Reilley[7h] have postulated the existence of disubstituted EDTA-cadmium complexes in the presence of excess EDTA, i.e.

$$\mathrm{Cd(EDTA)'} + \mathrm{EDTA} \rightleftharpoons \mathrm{(EDTA)Cd(EDTA)'} \rightleftharpoons \mathrm{Cd(EDTA)} + \mathrm{(EDTA)'}$$

This species should be highly immobilized in aqueous solution because of the presence of the number of negative charges. This degree of immobilization should lead to a dramatic shortening of the spin-lattice relaxation time for the cadmium nucleus. The preceding statement assumes that the ^{113}Cd spin-lattice relaxation mechanism(s) would be dominated either by dipole-dipole or chemical shift anisotropy processes.

Further evidence for the existence of chemical exchange between different species of Cd-EDTA at high pH values comes from the field dependence of the ^{113}Cd line width at pH 13.75; $\Delta\nu_{1/2} = 5$ Hz at 2.3 T and 20 Hz at 9.4 T. That is, the kinetic processes have become slower by a factor of 4 at 9.4 T with respect to the ^{113}Cd NMR chemical shift time scale in hertz. This contrasts with the ^{113}Cd line width for the low pH form(s) which is independent of the applied field strength ($\Delta\nu_{1/2} = 2$–3 Hz). Currently the actual identities of the solution species of Cd-EDTA at high pH are unknown. However, low-temperature, supercooled aqueous solution studies[22] and solid-state NMR experiments are being designed to further investigate the nature of these species.

Summary and Conclusions

The dependence of the ^{113}Cd chemical shift for Cd-EDTA as a function of pH in the range pH 3.0–13.8 has been determined. This striking pH dependence of the ^{113}Cd chemical shift clearly points out how informative NMR spectroscopy of metal nuclei can be. In an effort to understand the origins of this pH dependence, the ^{113}Cd spin-lattice relaxation time was determined at three field strengths (2.3, 4.7, and 9.4 T) and at selected values of pH. However, these data could not be properly analyzed without a corresponding determination of the ^{13}C spin-lattice relaxation times for the metal-bound ligand. These data afforded a value of $\tau_c = 1.1 \times 10^{-10}$ s for the low pH form. Thus, with this relatively "simple" anion it was found that the complex is near the region of intermediate correlation time. Within this region the value of $\eta_{\max}$ for ^{113}Cd changes rapidly with frequency, and frequency-dependent terms within the expressions for T_1^{-1} become increasingly important. Hence, the frequency dependence of these parameters must be included to properly interpret the experimental data. With a knowledge of $T_1^{\mathrm{DD}}(^{113}\mathrm{Cd})$ for Cd-EDTA in the presence and absence of deuterium in the ligand, it was determined that protons from water in the primary solvation sphere are providing a dipolar relaxation pathway for the ^{113}Cd nucleus. Hence, part of the observed pH dependence (pH 4-11) of the ^{113}Cd chemical shift, $T_1(^{113}\mathrm{Cd})$, and $\eta(^{113}\mathrm{Cd}\text{-}\{^1\mathrm{H}\})$ is due to the presence of a hydrated form of Cd-EDTA. It is essential to point out that the proper interpretation of the relaxation data was only afforded after a knowledge of the correlation time. Without this, the experimentally determined frequency dependence of T_1 may have been seriously misinterpreted. Therefore, the analysis of relaxation data of any highly charged metal nuclide must be preceded by a determination of τ_c for the complex.

Analysis of the ^{113}Cd relaxation data of Cd-EDTA at pH 13.8 illustrates how chemical kinetics can, under certain circumstances, dominate the measured value of T_1. These data argue the importance of hydroxylated forms of Cd-EDTA at this pH. Further, they also demonstrate the importance of examining relaxation parameters at widely separated field strengths.

Finally, the observed behavior of $T_1(^{113}\mathrm{Cd})$ and $\eta(^{113}\mathrm{Cd})$ for Cd-EDTA are in all probability a function of the nature of the counterion. The present work utilized the tetramethylammonium ion. However, other counterions may yield different results. These phenomena could arise because of the differences in the nature of the solvation of the Cd-EDTA anion/counterion complex. Further work on these systems is planned.

Acknowledgment. The authors acknowledge the NATO Science Affairs Division, Brussels (Research Grant No. 1831), the Danish Natural Science Research Council (J. No. 511-15401), the National Science Foundation Regional Nuclear Magnetic Resonance Facility at the University of South Carolina (CH78-18723), the National Institutes of Health (GM 26295), and the National Science Foundation (CH78-03115) for partial support of this research. Further, S.D. thanks DANIDA for the research fellowship. Finally, the authors thank Mr. K. E. Holst for synthesizing the EDTA-d_{12} ligand and the continuing support of Mr. P. Daugaard with the XL-100 spectrometer (Aarhus).

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NMR and Conductometric Studies of 2-Pyridyl-Substituted Carbanions. 2. Effects of Cation Size and Coordination

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Abstract: ^{1}H and ^{13}C NMR spectra of the lithium, sodium, and potassium salts of 2-ethylpyridine without and in the presence of crown ethers and cryptands indicate that the uncomplexed salts are present as contact ion pairs. Conductometric measurements carried out on the sodium salt confirm this conclusion and also indicate that the dibenzo-18-crown-6 and [2.2.2]cryptand complex of the sodium salt exist as a 1:1 crown complexed contact ion pair and a partially separated cryptate, respectively. The partial double-bond character of the C_α–C_2 bond leads to the occurrence of *E* and *Z* torsional isomers that are distinguishable by H_α–H_4 coupling. Coalescence of the CH$_3$ group for the Na, K, (Li, tetraglyme), and (Na, tetraglyme) salts in THF is observed at 105, >120, 65, and 95 °C, respectively. The *E*/*Z* isomer ratio, at least at higher temperatures, appears therefore to be thermodynamically controlled and decreases with increasing cation size and coordination. The ΔH of the equilibrium appears to be close to zero. This seems to indicate that differences in *E*/*Z* isomer ratios are entropy rather than enthalpy determined and may be due to restrictions on the rotation of the CH$_3$ group and the coordination sphere of the cation that is bonded in an allylic type fashion to C_α and N. Charge distribution within the anions was determined from ^{1}H and ^{13}C chemical shifts by using Me$_4$Si as internal standard and was found to be in qualitative agreement with CNDO/2 calculations.

Although the structure of ion pairs of delocalized hydrocarbon anions has been extensively studied in recent years,[1-3] relatively little detailed information is available about ion pairing in heteroatoms containing analogue anions in which the heteroatom

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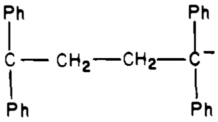
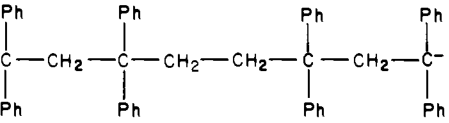
carries a substantial portion of the negative charge.[4,5]

Such systems are of considerable synthetic interest. For instance, substantial cation and solvent effects on stereochemistry have been demonstrated for enolates,[5] imines,[6] hydrazones,[7] oxazolines,[8] and other analogues,[9] and similar observations have been made for anionic polymerizations of vinyl monomers of the type $CH_2{=}C{-}C(Y){=}X$, where X = O or N and Y = O, N, or C.[10]

Previously, we reported that Li, Na, and Cs salts of **2** and **4** exist as tight ion pairs in relatively polar media such as THF and DME, although the Li and Na salts of **1** and **3** could be shown to exist as equilibrium mixtures of contact and separated ion pairs.[4b] Upon addition of crown ethers to the Na salts of **2** and **4**, **2** was converted to a crown separated ion pair, whereas **4** formed a crown complexed contact ion pair. These results were interpretable as due to extensive delocalization of charge into the 2- and 4-pyridyl rings, leading to a high charge density on nitrogen. For **3**, such a delocalization is not possible, and the anion closely resembles the corresponding hydrocarbon anion (**1**).





2, Py = 2-pyridyl
3, Py = 3-pyridyl
4, Py = 4-pyridyl

Subsequent studies of the stereochemistry of oligomerization of 2-vinylpyridine initiated by alkali salts of 2-ethylpyridine, according to eq 1, showed that with lithium and sodium as counterion this process yields isotactic oligomers.[11] With larger or more extensively solvated cations, the stereoselectivity is decreased. These results prompted us to take a more careful look at ion pairing of **5** and **6** as models of anions **7**–**9**.

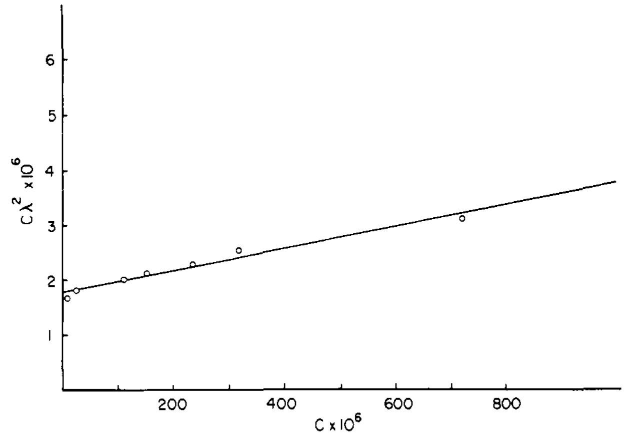
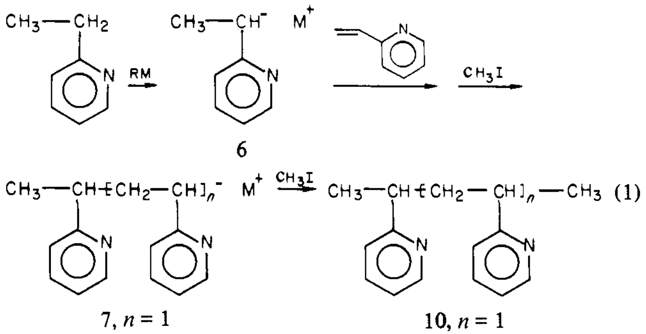


Figure 1. Wooster plot (eq 2) of sodio-2-ethylpyridine in THF at 25 °C.

Table I. Effects of Coordination by Dizenzo-18-crown-6 and [2.2.2] Cryptand on Ion Pair (K_1) and Triple Ion (K_2) Dissociation Constants of Sodio-2-ethylpyridine in THF at 25 °C

salt	solvent	K_1, M	K_2, M
Na-6	THF	1.4×10^{-10}	6.1×10^{-4}
	THF/dibenzo-18-crown-6[a]	1.5×10^{-9}	
	THF/[2.2.2] cryptand[a]	5.5×10^{-7}	

[a] Crown and cryptand in about 10% excess.

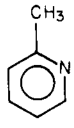


(1)

6

7, n = 1
8, n = 2
9, n = 3

10, n = 1
11, n = 2
12, n = 3



5

Results

UV/Visible and Conductance Studies. The sodium salt of 2-ethylpyridine (**6**) (see Experimental Procedures) was briefly investigated by UV/visible and conductimetric techniques. The UV spectrum of this salt matched that of the corresponding "living" poly(2-vinylpyridine) reported by Tardi and Sigwalt[12] and Fisher and Szwarc.[13] The absorption maximum at 321 nm was assumed to have the same extinction coefficient as that found for living poly(2-vinylpyridine) (ϵ = 10400). The spectrum was found to be independent of concentration in the 10^{-3}—10^{-6} M range. At the lowest concentration, however, the absorbance

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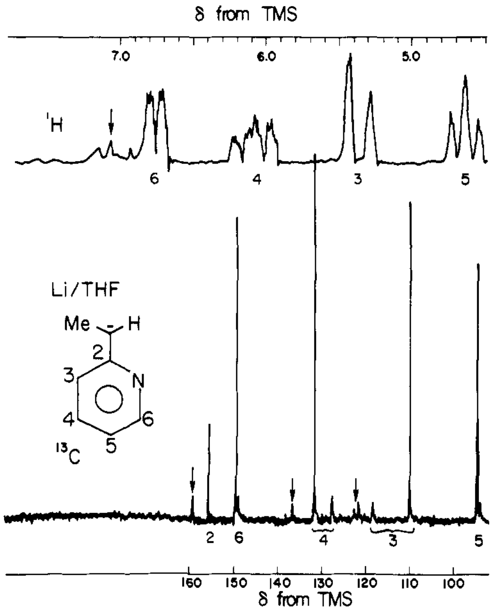


Figure 2. ^{13}C and ^1H NMR spectra of lithio-2-ethylpyridine in THF-d_8.

decreased rapidly with time, presumably due to the presence of a significant fraction of free ions. Addition of dibenzo-18-crown-6 to **6** did not result in an observable shift in the spectrum. Addition of [2.2.2]cryptand,[14] however, gave a red shift of about 7 nm, indicating at least partial ion pair separation. Conductance of the Na salt of **6** was measured over the 10^{-3}–10^{-7} M range. The Kraus–Brey plots of $1/\lambda$ vs. $C\lambda$ were strongly curved in the 10^{-4}–10^{-3} M region, indicating the presence of triple ions. The conductance data were replotted according to Wooster's equation.[15]

$$C\Lambda^2 = \Lambda_0^2K_1 + (2\Lambda_0\lambda_0 - \Lambda_0^2)K_1C/K_2 \qquad (2)$$

where Λ is the observed equivalent conductance, Λ_0 is the sum of the equivalent limiting conductances of cation and anion, λ_0 is the equivalent limiting conductance of the triple ion, and K_1 and K_2 are the dissociation constants of the ion pair and the triple ion, respectively. A plot of $C\Lambda^2$ vs. C (Figure 1) shows good linearity. From the value of the intercept, a value for K_1 of 1.8×10^{-10} M was determined, in good agreement with the value obtained from the limiting slope of the corresponding $1/\lambda$ vs. $C\lambda$ plot. From the slope of the $C\Lambda^2$ vs. C plot of **6**, the K_2 value is determined as 6.1×10^{-4}, indicating that triple ion formation is not extensive.

Thus, under the conditions of our NMR experiments (0.1–1.0 M) (see below), the proportion of triple ions can be estimated as less than 3%. The spectra are, therefore, most likely representative of ion pairs only.

In order to investigate the effects of cation coordinating agents on the structure of the ion pair, dibenzo-18-crown-6 and [2.2.2]cryptand were added to Na-**6**. In these cases, linear $1/\lambda$ vs. $C\lambda$ plots were obtained, and values of the ion pair dissociation constant could conveniently be obtained (Table I). The dissociation constant for the crown complex is increased about 10-fold, whereas that of the cryptand complex increased by a factor of about 4000. In neither case did the conductance of the solutions increase upon addition of crown ether or cryptand beyond that needed for a 1:1 complex, thus confirming the 1:1 stoichiometry of the complex.

NMR Measurements. The spectra of the recrystallized Li and K salts and the lithium [2.2.1]cryptate of **6** are shown in Figures 2–4. The ^1H NMR spectrum of the Li salt clearly shows the ring protons absorbing over a wide range in the order of increasing field strength: H_6 (δ 6.72), H_4(6.05), H_3 (5.32), and H_5 (4.58). Inspection of the ^1H spectrum of the potassio salt reveals a second set of absorptions which are most visible at H_4 (δ 5.78). The magnitude of the H_α–H_4 long range coupling constants for both H_4 signals indicates that the upfield signal is most likely due to the E isomer ($J_{\alpha\text{-}4}{}^E = 1.0$ Hz) (Figure 4). Weaker coupling is observed in the Z isomer ($J_{\alpha\text{-}4}{}^Z = 0.2$ Hz). Similar long range coupling was observed by Takahashi et al. for the 2-picolyl anion.[16]

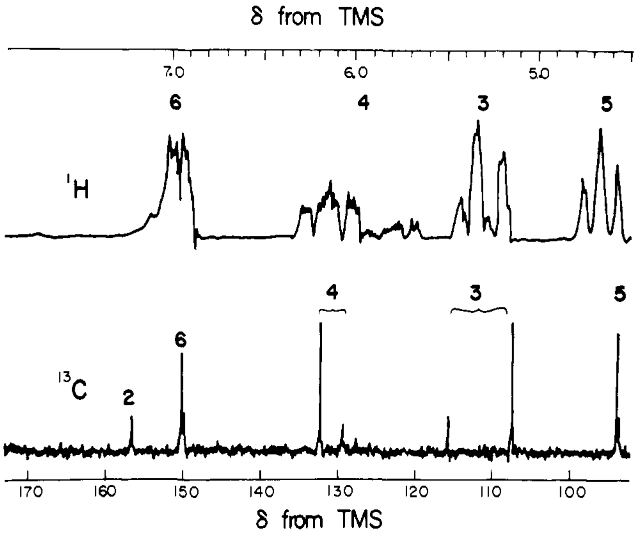


Figure 3. ^{13}C and ^1H NMR spectra of potassio-2-ethylpyridine in THF-d_8.

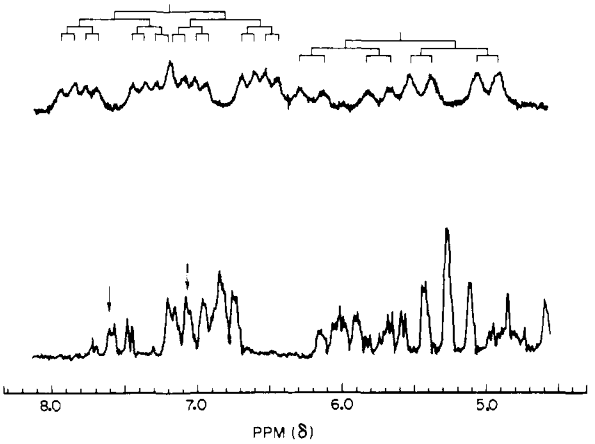
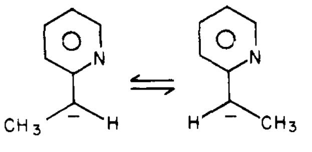


Figure 4. Proton NMR spectrum of the [2.2.1]cryptand complexed lithio-2-ethylpyridine in THF with expanded H_4 signal.



(3)

E *Z*

Integration of the ^1H NMR spectra affords the relative proportions of E and Z isomers of **6**. The ^{13}C NMR spectra also show evidence of E and Z carbanion isomers. For the K salt, the E/Z ratio obtained from ^1H and ^{13}C NMR is identical, indicating no complications due to NOE. Table II shows the relative abundance of the two isomers as a function of cation and solvent or coordinating agent. Larger cations and addition of stronger cation coordination compounds to the Li and Na salts shift the mixture of isomers toward the Z form, indicating that at least for the more extensively solvated ion pairs, we are dealing with an equilibrium.

Interestingly, the relative proportions of E and Z isomers do not appear to be affected by temperature. Thus, no significant change in the E/Z ratio is observed for the Na and K salt from

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Table II. Dependence of the Ratio (*E*)-6/(*Z*)-6 on Cation and Cation Coordination at 25 °C[a-c]

cation	solvent	$\Delta G^E - \Delta G^Z$, kcal/mol	(*E*)-6/(*Z*)-6
Li	THF	−1.77	19.00[e]
Li	THF/TG	−0.92	4.60
Li	THF/[2.2.1] cryptand	−0.35	1.78
Na	THF	−1.08	6.10
Na	THF/TG	−0.39	1.90
K	THF	−0.83	4.00
K	NH_3	0.12	0.82[d]

[a] Lithio salts prepared from 2-ethylpyridine and *n*-BuLi. Sodio and potassio salts prepared from the corresponding dianion tetramers of α-methylstyrene. [b] Salts were recrystallized from toluene- (or hexane-)THF mixtures. [c] Coordinating agents were added after salt formation. [d] Zoltewicz, J. A., private communication. [e] Determined by ^{13}C NMR spectroscopy.

Table III. Approximate (*E*)-6-(*Z*)-6 Coalescence Temperatures and Free Energies of Activation as a Function of Cation and Cation Solvation

cation	solvent	coalescence temp, °C	$\Delta G^{\ddagger}$, kcal/mol[a] $E \rightleftharpoons Z$
Li	TG	65	18.7
Na	THF	105	20.3
Na	THF/TG	95	20.6
K	THF	>120	>22

[a] Calculated according to ref 18.

−35 °C up to their coalescence tempertures (see Discussion).

High-temperature studies were performed to study the rate of interconversion between *E* and *Z* isomers of **6** by using the respective CH_3 absorptions. Slight temperature-dependent shifts, small chemical shift differences between *E* and *Z* isomers, and unequal isomer populations (see Table II) made line-width studies impractical so that enthalpies and entropies of activation for the reaction could not be determined.[17] However, approximate coalescence temperatures were obtainable providing some information on the effects of cation size and coordination on the apparent rotational barrier.[18] The results are shown in Table III. The barrier increases in the order Li, TG < Na, TG < Na < K. The Li salt was studied only in the presence of tetraglyme because of the high *E*/*Z* ratio (~19, see below). An attempt to study the effect of [2.2.1]cryptand on the coalescence of the Li salt failed due to the rapid decomposition at higher temperatures. The results indicate that the barrier is increased with increasing cation size and is slightly lowered upon addition of tetraglyme to the Na salt (see Discussion).

The high barrier to rotation suggested the possibility of measuring the rate constant for the $E \rightarrow Z$ interconversion at low temperatures and observing the relaxation to the new equilibrium. This was done by adding [2.2.1]cryptand to the Li salt at liquid nitrogen temperatures and letting the mixture warm up to −78 °C. The ^1H NMR spectrum taken about 20 min after the addition showed that the displacement toward the new equilibrium had occurred. Although a rate constant could not be measured, a lower limit of 7×10^{-4} s^{-1} could be calculated.

Table IV contains ^1H chemical shift data of the Li, Na, and K salts of **6** in THF with and without the presence of added coordinating agents. The ^1H chemical shifts show only a slight cation dependence with the largest shift at H_6 which is shifted upfield in the order K < Na < Li. The other protons show a weaker cation dependence with positions β, 4, and 5 showing downfield shifts with increasing cation radius. Positions H_α and H_3 show upfield shifts.

Addition of tetraglyme (TG) to the Na salt and [2.2.1]cryptand to the Li salt of **6** produced upfield shifts at H_3 and H_5. the addition of TG to the Li salt produced little change. The K/TG complex was not sufficiently soluble for study. The temperature dependence of the ^1H NMR chemical shifts of the alkali salts of **6** is shown in Table V. The K and Na salts show almost no temperature dependence. The Li salt shows upfield shifts at H_α, H_3, and H_5 with decreasing temperature, the largest shifts occuring at H_3 and H_5.

The ^{13}C NMR spectra of the Li, Na, and K salts of **6** are summarized in Table VI. The order of the chemical shifts is the same as that observed for the corresponding proton spectra. The presence of *E* and *Z* isomers is evident in all spectra, including that of the lithio salt. The C_2 absorption was assigned from a coupled ^{13}C NMR spectra that also confirmed the α-carbon resonance.

$^{13}C-^1H$ coupling constants for the Li and Na salt of **6** are given in Table VII together with those of pyridine. The ring coupling constants are equal or smaller compared to that of pyridine, consistent with the observation that increased negative charge density reduces the magnitude of $^{13}C-^1H$ coupling. $^1H-^1H$ ring coupling does not show a noticeable variation with cation or solvent.

CNDO/2 Calculations. Semiempirical and ab initio molecular orbital calculations have been used quite extensively to study ion pair structure, especially the nature of the carbon–lithium bond.[3h,19-22] In alkyllithiums, the calculations support the concept of prevalent covalent character. In the case of delocalized systems the organolithium compound appears to exist as either an undissociated ion pair or a dissociated ionic salt, and these experimental results have also been supported by the results of ab initio and semiempirical calculations.

The CNDO/2 method which was selected for this study has been widely used, and its strengths and weaknesses are well-known.[23] It is qualitatively good at predicting stable geometries with errors in bond length of about 0.1 Å and in bond angles of a few degrees. The calculated atomic charges are usually good to within a few hundredths of an electron, although the stability of compact geometries tends to be somewhat overestimated.

The calculations were begun on the picolyl anion–lithium ion pair by using bond angles and bond lengths reported for the pyridine ring.[24] The $C_\alpha-C_2$ bond length was first optimized in the free anion, assuming an sp^2 hybridization at C_α. The position of Li was then optimized for positions both in the nodal plane and above the delocalized carbanion. The hybridization at C_α was also varied to compare the energies of a delocalized anion and a "covalent" species with sp^3 hybridization at C_α. The calculations indicate that the optimum cation position is about 2 Å above the carbanion plane, equidistant between the C_α and N atom near C_2. By comparison, the lowest potential energy position of the Li ion in the nodal plane (with the cation coordinated to the nitrogen lone pair) was calculated to be 60 kcal higher in energy and thus seems unreasonable. These results are in qualitative agreement with the findings of Bongini et al.[19] who performed ab initio calculations on the allyllithium system and the results of Eizner and Erussalimsky[27] and Matsuzaki et al.,[3h] who carried

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Table IV. ^1H NMR Chemical Shifts in ppm from Internal Me_4Si for Li, Na, and K Salts[a] of 6 in THF at 38 °C

		CH_3		H_α		H_3		H_4		H_5		H_6	
cation	solvent	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*
Li	THF	1.38		3.13		5.32		6.05		4.58		6.72	
	THF/TG	1.38		3.13		5.28		6.05		4.57		6.75	
	THF/[2.2.1]-cryptand	1.37		3.13		5.18	5.37	6.03	5.68	4.50	4.28	6.78	7.02
Na	THF	1.40	1.50	3.13		5.32	5.40	6.15	5.75	4.68	4.55	6.85	
	THF/TG	1.37	1.43			5.08	5.08	6.03	5.68	4.48		6.85	
K	THF	1.43	1.53	3.07		5.27	5.35	6.15	5.78	4.67	4.63	6.97	

[a] Concentrations 0.1–1.0 M.

Table V. Temperature Dependence of the ^1H Chemical Shifts in ppm from Internal Me_4Si for Li, Na, and K Salts of 6 (*E* Isomer Only) in THF[a]

cation	*T*, °C	CH_3	H	H_3	H_4	H_5	H_6
Li	−44	1.37	3.07	5.18	5.98	4.47	6.15
	6	1.38	3.12	5.28	6.05	4.57	6.73
	38	1.38	3.13	5.32	6.05	4.58	6.72
Na	−57	1.37	3.13	5.25	6.13	4.65	6.87
	−35	1.38	3.13	5.30	6.15	4.67	6.87
	38	1.40	3.13	5.32	6.15	4.68	6.85
	102	1.42	3.13	5.32	6.15	4.70	6.85
	−35	1.40	3.05	5.23	6.15	4.67	7.00
	38	1.43	3.07	5.27	6.15	4.67	6.97
	108	1.43	3.07	5.28	6.15	4.67	6.95

[a] Concentrations 0.1–1.0 M.

out CNDO/2 calculations on a variety of enolates and the 2-phenylbutane anion, respectively. These calculations pertain to the ion pair in the gas phase. However, calculations which have included solvation of the cation (water molecules or dimethyl ether) have shown that the effect of solvation continues to favor the relative stability of the cation above the plane.[19],[22] Since coordination of the cation at a position in the nodal plane adjacent to the methylene could result in steric problems, calculations were also executed with the methylene unit twisted out of plane. The results indicated that the loss of overlap with the ring was much more costly than the benefits derived from lessening of steric repulsions and improved overlap between the C_α annd the Li orbitals.

The charge distribution and π bond orders calculated for the optimized upaired picolyl anion is shown in Table VIII. The bulk of the negative charge is located at C_α and N, resulting in a charge distribtion similar to an allylic system.

Calculations were also carried out for the 2-ethylpyridyl anion. The optimum conformation of the methyl group was determined for both *E* and *Z* forms by calculations on the free anion. The energy difference between the *E* and *Z* isomers was found to be very slight, with the *Z* isomer being favored by 0.14 kcal/mol.

Discussion

Ion Pairing. The relationship between charge delocalization and the structure of ion pairs of hydrocarbon anions is well documented.[1-3] The ion pair tends to become "looser" with increasing anion delocalization, and under the right conditions, this is reflected in an increasing fraction of separated ion pairs. This, however, is not necessarily the case of anions where an electronegative nitrogen is present in the aromatic ring. For instance anions **2** and **4** have been shown to be considerably tighter than the hydrocarbon anion **1**.[4b] This is readily understood on the basis of extensive π delocalization of charge onto nitrogen in **2** and **4**. This is not possible for the 3-pyridyl substituted anion **3**, and indeed this anion resembles **1** in its ion pairing properties.

The present case documents this trend further. The Na salt of **2** and **6** in THF were shown to be equal to 3.7×10^{-7}[4b] and 1.1×10^{-10} M, respectively.

This illustrates the substantial effect due to the additional delocalization by the phenyl group in **2**. Since the Li, Na, and K salts of **2** were shown to be contact ion pairs in THF at all temperatures, this should also be the case for the corresponding less delocalized salts of **6**. This is confirmed by the considerable differences in the NMR spectra of the three salts without and in presence of strongly coordinating agents. The tightness of the ion pair of Na-**6** is furthermore illustrated by a comparison with the corresponding benzylic contact ion pair which is dissociated about a thousand times more in THF ($K_d = 1.5 \times 10^{-7}$ M).[25] This appreciable difference in dissociation constant is consistent with a very substantial concentration of electron density onto nitrogen, thus giving anions such as **5** and **6** nitranion character.

Addition of dibenzo-18-crown-6 to the Na salt of **6** increased the dissociation constant to 1.5×10^{-9} M (about 10 times). The K_d of the corresponding complex of **2** was shown to be about 4×10^{-6} M, a value characteristic of separated ion pairs. The 18-crown-6 complex of Na-**6** therefore exists most likely as a crown complexed contact ion pair. Upon addition of the [2.2.2]cryptand, however, the dissociation constant of the resulting complex was increased ~4000-fold to 5.5×10^{-7} M, indicating at least partial ion pair separation, and this is confirmed by the 8-nm red shift which was not observed upon addition of the crown ether (see Results).

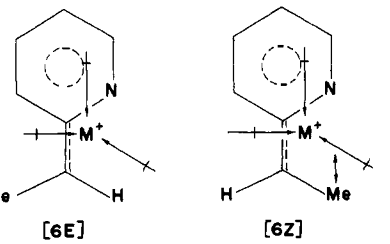
The extensive delocalization into the 2-pyridine ring demands a substantially restricted rotation along the C_α–C_2 bond. This is consistent with the calculated high C_α–C_2 π bond order (Table VIII) and is confirmed by the ^1H and ^{13}C NMR measurements that indicate the existence of *E* and *Z* stereoisomers for the alkali salts of **6**. Restricted bond rotation on similar 2-picolyl anion lithio salts has been observed by Takahashi et al.[16] and Matsuzaki et al. for the 2-phenylbutane anion.[3h]

The effects of cation size and coordination on the ratio of isomers (*E*)-**6** and (*Z*)-**6** (Table II) is of considerable interest. Increasing cation size and coordination tend to lower the (*E*)-**6**/(*Z*)-**6** ratio. Similar observations have been made with oxazoline substituted analogues,[8] enolates,[5a] anions of hydrazones[7] and allylic anions,[26] and correlations with the stereochemical behavior of these anions have been made.[5-9] For the enolates[5] and oxazoline analogues,[8] the ratio of *E* and *Z* stereoisomers was show to be kinetically determined at the conditions under which they were generated (generally below −30 °C). We believe that in the present case the ratio of *E* and *Z* isomers is thermodynamically controlled for the following reasons: First, the effects of cation size and coordination constitute a pattern consistent with ther-

Table VI. ^{13}C NMR Chemical Shifts of Li, Na, and K Salts of 6 in THF[a] (ppm from Me_4Si) at 35 °C

	C_β		C_α		C_2		C_3		C_4		C_5		C_6	
cation	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*
Li	13.5		68.4		156.7		110.3	118.9	132.5	128.5	94.9	94.7	150.4	149.8
Na	13.6		65.9		157.6		109.2	126.8	133.5	130.4	95.6	95.4	151.5	150.8
K	14.1		67.1		157.8		108.3	116.8	133.3	130.4	94.7	94.4	151.4	151.0

[a] Concentrations 0.1–1.0 M.



[6E] [6Z]

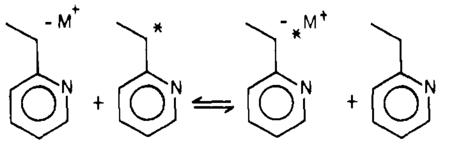
Figure 5. Schematic representations of nonbonded interactions between metal ion coordination sphere and methyl group in alkali salts of **6**.

Table VII. $^{13}C-^{1}H$ Coupling Constants (in Hz) of Alkali Salts of 6 in THF at 35 °C

cation	C_β	C_α	C_3	C_4	C_5	C_6
Li	125	147	156	150	163	162
Na	122	146	154	150	160	159
pyridine			163	152	163	170

modynamical control. Second, and more importantly, the addition of the [2.2.1]cryptand to the Li salts at dry ice temperatures leads to a rapid change in the (*E*)-**6**/(*Z*)-**6** ratio. Moreover, when this solution is warmed to room temperature, the isomer ratio is identical with that obtained by addition of cryptand at ambient conditions. Third, the observed coalescence of the Na and the glymated Li and Na salts supports the existance of an equilibrium at least at the higher temperatures.

It appears most likely that the carbanion isomerization occurs through bond rotation and not through the proton-transfer mediated process (eq 4).



(4)

For example, in the glymated Na salt, broadening due to such an exchange process could not be observed at 100 °C, 13 °C above the *E*–*Z* coalescence temperature, even though the difference in chemical shift of the CH_2 groups of 2-ethylpyridine and its anion is quite small ($\Delta\delta = 0.12$ ppm).

The equilibrium between the geometric isomers (*E*)-**6** and (*Z*)-**6** shows an interesting dependence on cation and solvent as shown in Table II. Provided that the cation is located between C_α and N, such as trend could be explained on the basis of nonbonded interactions between the CH_3 group and the coordination sphere of the cation as shown schematically in Figure 5. Such an interaction is expected to be particularly important for the peripherally solvated Li ion, which is in close proximity to the π system. Coordination by tetraglyme and especially by the [2.2.1]cryptand should increase the carbanion–lithium distance, thus decreasing such nonbonded interactions. Another factor to be considered is that solvating agents may coordinate in such a way as to be sterically less demanding than a solvation shell consisting of several THF molecules. The trends observed for the larger cations are consistent with the above explanations. Not only is the interionic distance increased, but the large ions tend to be less solvated as well.

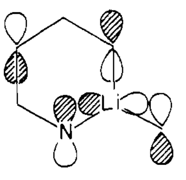


Figure 6. Overlap of Li 2p orbital with HOMO of the 2-picolyl anion.

The cryptated lithio salt in THF and the potassium salt in liquid NH_3 may actually approximate the free anion and were the only two systems to show low *E*/*Z* ratios. The *Z* isomer should be slightly preferred according to our calculations.

Cation and solvent effects on *E* and *Z* carbanions have recently been shown by a number of authors.[5,8,26] In a number of cases, the ratios of carbanion isomers were shown to be kinetically controlled. Our results resemble somewhat those reported by Schlosser and Hartmann[26a] on cation and solvent effects on *E*/*Z* ratios of 2-alkenyl metallic compounds. In this case, the larger and more extensively solvated cations increasingly favor the *Z* form, indicating the inherent greater preference of the free anion for the *Z* form. This was attributed to the formation of hydrogen bonds between the alkyl group and the electron-rich terminal carbon atom. Such a rationalization may apply to our case, provided that such an interaction is more important for the more negatively charged nitrogen atom than for C_3.

Variation of temperature from the coalescence temperature of −78 °C does not produce a measurable change in the (*E*)-**6**/(*Z*)-**6** ratio within experimental error. Even though our data do not allow us to conclude that equilibration occurs for all systems at all temperatures, our data appear to indicate that the ΔH of the (*E*)-**6** ⇌ (*Z*)-**6** interconversion is very small. This means that variations with cation and solvent must be explained on the basis of entropy considerations. Thus the effect of the steric repulsions between the solvation shell of the cation and the methyl group may lead to restrictions of the rotation of the methyl group and the rotation of the solvent molecules coordinated to the cation. It appears therefore that the *Z* isomer is slightly favored for the free anion, but the presence of a cation with its solvation shell apparently produces entropy effects which favor the *E* isomer.

Anion Geometry. The observation of two isomeric forms in ^1H and ^{13}C NMR spectra is indicative of double-bond character about the C_2–C_α bond and significant sp^2 character at C_α. The magnitude of ^{13}C–^1H coupling is related to the s character at carbon. Although this relationship has been abused when other factors have been ignored, it remains useful.[27] The ^{13}C–^1H coupling constant of 149 Hz at C_α is well above that expected for sp^3 hybridized carbon, especially considering that negative charge decreases coupling. In fact, the ^{13}C–^1H coupling constant is close to those of the ring carbons (Table VII). These findings are in agreement with the geminal coupling constants reported in 1- and 2-methylnaphthalene alkali salts, which also indicated sp^2 hybridization for C_α.[3d]

Charge Distribution. Calculations performed on the 2-picolyl anion predicted the charge distribution shown in Table VIII with approximately two-third of the negative charge localized on the nitrogen and the α-carbon. Considering that the presence of a cation should further polarize the anion, it appears therefore that 2-alkylpyridyl carbanions may be essentially ambient anions, with some delocalization onto carbons 3 and 5.

Negative charge density is associated with upfield shifts in both ^1H and ^{13}C NMR.[28,29] The ^{13}C NMR technique is considered

Table VIII. Charge Distribution and Differential Charge Distribution of Anions 5 and 6

	C_α	C_2	C_3	C_4	C_5	C_6	N
ρ of 5 (calcd)[b]	−0.36	0.20	−0.14	0.06	−0.16	0.12	−0.32
Δρ of 5 (calcd)[c]	−0.34	0.06	−0.09	0.01	−0.12	0.02	
Δρ of 5 (exptl)[d]	−0.43	−0.05	−0.08	−0.03	−0.17	~0	
Δρ of 6 (exptl)[e]	−0.50	0.03	−0.05	−0.03	−0.15	~0	
π bond order of 5[b]	C_α-C_2, 0.70	C_2-C_3, 0.48	C_3-C_4, 0.75	C_4-C_5, 0.58	C_5-C_6, 0.66	C_6-N, 0.68	N-C_2, 0.47

[a] ρ, charge density. [b] Based upon CNDO-2 calculations (see text). [c] Calculated difference in charge density between 2-picoline and its anion 5. [d] Calculated from ^{13}C chemical shifts using 160 ppm/electronic charge. For Cα, 2-vinylpyridine was selected as reference compound (see text). [e] Determined from the data of ref 16.

more reliable for determination of charge densities because anisotropy plays a less important role in determining chemical shifts.[29,30] Changes in charge densities may be calcuulated by measuring upfield shifts relative to a model compound and using a shift of 160 ppm per electron.[29-33] Table VIII shows the results of CNDO/2 calculations for the change in charge distribution between 2-picoline and the 2-picolyl anion. 2-Methylpyridine was chosen as the reference compound for all atoms except for the α-carbon which is apparently largely sp^2 hybridized and was compared to the corresponding α-carbon in 2-vinylpyridine. The agreement is satisfactory and indicates that the calculated charge distribution is consistent with experimental values.

^1H NMR studies of alkali metal salts of 1- and 2-methylnaphthalenes revealed systematic variations in chemical shifts as a function of cation radius, which were explained in terms of increasing polarization of the anion toward the C_α with smaller cations.[3d] The chemical shifts tabulated in Tables V and VI for the Li, Na, and K salts of **6** do not reveal such a pattern. This may be an indication that the cation is not as closely associated with C_α in salts of **6** as in the methylnaphthyl salts.

A change in the solvation of the cation should likewise affect the charge distribution. ^1H NMR spectra of Li and Na salts of **6** described in Table IV show significant upfield shifts at H_3 and H_5 with the addition of the cation solvating agents tetraglyme and [2.2.1]cryptand. The Li salt showed only small upfield shifts with the addition of tetraglyme, but the addition of [2.2.1]cryptand produced rather large shifts. The shift of C_α could not be studied due to absorptions of the tetraglyme and the [2.2.1]cryptand. Thus, increasing cation solvation appears to result in less polarization of the anion by the cation. Similarly, as solvation increases at lower temperatures, H_3 and H_5 would be expected to experience upfield shifts. In accordance with this prediction, the Li salt, for which peripheral solvation should be the most important due to its small size, shows the greatest temperature dependence (Table V). Although upfield shifts occur at all positions, H_3 and H_5 do show the largest change. However, the shifts are much less than those associated with addition of solvating agent. This result agrees with conductance measurements on similar 2-pyridyl substituted carbanions that indicate very little additional solvation of Li and Na counterions upon cooling the solutions from 25 to −78 °C.[4b]

The CNDO/2 calculations carried out on the unsolvated 2-picolyllithium ion pair indicate a strongly preferred cation position above the π system equidistant between C_α and N. For the corresponding ion pair of **6**, a similar situation should prevail. The above plane position of Li allows overlap between a Li orbital and the HOMO of the anion as shown in Figure 6.[3h,j] Moreover, a solvated cation located in the nodal plane would suffer peri interactions with the methyl group in (*Z*)-**6**. This would be inconsistent with the fact that increasing cation coordination appears to favor the *Z* isomer.

These findings correlate with ^1H and ^7Li NMR investigations of fluorenyl salts which demonstrated the cation to be above the ring as determined by upfield shifts of the Li and the cation solvating agents complexed to the cation.[34,35] Likewise, a similar allylic-type position was suggested for Li salts of 1- and 2-methylnaphthalenes.[3d] Furthermore, in crystals of benzyllithium ethylenediamine, the Li is coordinated in an allylic manner.[36] Thus, it seems that the anion is capable of competing with the solvent for a second coordination site. This type of structure has also been suggested in a number of CNDO/2 studies of Li salts of compounds with allylic-type charge distributions.[19-22]

The effects of metal ion size and coordination on coalescence temperature (Table III) are puzzling. Addition of tetraglyme to the Na salt appears to lower the rotation barrier slightly. On the other hand, the presence of larger cations seems to lead to higher coalescence temperatures, in agreement with the results obtained by Sandel et al.[37] for the lithium, sodium, and potassium phenyl allyl salts in THF. unfortunately, these effects do not seem to correlate in a simple fashion with changes in charge distribution evaluated by ^{13}C or ^1H NMR (Tables IV–VI). This may be part due to the fact that changes in cation size are inevitably accompanied by changes in solvation as well and the fact that at present we do not have experimental data revealing a measure of charge density on nitrogen atom. Further work along these lines is in progress.

Experimental Procedures

Solvents. THF was purified as reported previously by distillation from benzophenone dianion alkali salts or directly from blue solutions of Na–K alloy in THF. Tetraglyme was distilled from CaH_2 into a flask containing Na–K alloy, followed by distillation on the vacuum line into ampules equipped with breakseals. Dibenzo-18-crown-6, [2.2.1]-, and [2.2.2]cryptand (PCR, Gainesville, FL) were dried on the vacuum line overnight, dissolved in THF, and stored as solutions in vacuo in breakseals.

Carbanion Salts. 2-ethylpyridine was fractionally distilled, stirred over CaH_2, degassed and distilled in vacuo onto a dried carbanion salt solution such as lithio- or sodio-2-ethylpyridine and redistilled in vacuo into glass ampules equipped with breakseals. The lithio, sodio, and potassio salts were prepared, respectively, by reaction of 2-ethylpyridine in THF at −78 °C with *n*-BuLi and the sodium or potassium salts of the α-methylstyrene tetramer (prepared with the sodium or potassium mirrors and a THF solution of α-methylstyrene). The salts were purified by recrystallization as follows: THF was evaporated from the solutions until almost dry, and toluene or hexane were distilled in. The resulting solution was placed in the freezer (−20 °C). Crystallization usually occurred within a few hours. The crystals were filtered in vacuo and washed with cold toluene or hexane. Residual THF was then removed on the vacuum line prior to adding THF-d_8.

Conductance. All experiments were carried out under high vacuum in an apparatus equipped with quartz optical cells and a conductometric cell. Conductances were measured on a "General Radio" automatic capacitance bridge assembly, 1680-A, at a frequency of 1 kHz.

NMR Measurements. 60- and 100-MHz ^1H NMR spectra were obtained with a Varian A-60 and XL-100 MHz spectrometers using tetramethylsilane as internal standard. ^{13}C (25.2 MHz) spectra were obtained with a Varian XL-100 spectrometer using Me_4Si as internal standard. At the same temperature, chemical shifts were reproducible to about ±4 Hz. Approximately 1000–5000 average transients were necessary for satisfactory signal-to-noise ratios. Temperature of the sample was controlled to ±2 °C and was measured before and after each spectrum was taken.

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