	$J_{2,4}$	1.1 ± 0.2	1.1 ± 0.1	1.0 ± 0.1
	$J_{3,4}$	7.5 ± 0.2	7.5 ± 0.1	7.1 ± 0.2
	$J_{5,6}$	8.1 ± 0.1	8.1 ± 0.1	8.1 ± 0.1
	$J_{5,7}$	1.2 ± 0.1	1.3 ± 0.1	*a*
	$J_{6,7}$	6.6 ± 0.1	6.6 ± 0.1	*a*
	$J_{6,8}$	1.0 ± 0.2	1.4 ± 0.1	1.2 ± 0.1
	$J_{7,8}$	8.4 ± 0.2	8.3 ± 0.1	*a*
	$\alpha J_{7a,b}$		0.0[b]	
2-Naphthylmethyllithium	$J_{1,3}$	2.0 ± 0.1	2.0 ± 0.1	*a*
	$J_{3,4}$	8.9 ± 0.2	8.7 ± 0.2	*a*
	$J_{5,6}$	8.0 ± 0.1	8.0 ± 0.1	7.6 ± 0.1
	$J_{5,7}$	*a*	*a*	1.2 ± 0.2
	$J_{6,7}$	*a*	*a*	6.6 ± 0.1
	$J_{6,8}$	*a*	*a*	1.0 ± 0.1
	$J_{7,8}$	*a*	*a*	8.6 ± 0.1
	$\alpha J_{a,b}$		1.4 ± 0.1[b]	

[a] Large uncertainty because of overlap. [b] Measured in THF-d_8 at −40°.

Table III. Chemical Shifts (δ, ppm) from TMS in the Naphthylmethyl Anions in THF-d_8 at 29°[a]

1-Naphthylmethyl anion			2-Naphthylmethyl anion		
Proton	Sodium	Potassium	Proton	Sodium	Potassium
2	5.764	5.467	1	5.525	5.20*
3	6.290	6.149	3	6.271	
4	5.342	5.065	4	6.400	
5	6.878	6.731	5	6.587	6.45*
6	6.760	6.676	6	5.838	5.69*
7	6.520	6.385	7	6.434	
8	7.501	7.367	8	6.311	
α_a	2.946[b]	3.188	α_a	2.359[b]	
α_b	2.703[b]	2.914	α_b	2.248[b]	

[a] See Table I, footnote *a*. [b] At −40°.

Least-squares fittings of many of the spectra were performed with the LOACOON-III computer program of Bothner-By and Castellano.[27] The best-fit data are summarized in Tables I–IV. The chemical shifts marked with an asterisk are probably accurate to ±0.03 ppm. In these particular cases the LAOCOON-III program could not be employed to obtain more accurate values because of overlap or broadness of the spectral lines. The remainder of the chemical shifts are believed to be accurate to ±0.01 ppm, since some of the frequency measurements obtained with different, independently prepared samples varied by approximately this amount. (The error estimates obtained from the LAOCOON-III program for individual samples were smaller by a factor of 10.) No variations in the coupling constants from sample to sample were apparent, so the error estimates obtained from the LAOCOON-III program were assumed to be valid.

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(27) The LAOCOON-III program was obtained from the Quantum Chemistry Exchange Program, University of Indiana.

Table IV. Coupling Constants in the 1- and 2-Naphthlymethyl Anions

	Protons	Sodium (THF)	Potassium (THF)
1-Naphthylmethyl anions	$J_{2,3}$	8.0 ± 0.1	8.1 ± 0.1
	$J_{2,4}$	1.1 ± 0.1	1.2 ± 0.1
	$J_{3,4}$	7.4 ± 0.1	7.3 ± 0.1
	$J_{5,6}$	8.2 ± 0.1	8.3 ± 0.1
	$J_{5,7}$	1.3 ± 0.1	1.3 ± 0.2
	$J_{6,7}$	6.6 ± 0.1	6.7 ± 0.2
	$J_{6,8}$	1.4 ± 0.1	1.3 ± 0.1
	$J_{7,8}$	8.3 ± 0.1	8.2 ± 0.1
	$\alpha J_{a,b}$	2.2[a]	1.9
2-Naphthylmethyl anions	$J_{1,3}$	2.0 ± 0.1	
	$J_{3,4}$	8.8 ± 0.1	
	$J_{5,6}$	7.7 ± 0.1	
	$J_{5,7}$	1.5 ± 0.1	
	$J_{6,7}$	6.8 ± 0.1	
	$J_{6,8}$	1.5 ± 0.1	
	$J_{7,8}$	8.4 ± 0.1	
	$\alpha J_{a,b}$	2.8[a]	

[a] At −40°.

Table V. Kinetic Data for Methylene Rotation in THF-d_8 for the 1- and 2-Naphthylmethyl Organometallic Compounds

	1-Naphthylmethyl			2-Naphthylmethyl	
	Lithium	Sodium	Potassium	Lithium	Sodium
Δ_{AB}, ppm	0.284	0.182	0.27	0.080	0.134
J_{AB}, Hz	0.0	2.2	1.9	2.2	2.8
$\Delta H^{\ddagger}$, kcal/mol	13.3 ± 0.1	15.2 ± 0.1	(18.2)[a]	12.8 ± 0.2	17.8 ± 0.4
$\Delta S^{\ddagger}$, cal/deg, 0°	1.5 ± 0.6	1.5 ± 0.3		0.3 ± 1.0	11.5 ± 1.6
$\Delta G^{\ddagger}$, kcal/mol, 0°	12.9 ± 0.3	14.8 ± 0.2	(17.8)[a]	12.8 ± 0.5	14.6 ± 0.9

Temp, °K	Rate, sec^{-1}	Temp, °K	Rate, sec^{-1}	Temp, °K	Rate, sec^{-1}	Temp, °K	Rate, sec^{-1}	Temp, °K	Rate, sec^{-1}
252	11.3 ± 0.3	280	6.2 ± 0.4	353	10	243	6.0 ± 0.5	275	5.5 ± 0.1
262	30.5 ± 1.2	286	11.1 ± 0.3			248	10.7 ± 0.2	280	9.7 ± 0.4
272	83.0 ± 3.0	291	18.1 ± 0.5			253	18.8 ± 0.4	286	17.7 ± 0.3
282	203.0 ± 1.4	297	31.8 ± 0.6			263	49.1 ± 0.7	291	35.3 ± 0.9
292	506.0 ± 7.1	313	122.0 ± 1.7					297	60.0 ± 0.8
								302	111.0 ± 1.4

[a] Calculated for comparison by assuming $\Delta S^{\ddagger} = 1.5$ cal/deg.

The following pertinent data are not included in the tables. The nmr spectra of both 1-naphthylmethylsodium and 2-naphthylmethylsodium in HMPA solution were virtually identical with the spectra of the corresponding lithium compounds in HMPA solution. Chemical shift measurements for each pair of spectra were identical within ±0.01 ppm.

The pmr spectra of all the naphthylmethyl salts in both THF and ethyl ether solution were temperature dependent. Spectra of the lithium compounds in ethyl ether solution were only weakly temperature dependent: chemical shifts at −30° were 0.02–0.04 ppm upfield from the 29° values. Similar weak temperature dependence was evident in the spectrum of 1-naphthylmethylpotassium in THF solution. Larger variations in the chemical shifts were found in the spectra of the sodium and lithium compounds in the THF solution. At −40°, upfield shifts of 0.05–0.10 ppm were observed for the ring protons of 1- and 2-naphthylmethyllithium, and 0.10–0.20 ppm for 1- and 2-naphthylmethylsodium.

Spectra of the Methylene Protons. Rotational Barriers. The pmr spectra of the methylene protons of all compounds studied except 2-naphthylmethylpotassium were observed in THF-d_8 solution. In each case, the peaks showed a temperature dependence characteristic of restricted rotation about the ring–methylene bond. At low temperature separate peaks were observed for each proton, whereas at higher temperature they coalesced into a single peak. At temperatures where exchange broadening occurred, the rates of methylene rotation were obtained by computer-fitting the experimental spectra to the theoretical AB line-shape function of Heidberg,[28] *et al.*, using a least-squares technique.[29] The data are summarized in Table V. Some of the relative chemical shifts (ΔAB values) were actually slightly temperature dependent, requiring that this be treated as an adjustable parameter for proper fitting of the experimental curves to the theoretical line-shape function. The error estimates quoted were generated in the least-squares program. Uncertainties in the ΔAB values and other systematic errors in the data, such as uncertainties in the temperature measurements and natural line widths, were difficult to account for, and they may have caused greater uncertainties in the rates and activation parameters than those which are quoted. In particular, the large entropy of activation calculated for 2-naphthylmethylsodium should be questioned since it differs greatly from the rest of the data.

Under conditions of rapid exchange, the methylene proton bands of the anions were approximately 1-Hz wide at half-height. In the slow exchange region they were somewhat broader due to benzylic coupling and, in some cases, to loss of resolution at low temperatures. In order to minimize errors resulting from natural line width uncertainties, rate data obtained when the exchange-broadened peaks were less than 3-Hz wide were discarded.

The spectrum of the methylene protons of 1-naphthylmethylpotassium in THF-d_8 was a well-resolved AB quartet at room temperature. No significant exchange broadening occurred at temperatures below 70°. At 80° the exchange was sufficiently rapid to allow a calculation of the rate of rotation, but the spectrum of the

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(28) J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, **41**, 1003 (1964).

(29) An iterative procedure based upon the method of Gauss (K. L. Neilson, "Methods In Numerical Analysis," 2nd ed, Macmillan, New York, N. Y., 1964, p 308) was used. The A–B chemical shift difference (ΔAB), J_{AB} and the exchange lifetime τ were treated as adjustable parameters. Optional output also provided superimposed plots of the observed and calculated AB spectra.

anion rapidly deteriorated upon heating the sample further.

Discussion

General Characteristics. The physical and spectroscopic properties of the naphthylmethyl alkali metals are those normally associated with essentially ionic compounds. Thus, they are colored solids which are virtually insoluble in hexane. The lithium compounds are monomeric even in weakly basic solvents such as diethyl ether.[30] The pmr spectra are quite unlike those of covalent aromatic compounds in that the chemical shifts of the ring protons are spread out over a much wider area of the spectrum. Recognizing the relationship between chemical shifts and charge densities,[24-26] the large upfield shifts of these protons relative to naphthalene (some nearly 3 ppm) indicate considerable negative charge delocalization into the rings of the anions. The observance of appreciable barriers to rotation about the ring–methylene bonds further attest to this delocalization. The small couplings between the methylene protons (0–2.8 Hz) are characteristic of those bonded to sp^2-hybridized carbon, rather than sp^3. All these properties are consistent with an essentially ionic formulation for the compounds.

In the ether solvents the compounds obviously do not exist as completely dissociated or solvent separated ions, because the pmr spectra show strong cation dependence (compare Table I and III). The spectra in THF move to higher field in the order $Li < Na < K$, indicating that polarization of the carbanion by lithium is greater than sodium, which is greater than potassium. These trends in the pmr spectra are those associated with species commonly called contact ion pairs.[7] Since polarization of the anion by the cation apparently decreases the ring electron densities, the interaction between them must occur primarily at the methylene carbon.[15]

The effects of solvent polarity on the electronic and pmr spectra are also in accord with the identification of contact or tight ion pairs in ether solvents. In both cases the spectral shifts can be interpreted in terms of decreased polarization of the anion by the cation in the more polar solvent. The bathochromic shifts in the electronic spectra of the lithium compounds in THF relative to ether are attributable to this effect.[31] The shapes of the spectra in the two solvents are basically similar, suggesting no gross changes in the species involved. Similarly, the upfield shift of the pmr spectra in THF relative to ether (Table I) indicate greater delocalization of negative charge in the more polar solvent. Using the contact ion pair model, these shifts can be rationalized by assuming that solvation of the cation tends to disperse its charge, thereby reducing its ability to polarize the anion.

The chemical shift variations could also be attributed to the shifting of an equilibrium between contact and solvent separated ion pairs, more polar solvent favoring the latter species.[7] However, such an interpretation is rendered unlikely by the similarity of the electronic spectra in ether and THF, and by the relatively small temperature dependence of the ring proton chemical shifts. Low temperature greatly favors solvent separation of lithium and sodium salts in THF.[12] If solvent separation in the naphthylmethyl salts occurred to an appreciable extent, one would expect a relatively large temperature dependence of the ring chemical shifts. This would be especially true of the lithium compounds, since solvent separation of lithium salts is favored in THF compared with the corresponding sodium compounds.[12] In the naphthylmethyl salts, however, the temperature dependence of the ring proton chemical shifts of the sodium compounds is greater than that of the lithium. Thus we conclude that in the ether solvents, the naphthylmethyl alkali metals exist primarily as contact ion pairs.

In HMPA, the pmr spectra of the lithium and sodium compounds were identical, indicating that the compounds exist as either solvent separated ion pairs or free ions. A distinction between the two cannot be made from the present data because their spectroscopic properties should be similar.[32] (It has been reported[33] that 10^{-3} M solutions of 1:1 electrolytes in HMPA are completely dissociated.) Whatever the state may be, the anions are free in the sense that they are not appreciably perturbed by interaction with the alkali metal cations. This is further illustrated by the fact that the spectra of the lithium compounds in HMPA are considerably upfield compared with those of the potassium compounds in THF. Thus, in HMPA the highly solvated lithium ion polarizes the anion less than does potassium in THF.

Structure of Contact Ion Pairs in Solution. Polarization of the anions in the contact ion pairs apparently increases the electron density at the methylene carbons, since the ring electron densities decrease. Waack, *et al.*,[15] have interpreted similar data from benzyllithium as indicating partial σ or localized bonding. The variations in pmr chemical shifts with cation size and solvent polarity in the naphthylmethyl salts support such an interpretation. The effects of cation size will be discussed first.

Hogen-Esch and Smid[6] found a linear relationship between electronic excitation energies for the contact ion pairs of the fluorenyl salts and the inverse of the cation radius. Cox[7] reported a similar relationship between chemical shifts and cation size. The proton chemical shifts of 1- and 2-naphthylmethyl salts in THF also obey this relationship. This is most effectively illustrated when the chemical shifts relative to naphthlene (δ_N's) are plotted *vs.* the inverse of the Goldschmidt[34] radii as shown in Figures 3 and 4. This tends to cancel out the effects of ring current anisotropy,[35] allowing electron density effects to dominate the chemical shifts.

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[30] It is assumed that the organolithiums are monomeric in the more polar THF and HMPA solvents as well, since stronger coordination of the solvent to the cation is expected to reduce the tendency for oligomerization. For example, allyllithium is highly associated in ether, but in THF the tendency to associate is greatly reduced (see ref 8). Association has not been investigated in sodium and potassium compounds.

[31] R. Waack, M. A. Doran, and P. E. Stevenson, *J. Amer. Chem. Soc.*, 88, 2109 (1966).

[32] L. I. Chan and J. Smid, *ibid.*, **90**, 4654 (1968).

[33] M. Szwarc, *Accounts Chem. Res.*, **2**, 87 (1969).

[34] "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1962, p 3519.

[35] One might also justify the use of the methylnaphthylenes as chemical shift standards. The methyl carbons are sp^3 hybridized; however, the evidence is presented that the methylene carbons in the anions are sp^2 hybridized. Thus the substituent methyls may influence the ring chemical shifts in a manner quite different from the anion methylene carbons. The relatively constant abscissa intersection when naph-

Table VI. Comparison of Observed Chemical Shifts in THF with Those Calculated Using Eq 1

	Proton	Lithium salts Obsd	Lithium salts Calcd	Sodium salts Obsd	Sodium salts Calcd	Potassium salts Obsd	Potassium salts Calcd
1-Naphthylmethyl salts	2	1.38	1.40	1.66	1.70	1.95	1.89
	3	0.96	0.94	1.13	1.14	1.27	1.27
	4	2.04	2.03	2.46	2.47	2.74	2.75
	5	0.74	0.76	0.92	0.93	1.07	1.03
	6	0.57	0.55	0.66	0.67	0.74	0.75
	7	0.76	0.75	0.90	0.92	1.04	1.02
	8	0.78[a]	0.78	0.93[a]	0.94	1.06[a]	1.05
2-Naphthylmethyl salts	1	1.90	1.90	2.28	2.31	2.60	2.57
	3	0.98	0.96	1.15	1.17		1.30
	4	1.18	1.17	1.40	1.42		1.58
	5	0.98	0.99	1.21	1.21	1.35	1.34
	6	1.32	1.30	1.58	1.58	1.73	1.76
	7	0.83	0.82	0.99	1.00		1.11
	8	1.23	1.23	1.49	1.49		1.66

[a] 0.63 ppm has been added to correct for steric interaction.

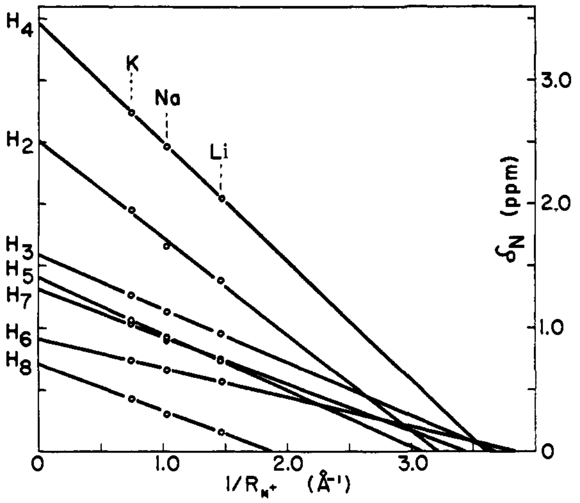

Figure 3. Relationship between the chemical shifts relative to naphthalene (δ_N) and the inverse of the cationic radius in 1-naphthylmethyllithium, -sodium, and -potassium.

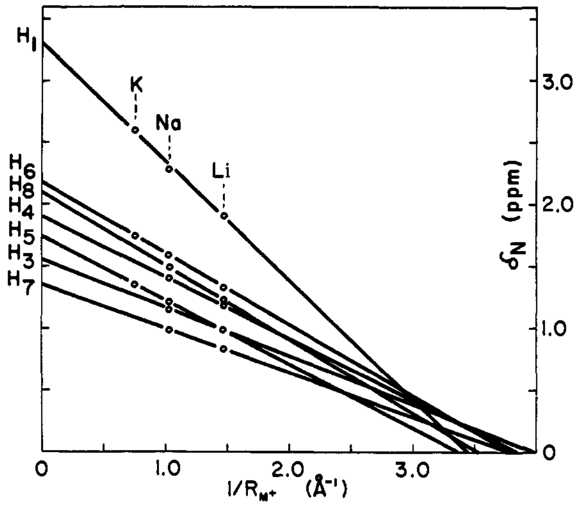

Figure 4. Relationship between the chemical shifts relative to naphthalene (δ_N) and the inverse of the cationic radius in 2-naphthylmethyllithium, -sodium, and -potassium.

Table VII. Comparison of $\delta_{N\infty}$ and δ_N (HMPA)

	Proton	$\delta_{N\infty}$ ($R_{M^+} = \infty$)	δ_N(HMPA)	Difference
1-Naphthylmethyl anion	2	2.41	2.12	−0.29
	3	1.62	1.59	−0.03
	4	3.50	3.17	−0.33
	5	1.31	1.48	+0.17
	6	0.96	1.07	+0.11
	7	1.30	1.43	+0.13
	8	1.34	0.77 (1.40)[a]	+0.06
2-Naphthylmethyl anion	1	3.27	2.97	−0.30
	3	1.66	1.62	−0.04
	4	2.01	2.07	+0.06
	5	1.71	1.83	+0.12
	6	2.24	2.25	+0.01
	7	1.42	1.45	+0.03
	8	2.12	2.14	−0.02

[a] H_8 corrected for steric interaction by adding 0.63 ppm.

A consistent linearity is apparent in the plots in Figures 3 and 4. Furthermore, when the lines are extrapolated to the abscissa, all except H_8 in the 1 isomer (which will be considered later) tend to intersect this axis at a common point, 3.5 Å^{-1}. The scatter is probably due mainly to experimental error, since changing the chemical shifts by only 0.02 ppm would cause considerable change in the points of intersection. This suggests that the chemical shifts may be represented by a single linear relationship with only one adjustable parameter

$$\delta_N = \delta_{N\infty}(1.0 - 1/3.5R_{M^+}) \qquad (1)$$

where the $\delta_{N\infty}$'s roughly correspond to the intercepts in Figures 3 and 4, but are adjusted to best-fit the equation. Table VI lists the observed δ_N values and the corresponding values calculated from eq 1. (The best-fit $\delta_{N\infty}$ values are listed in Table VII). The agreement is excellent!

As mentioned above, H_8 in the 1 isomer behaves anomalously, having an abscissa intersection of only 1.9 Å^{-1} in Figure 3. In a planar anion this hydrogen interacts sterically with one of the methylene protons in the same manner as the 4 and 5 protons of phenanthrene, causing a downfield shift relative to the other aromatic protons. If a steric factor increment of 0.63 ppm is added to all the H_8 δ_N's, this line in Figure 3 would cross the abscissa at 3.5 Å^{-1} with the others, and the adjusted chemical shifts follow eq 1. The excellent

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thylene is used as a standard is probably the best justification for its use instead of the methylnaphthalenes.

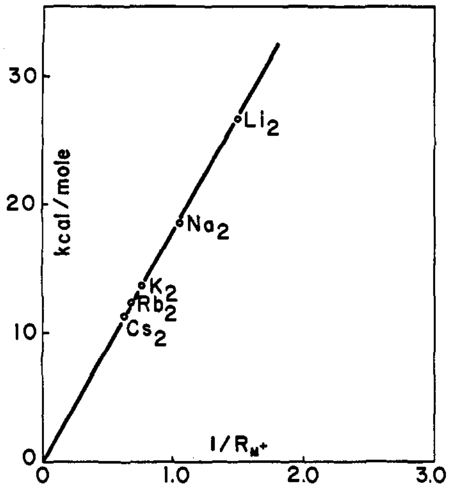

Figure 5. Relationship between the bond energies of homonuclear diatomic alkali metal molecules and the inverse of their respective ionic radii.

agreement of this independently derived steric factor with that of Cheney[23] (0.54 ppm) is good evidence for anion planarity in all of the 1-naphthylmethyl contact ion pairs, and sp^2 hybridization of the methylene carbon. The sp^2 hybridization is further substantiated by the small (0–3 Hz) coupling constant between the methylene hydrogens in both series of organometallic compounds.

Let us turn now to the significance of the linear chemical shift relationship in eq 1. When the cation size approaches 0.29 Å, the chemical shifts approach those of naphthalene ($\delta_N = 0$). If we assume that the δ_N of each hydrogen is proportional to the electron density on the carbon bearing that hydrogen,[24-26] then the point where $1/R_{M^+} = 3.5$ corresponds to a hypothetical contact ion pair in which the cation polarizes the anion to such an extent that the electron density on each ring carbon approaches that of naphthalene. Actually, this corresponds to a localized (or essentially covalent) bond since the electron pair must be localized at the α carbon. Going to the other extreme, at infinite cation size the δ_N's approach $\delta_{N\infty}$. Clearly this would correspond to the free ions, or a completely delocalized carbon–metal bond. Although we cannot induce ion separation in pure THF, the δ_N's of the solvent separated or free ions in HMPA should approximate the latter extrapolated values. In Table VII the chemical shifts of the aromatic protons of the anions in HMPA relative to naphthalene in the same solvent are compared to the δ_N values. In spite of the difference in solvent the agreement is fairly good.

Having established the δ_N's of the free ions and covalent species, it is logical to conclude that the observed linear relationship results from partially localized bonding (covalent character) in the contact ion pairs, the term $(1.0 - 1/3.5R_{M^+})$[36] in eq 1 representing the fractional delocalization of the carbon–metal bond. In this context, the bonding of carbon to lithium, sodium, and potassium in the contact ion pairs in THF solution can be thought of as being 58, 71, and 79% delocalized, respectively.

In eq 1, we suggest that the ability of the alkali metals to form localized bonds with carbon is proportional to $1/R_{M^+}$. This leads to the question of why the localized character should depend on this particular variable. Although this question is still being investigated, a simple rationale can be presented at this time. The interaction between anion and cation apparently polarizes the anion by increasing the electron density in the region between the methylene carbon and the cation. The region around the cation may be thought of as a potential well. The probability of finding an electron in this well should depend upon its depth, which is the electrostatic potential at the surface of the cation. If the cation is regarded as a rigid sphere, this potential is inversely proportional to the cation radius.

If the above rationale has merit, one might expect that the bond energies of the alkali metal diatomic molecules would also be a function of the ionic radii. This is indeed the case. A plot of the alkali metal homonuclear diatomic bond energies *vs.* the reciprocals of their Goldschmidt radii,[34] Figure 5, reveals a proportionality to within experimental error. Thus the correlation of ion pair properties with $1/R_{M^+}$ which was presented above could have been made with the alkali metal bond energies instead. This is additional justification for calling the ion pair bonding partially localized or covalent.

Using Hückel molecular orbital theory, a linear relationship between localized character and δ_N values comparable with eq 1 may be derived if the δ_N values are assumed to be proportional to charge densities on the ring carbons:[24-26]

$$\delta_{N\mathrm{t}} = Aq_\mathrm{t} \qquad (2)$$

where $\delta_{N\mathrm{t}}$ refers to the proton attached to carbon t, q_t is the charge on carbon t, and A is a proportionality constant. To the extent that the carbon–metal bond is localized, $\beta_{\mathrm{m-r}}$, the resonance integral between the methylene 2p orbital and that on the adjacent ring orbital is reduced from the usual β_{cc} in the free anion. The variation of the ring charges with $\beta_{\mathrm{m-r}}$ can be calculated to a sufficient approximation using atom–bond polarizabilities,[37] $\pi_{\mathrm{m-r,t}}$:

$$\partial q_\mathrm{t}/\partial\beta_{\mathrm{m-r}} = 2\pi_{\mathrm{m-r,t}} \qquad (3)$$

$$q_\mathrm{t}' = q_\mathrm{t} + 2\pi_{\mathrm{m-r,t}}\Delta\beta_{\mathrm{m-r}} \qquad (4)$$

The pertinent atom–bond polarizabilities have been tabulated for the 1- and 2-naphthylmethyl anions by Coulson and Streitwieser.[38] In Table VIII these are compared with the HMO ring charges, and in both anions the $\pi_{\mathrm{m-r,t}}$ values are proportional to the corresponding q_t. Thus, we can rewrite eq 4 as

$$q_\mathrm{t}' = q_\mathrm{t}(1 - b\Delta\beta_{\mathrm{m-r}}) \qquad (5)$$

b being a proportionality constant (0.90 for the 1 isomer and 1.06 for the 2 isomer). Substituting eq 2 into 5 gives

$$\delta_N = \delta_{N\infty}(1 - b\Delta\beta_{\mathrm{m-r}}) \qquad (6)$$

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(36) In our preliminary communication (ref 1) the term $(1 - 1/3.5R_{M^+})$ was interpreted as the ionic character of the carbon–metal bond. Although this interpretation is tenable, we now feel that it is more accurately identified with the delocalization of the bond. "Localized character" may or may not be synonymous with covalent character, depending upon the one's definition of the latter term.

(37) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **191**, 39 (1947); **192**, 16 (1947).

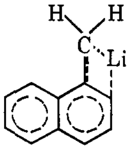
(38) C. A. Coulson and A. Streitwieser Jr., "Dictionary of π-Electron Calculations," Pergamon Press, New York, N. Y., 1965, pp 188–191.

Table VIII. Comparison of Ring Charges (q_t) and Atom–Bond Polarizabilities ($\pi_{m-r,t}$)

		1	2	3	4	5	6	7	8	9	10
1-Naphthylmethyl anion	q_t	0.000	0.200	0.000	0.200	0.050	0.000	0.050	0.000	0.050	0.000
	$\pi_{m-r,t}$	0.000	0.180	0.000	0.180	0.045	0.000	0.045	0.000	0.045	0.000
2-Naphthylmethyl anion	q_t	0.235	0.000	0.059	0.000	0.000	0.059	0.000	0.059	0.000	0.059
	$\pi_{m-r,t}$	0.249	0.000	0.062	0.000	0.000	0.062	0.000	0.062	0.000	0.062

Thus, if we identify $(1 - b\Delta\beta_{m-r})$ with the per cent delocalization of the carbon–metal bond, eq 6 is equivalent in behavior to eq 1. It is a linear relationship with δ_N's approaching $\delta_{N\infty}$ for complete delocalization, and approaching zero (the chemical shifts of naphthalene) as the bond becomes largely localized.

We turn now to the effects of solvent polarity on the spectra of 1- and 2-naphthylmethyllithium. Polar solvents enhance those properties of the organolithium compounds which are generally associated with greater ionic character. In the delocalized systems these effects have been attributed to a stronger coordination of the solvent with cation,[39] which decreases the interaction between cation and anion and allows greater charge delocalization in the latter. This gives rise to red shifts in the electronic spectra[33] and upfield shifts in the pmr spectra of the aromatic protons.[9,40] The electronic and pmr spectra of 1- and 2-naphthyllithium vary with solvent according to the established trends, with two exceptions. Notice in Table I that the resonances of proton 2 in the 1 isomer and proton 1 in the 2 isomer occur at *higher* field in ether than in THF. This suggests that in ether the cation polarizes the anion in a different manner than in the other solvents. The anomalous behavior is not entirely due to the proximity of these protons to the methylene carbon, since proton 3 in the 2 isomer is similarly situated and is not anomalous. It is significant that HMO theory predicts that carbon 1 in the 2-naphthylmethyl anion will bear twice as much negative charge as carbon 3. We suggest that the anomalous upfield shifts are the result of a strong polarization of the anion caused by a shifting of the equilibrium position of the cation in the contact ion pair toward the ring carbon bearing the proton whose shift is anomalous. Structurally, this suggests that in ether the lithium ion may interact with a ring carbon as well as the methylene group, as in **6** and **7**. Allylic interactions similar to this have been reported in certain benzyl transition metal complexes.[41–43] Further support for this idea lies in the fact that in benzyllithium triethylenediamine crystals,[16] the lithium ion is coordinated to the benzyl group in a manner remarkably similar to the allylically coordinated transition metals. A similar type of structure has been suggested for certain allylic lithium compounds.[10,11] It appears that in the poorly coordinating ether solvent, or when there is a deficiency of solvent such as in the solid state, the anion may successfully compete for a second coordination site on the cation. This may be the beginning of a transition from the largely ionic, monomeric, delocalized ion pairs in THF to an oligameric, mainly covalent structure of the alkyllithiums in nonpolar solvents. Transitions between ionic and covalent structures with decreasing solvent polarity have been reported previously.[11,15]



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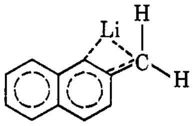

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Rotational Barriers. Another indication of partial carbon–metal bond localization in the contact ion pairs comes from the variations in the barriers to rotation[9,44] about the methylene–ring bonds with cation size. The barriers increase in order Li < Na < K (Table V). These data parallel the chemical shift behavior and reinforce the bonding concepts presented above. Partially localized bonding in the contact ion pair would be expected to decrease the π-bond order between the methylene carbon and the ring, thereby reducing the barrier to rotation.

Thus far we have discussed partially localized bonding in the contact ion pairs in terms of a hybrid structure. Another model which has been suggested to account for the properties of partially ionic organometallic compounds is an equilibrium between covalent and ionic species.[9,44–46] The rotational barrier data serve to distinguish between these two models.

Superficially, both the chemical shift and rotational barrier data can be rationalized by assuming equilibria between covalent and ionic species. If the equilibria were rapid enough, the chemical shifts would depend on the mole fraction of ionic (n_I) and covalent (n_C) forms, and their chemical shifts (δ_{NI} and δ_{NC}).

$$\delta_{Nt} = n_I\delta_N + n_C\delta_{NC} \qquad (7)$$

If δ_{NI} and δ_{NC} are assumed to be $\delta_{N\infty}$ and zero, respectively, the resulting equation predicts the linear chemical shift behavior found in eq 1. The lithium compounds would require approximately 42% of the covalent species, however, and this is not reconcilable with an appreciable barrier to rotation about the methylene–ring bonds. Thus the presence of these barriers indicates that the chemical shift behavior cannot result from an equilibrium.

We cannot rule out the possibility, however, that the mechanism for rotation does involve imperceptible amounts of covalent species in equilibrium with the ion pairs. Bates,[47] *et al.*, invokes this mechanism for ro-

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[39] It is generally accepted that aprotic solvents, such as ethers and HMPA, solvate cations primarily. (See ref 6, 15, and V. H. Normant, *Angew. Chem.*, **79**, 1029 (1967).)

[40] R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, **85**, 4042 (1963).

[41] R. B. King and A. Fronzaglia, *ibid.*, **88**, 7091 (1966).

[42] F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 5418 (1968).

[43] F. A. Cotton and T. J. Marks, *ibid.*, **91**, 1339 (1969).

[44] R. B. Bates, D. W. Grosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

[45] E. Grovenstein, S. Chondra, C. E. Collum, and W. E. Davis, Jr., *J. Amer. Chem. Soc.*, **81**, 1769 (1959).

[46] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954, Chapter 4.

[47] R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, Abstracts of Papers presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, ORGN 144.

tation in the pentadienyl anions in THF solution. This conclusion was reached because the rotational barriers increased with dilution, presumably due to a shifting of the equilibrium toward the ionic species. This argument applies only if the ions are appreciably dissociated, which is an unlikely possibility in THF. An increase in the degree of association with increasing concentration would provide an alternate explanation for this effect.

On the other hand, Heiszwolf, Van Drunen, and Kloosterziel[48] argue that internal rotation in *cis*-3-methyl-*trans*-1-phenylallylpotassium in liquid ammonia occurs *via* the ionic species because rates of rotation were not affected by a 130% increase in potassium ion concentration. Again the argument is sound only if appreciable amounts of free ions are present, since the equilibrium between ions pairs and covalent species should be independent of cation concentration. Thus the precise mechanism for rotation in delocalized carbanions must await further definitive experiments.

Conclusions

The alkali metal derivatives of 1- and 2-methylnaphthalene exist as contact ion pairs in THF and ether at ambient temperature, whereas the lithium and sodium compounds are solvent separated or free ions in HMPA. In all cases the hybridization of the methylene carbon is sp^2 and the methylene hydrogens lie in or near the plane of the aromatic rings.

In the contact ion pairs, the cation–anion interaction takes place mainly at the sp^2-hybridized methylene carbon, although in ether there appears to be an allylic type of coordination with the ring π system as well in the lithium compounds. The spectra of the contact ion pairs suggest partial localization of the carbon–metal bonds, which decreases with increasing cation solvation and cation size. The delocalization of the C–Li, –Na, and –K bonds evaluated from chemical shift variations is 58, 71, and 79%, respectively. This partial delocalization does not result from rapid equilibria between ionic and covalent forms.

Experimental Section

A combination of syringe and vacuum line techniques was used in solvent purification, preparation of the alkali metal organometallic compounds, and sample handling.

Purification of Solvents. Reagent grade ethyl ether and THF were distilled from a solution of the potassium ketyl of benzophenone and stored under vacuum in a solution of the potassium radical anion salt of anthracene. Butyllithium was added to reagent grade hexane, and the solution was stored under vacuum. These solvents were distilled from the storage vessels immediately prior to use. It was impractical to distill HMPA through the vacuum manifold because of its low volatility. It was purified by distillation from a solution of triphenylmethyllithium directly into breakseal tubes for storage and transfer.

1-Naphthylmethyltributyltin. Under nitrogen, a Grignard reagent was prepared in the usual fashion from 18 g (an excess) of magnesium turnings and 29 g (0.165 mol) of 1-chloromethylnaphthalene in 200 ml of dry ether. To this 53 g (0.163 mol) of tributyltin chloride in 50 ml of ether was added dropwise with stirring. The stirring was continued for 4 hr, after which the mixture was cooled in an ice bath and hydrolyzed with water. The solid was removed by filtration and washed several times with petroleum ether, the washings being added to the filtrate. The organic layer was separated, dried and evaporated. A small amount of solid precipitated at this point and was filtered off. Recrystallization twice from benzene yielded 1.0 g of material identified as 1,2-di-(1-naphthyl)ethane by its nmr spectrum and 163–165° melting point (lit.[49] 163–165°).

The remainder of the organic layer was vacuum distilled through a 12-in. Vigreux column to yield 58 g (83%) of 1-naphthylmethyltributyltin, bp 170° (0.05 mm). Its nmr spectrum was in agreement with the assigned structure.

2-Naphthylmethyltributyltin. The preparation of the title compound was very similar to the 1 isomer; 45 g of 2-bromomethylnaphthalene (0.20 mol) and 64 g (0.20 mol) of tributyltin chloride were used. Work-up as before gave 0.5 g of 1,2-di(2-naphthyl)ethane, mp 187.5–189.5° (lit.[50] 184–186°), and 57.2 g (67%) of 2-naphthylmethyltributyltin, bp 171–175° (0.05 mm). The nmr spectra of the products were in agreement with the assigned structures.

Preparation of Organometallic Compounds by the Method of Seyferth and Weiner.[18] The procedures used in the preparation of 1- and 2-naphthylmethyllithium were essentially identical. Similar procedures were also used for the preparation of all the sodium and potassium compounds. Thus two examples will suffice to illustrate these preparations. The sodium and potassium compounds prepared by this method were found by flame photometric analysis to contain lithium to the extent of 14–28 mol %.

1-Naphthylmethyllithium. To a solution of 1.20 g (2.8 mmol) of 1-naphthylmethyltributyltin in 2.0 ml of hexane and 2.0 ml of ethyl ether was added 1.5 ml of 2.25 *M* butyllithium in hexane (20% excess), with stirring. The monoetherate of 1-naphthylmethyllithium precipitated as a yellow-orange crystalline solid over a period of 1.5 hr. The solid was filtered off, washed several times with hexane, and dried under vacuum.

1-Naphthylmethylsodium. When a mixture of 0.45 g (4.5 mmol, of sodium *tert*-butoxide and 1-naphthylmethyltributyltin in 4.0 ml of hexane was treated with 2.6 ml of 2.25 *M* butyllithium in hexane, the mixture immediately turned rust brown. The mixture was stirred for 5 hr whereupon a rust-colored solid precipitated. This was filtered, washed six times with 5-ml portions of hexane, and dried under vacuum.

Preparation of 1-Naphthylmethylsodium and -potassium by the Method of Williams, Levy, and Pearson.[20] The procedure was identical for both compounds. The preparation of 1-naphthylmethylsodium will illustrate this procedure. A sodium mirror was prepared by vacuum distilling 150 mg (6.5 mmol) of sodium through a series of three bulbs, and then into a reaction vessel. A solution of 50 mg (0.19 mmol) of 1,2-di(1-naphthyl)ethane in 0.50 ml of THF and 0.05 ml of tetramethylsilane was admitted. The mixture was agitated for about 1 hr to ensure complete reaction. The solution was then filtered into an nmr tube attached to the reaction vessel, and the sample was sealed under vacuum.

Isopiestic Molecular Weight Measurements. An accurately weighed sample (*ca.* 40 mg, 0.16 mmol) of triphenylmethane was introduced into one leg of a volume-calibrated H tube. The tube was evacuated and flushed with nitrogen. Then 3.0 ml of a saturated solution of recrystallized (from ether) naphthylmethyllithium was introduced into the second leg of the H tube. This solution was frozen in liquid nitrogen, and the apparatus was again evacuated. An extra 4–5 ml of ether was distilled into the apparatus, whereupon it was sealed and submerged in a constant temperature bath at 25°. Equilibration was considered to be complete when there was no change in the volume of either solution for a 48-hr period. The equilibrium was then disturbed by cooling one leg, and equilibrium was approached from the opposite side.

Acid–base titration was used to determine the amount of organometallic compound present. Water was introduced into the sample leg *via* a breakseal tube. The apparatus was then opened, the ether solvent was evaporated, and an excess of standard acid was introduced. This was back titrated with standard base.

Finally, the organic residue from the sample leg was taken up in carbon tetrachloride, dried, and filtered into an nmr tube to check for contaminants (such as tetrabutyltin). If any indication of contamination was found in the spectrum, the data were discarded. This procedure yielded molecular weights of 139 and 137 for the 1- and 2-naphthylmethyllithium in ether, respectively. This is within experimental error of the 144 molecular weight calculated for monomeric species.

Sample Preparation and Spectroscopic Procedures. Solutions of 1- and 2-naphthylmethyllithium in THF and HMPA were pre-

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(48) G. J. Heiszwolf, J. A. A. Van Drunen, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, 88, 1377 (1969).

(49) *Beilstein*, 3rd ed, 5, 2496.

(50) *Ibid.*, 5, 2497.

pared from the monoetherates by adding the more polar solvent and distilling out the ether under vacuum. The complete removal of ether from the THF solutions required evaporation to dryness twice, followed by dilution with enough THF to bring the sample to the required concentration.

Samples for electronic spectra were transferred to evacuated cells by means of breakseal tubes. Spectra were run at approximately 10^{-2} and 10^{-3} *M* using a 1.0-mm cell equipped with a removable 0.9-mm spacer. The spectra were recorded on a Cary 14 spectrophotometer.

The nmr samples were filtered through a sintered glass filter into an nmr tube attached to the vacuum apparatus and sealed under vacuum. Spectra were recorded on a Varian HA 100 spectrometer in frequency sweep mode using solvent peaks for a lock. Frequency measurements were made using a frequency counter and the chemical shifts were referenced to TMS by adding the chemical shift of the lock peak. In THF and HMPA the methylene protons could not be observed because of overlap with the solvent peaks. In the case of THF this was remedied by the use of THF-d_8 as a solvent. TMS was used for a lock in these samples.

Temperatures were measured using the Varian-supplied methanol and ethylene glycol samples. Frequency measurements of the methanol peaks in the −5 to +10° range were not reproducible because the peaks are very broad. Interpolation was therefore necessary. In the vicinity of 40°, temperature measurements with the two samples agreed to ±1°.

Chemical Shifts of Naphthalene in THF and HMPA. The 100-MHz spectra of 0.20 *M* solutions of naphthalene in CCl_4, THF, and HMPA were obtained. The patterns were all very similar, but reasonably large shifts in the α and β proton patterns were apparent. Using the value of Cooper and Manatt[51] for the chemical shift between the α and β protons (35.7 Hz) and the midpoint between their patterns in the CCl_4 spectrum (7.56 ppm), the chemical shifts are calculated to be 7.74 and 7.38 ppm, respectively, for the 0.2 *M* solution.[52] In THF the α and β patterns were 0.06 and 0.04 ppm downfield from the corresponding patterns in CCl_4. The α and β chemical shifts in THF are then approximately 7.80 and 7.42 ppm, respectively. In HMPA the patterns were shifted downfield 0.22 and 0.12 ppm, making the approximate chemical shifts 7.96 and 7.50 ppm.

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[51] M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **91**, 6325 (1969).

[52] The naphthalene chemical shifts were observed to be quite concentration dependent.

Dependence of Mechanism on pH for Deuterium–Hydrogen Exchange in 1-Methyltetrazole-5-*d*. Transition Metal Ion Catalysis of a Deprotonation Process

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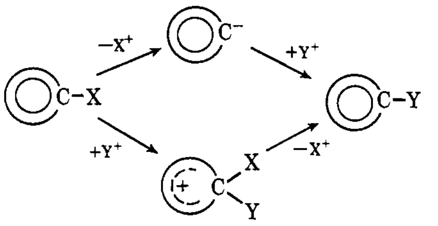
Abstract: The pH–rate profile of protium for deuterium exchange of 1-methyltetrazole-5-*d* in aqueous solution at 67.6° has been determined and used as a control experiment in a demonstration that σ complexation of a heteroaromatic substrate with a transition metal cation (Cu^{2+} and Zn^{2+} used) can have a major rate-enhancing effect on processes in which substrate ring substituents are eliminated to produce formal sp^2 carbanion intermediates. The control experiment is itself of interest, since in addition to a flattened exchange rate minimum at pH 4, a rate maximum is found at $-H_0$ 1–1.5, well below the experimental H_0 (*ca.* −2.4) for half-protonation of 1-methyltetrazole.

Electrophilic substitution at annular positions in heteroaromatic compounds *via* carbanionic intermediates (mechanism 1) has been amply and rigorously documented[1] and in many systems rivals in importance the much better known pathway 2 involving initial addition of the electrophilic reagent at the carbon atom being substituted. Moreover, the synthetic transformations which may readily be accomplished by each route are usually complementary because positional specificities and reaction condition requirements are ordinarily quite different.

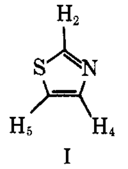


(1)

(2)

The present investigation has two origins: first, a desire to devise practical methods to increase the facility of electrophilic substitution by the ionization pathway 1 and thus increase its utility; and second, a suspicion that catalytic mechanisms are available by which biological systems could make greater use of this process than would be expected from predicted reactivities. The analysis which led to the specific experiments reported here is outlined below.

In OD^-–D_2O at 31°, thiazole (I) readily undergoes H–D exchange of H_2 and H_5 (relative rate 1:0.9) by a simple ionization pathway, rate = k_2[thiazole][OD^-].[2] N-Alkylation (→II) produces a vast selective increase



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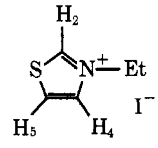

II

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[1] Though this area has never been generally reviewed, references are too numerous to reproduce here. Some of this work and leading references to most of the remainder can be found in the papers cited in ref 2–10.

[2] R. V. Kendall, Dissertation, The Pennsylvania State University, 1970; R. A. Olofson, J. M. Landesberg, K. N. Houk, and J. S. Michelman, *J. Amer. Chem. Soc.*, 88, 4265 (1966).