NMR Studies of Arylmethyl Anions with Nitrogen Heterocyclic Rings

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[1]H and ^{13}C chemical shifts for anions of 2-, 3- and 4-benzylpyridine as a function of cation, temperature, and solvent are reported. For 2-benzylpyridine and 3-benzylpyridine restricted rotation about the C_α–C_1 bond leads to E and Z isomers. Charge distributions calculated from ^{13}C chemical shifts indicate a shifting of charge to the pyridyl ring in the order 4-BP > 2-BP > 3-BP with concurrent charge decrease in the phenyl rings. Ion pair studies indicate that the lithium salts are tight ion pairs in THF with cation coordination to nitrogen in all anions. Coalescence phenomena lead to estimates of the rotational barriers. The barriers for phenyl ring rotation decrease in the order 3-BP > 2-BP > 4-BP and the barriers for the pyridyl rings increase in the same order 3-BP < 2-BP < 4-BP. The lithium ion has an enhanced effect on charge distribution and rotational barrier.

Carbanion stability is determined by inductive, hybridization, and delocalization phenomena.[1] Arylmethyl carbanions have served as useful models for the delineation and assessment of these effects.[2–4]

The base strength of a considerable number of anions is available from equilibrium acidity studies.[4] In many cases the effects of substituent and ion pairing are well-known.[4d,e] Electrochemical methods provide another useful means of studying anion stabilities.[5] The one-electron oxidation of the anions relates the anion and corresponding radical stabilities. For di- and triarylmethyl anions substituent effects on the oxidative processes provide estimates of both electron-donating and electron-withdrawing substituents on carbanion and radical stabilities.[5] Thus, pK and E_{oxid} values are related to anion stabilities.[5a]

Additionally, nuclear magnetic resonance methods have provided insight into the contributions of the several factors affecting stability. For example, delocalization in diarylmethyl anions leads to enhanced anion stability and to varying degrees of π bonding to the benzylic carbon. This π bonding leads in turn to restricted aryl rotation. We,[6a] and others,[6b] have utilized dynamic NMR studies of aryl restricted rotation in metal salts of diarylmethyl anions as a quantitative measure of π bonding.

NMR chemical shifts and coupling constants provide information about charge and structure of the arylmethyl anions. Thus, ^{1}H and ^{13}C NMR are used to estimate charge densities at the various positions.[7] Ion-pairing effects are often conveniently characterized by the cation,

solvent, and temperature dependencies of these values.[7d,8] Structural and steric effects can be studied from the magnetic shielding/deshielding effects caused by proximity and the known geometric dependence of these terms.[3,9]

For unsymmetrical diarylanions, electron-donating (methyl),[6a] electron-withdrawing (trimethylsilyl),[6a] and the more powerful tricarbonyl chromium substituents have been studied.[6c] In the main, these substituent effects provide significant but perhaps not major perturbations of the carbanion system. In the present study we utilize nitrogen heterocycles as one of the aryl rings for studies of a major substituent effect.

The introduction of a highly electronegative nitrogen atom in the ring has dramatic effects facilitating anion formation[10] and has been utilized synthetically for over 70 years.[11] During the past 15 years investigations to quantify and delineate the effect have provided considerable insight.[12] In the main, methyl- and alkylpyridines have served as model systems.

The equilibrium acidities of 2-, 3-, and 4-methylpyridine of 34, 37.7, and 32.2 pK units in tetrahydrofuran, respectively, reveal anion stabilization relative to toluene of some 7 to 14 kcal/mol.[13] Nuclear magnetic resonance studies of these and related anions show extensive charge delocalization.[12] The methylene carbon is essentially sp[2]-hybridized and considerable charge can be assigned to the ring nitrogen. In tetrahydrofuran solution the lithium salts are tight ion pairs.[12d] Restricted aryl rotation has been found for 2-pyridylmethyl compounds and 2- and 4-pyridylethyl compounds.[12a,d,14a] Aryl rotational barriers in the range 18.7 to 22.7 kcal/mol have been recorded. This is compared with barriers of 14 to 18 kcal/mol for related carbocyclic analogues.[15]

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In this work nitrogen-substituted diarylmethyl anions have been studied. The anions of 2-, 3-, and 4-benzyl-pyridines (2-BP, 3-BP, and 4-BP) were selected. Recent work provides pK values of the parent heterocycles of 28.4, 30.2, and 25.2, respectively.[13] Accordingly, the anions have both enhanced and varying stabilities relative to the di-phenylmethyl anion (DPM). Stabilization energies of 6.3, 3.8, and 10.7 kcal/mol, respectively, can be estimated. Additionally, ion-pairing studies on related systems of alkali salts of 2-, 3-, and 4-pyridine type diaryl carbanions have been studied with UV/vis spectroscopy.[14b] We have utilized NMR methods to probe the contributing factors for these stability terms.

Experimental Section

Methods. Proton NMR spectra were obtained on 60-MHz Varian EM-360, 90-MHz Bruker WH-90, and 300-MHz Varian XL-300 FT spectrometers. Carbon-13 NMR spectra were obtained at 22.64 MHz on a Bruker WH-90 FT spectrometer and at 75.4 MHz on a Varian XL-300 FT multinuclear spectrometer. Samples contained tetramethylsilane (Me$_4$Si) as an internal standard. Deuterium locking source for the anion samples (15 to 20% vol) was benzene-d_6, toluene-d_8 or dimethyl-d_6 sulfoxide. Toluene-d_8 also served as an aid for freezing point depression. Mass spectral data were obtained on an AEI MS-902 high resolution electron impact mass spectrometer.

Materials. The 2-, 3-, and 4-benzylpyridine heterocyclic compounds were all commercially available (Aldrich). n-Bu-tyllithium (n-BuLi) was 1.6 or 2.6 M in hexane (Aldrich). Tet-ramethylethylenediamine (TMEDA) (Aldrich) was distilled from calcium hydride. Diisopropylamine (Aldrich) was stored over molecular sieves. Dimethyl sulfoxide (Me$_2$SO) (Fisher) was purified by heating with CaH$_2$ to 70 °C for 2 h under N$_2$ and then vacuum-distilled. Tetrahydrofuran (THF) was predried over sodium and then distilled from sodium–benzophenone ketyl with ~1% Me$_4$Si added. Potassium *tert*-butoxide (KO-*t*-Bu) and α-methylstyrene (Aldrich) were used directly.

2,6-Dideuterio-4-benzylpyridine. The procedure for α-deuteration of pyridine using a cobalt catalyst by Calf and Garnett[16] was followed. To 200 mg (3.4 mmol) of Co [from Co(CH$_3$COO)$_2$·4H$_2$O or CoCl$_2$·6H$_2$O] dissolved in 50 mL of distilled water was slowly added 800 mg (21.2 mmol) of NaBH$_4$. The water was decanted and finely divided Co was washed to neutral pH with distilled water and finally with 50% D$_2$O. The wet slurry of reduced Co was transferred to a 20 × 2 cm thick-walled reaction tube which had been flushed with argon. The Co was allowed to settle and the bulk of the water layer was withdrawn with a long Pasteur pipet. The tube was then charged with 9 mL (9.5 g, 5.6 × 10^{-2} mol) of 4-benzylpyridine and 2.5 mL (14 × 10^{-2} mol) of D$_2$O, cooled in dry ice, and sealed. The reaction was allowed to proceed in a N$_2$-pressurized cylindrical high-pressure oven apparatus at 135–140 °C, 400 psi, for 5 days. The reaction mixture was removed with a long Pasteur pipet, and the product was separated from the water layer by a series of centrifugations and dried over CaSO$_4$/CaH$_2$. Yield: (61%: 5.5 mL, 5.8 g, 3.4 × 10^{-2} mol). Analysis of the deuteriated compound by ^{1}H NMR revealed ~55% deuteration at positions 2 and 6 as well as ~25% deuteration at C$_\alpha$.

^{1}H NMR (CDCl$_3$): 8.43 ppm (d, 0.9 H), 7.27–6.92 (m, 7 H), 3.85 (s, 1.6 H), 3.83 (s, 0.6 H). ^{13}C NMR (CDCl$_3$): 149.83 ppm (s, 1 C), 149.78 (s, 2 CH), 149.43 (t, 2C D; J_{c-d} = 27.1 Hz), 138.81 (s, 1 C), 128.95 (s, 2 CH), 128.64 (s, 2 CH), 126.59 (s, 1 CH), 124.09 (s, 2 CH), 123.93 (s, 2 CHαD), 41.10 (s, 1 CH$_2$), 40.77 (t, 1 CHD; J_{C-D} = 20.6 Hz). Mass spectrum: m/e 173 (d_4), 172 (d_3), 171 (d_2), 170 (d_1), 169 (d_0).

2,6-Dideuterio-3-benzylpyridine. This compound was prepared in a manner similar to that described above for 2,6-di-deuterio-4-benzylpyridine using 9 mL, (9.4 g, 5.5 × 10^{-2} mol) of 3-benzylpyridine and 2.5 mL (14 × 10^{-2} mol) of D$_2$O. Yield: 8

mL, 8.34 g (4.9 × 10^{-2} mol, 83%). Analysis of the deuterated compound by ^{1}H NMR revealed ~65% deuteration at positions 2 and 6 as well as ~30% deuteration at C$_\alpha$.

^{1}H NMR (Me$_2$SO-d_6): 8.59 ppm (s, 0.6 H), 8.48 (d, 0.6 H), 7.57 (d, 1 H), 7.27–7.17 (m, 6 H), 3.95 (s, 1.4 H), 3.80 (s, 0.2 H). ^{2}H NMR (Me$_2$SO): 8.60 ppm (s, 1 D), 8.48 (s, 1 D), 3.78 (s, 1.4 D). ^{13}C NMR (CDCl$_3$): 150.27 ppm (s, 1 CH), 149.90 (t, 1 CD; J_{C-D} 26.2 Hz), 147.75 (s, 1 CH), 147.42 (t, 1 CD; J_{C-D} = 27.2 Hz), 138.98 (s, 1 C), 136.60 (s, 1 C), 136.57 (s, 1 CαD), 129.04 (s, 2 CH), 128.88 (s, 2 CH), 126.69 (s, 1 CH), 123.66 (s, 1 CH), 123.53 (s, 1 CHαD), 39.16 (s, 1 CH$_2$), 38.86 (t, 1 CHD; J_{C-D} = 21.9 Hz). Mass spectrum: m/e 172 (d_3), 171 (d_2), 170 (d_1), 169 (d_0).

Anion Preparation. Anions were prepared on an Ace Glass No-Air vacuum-inert gas delivery system. All glassware was oven-dried, assembled while hot, and then flame-dried, evacuated, and purged with argon three times before use. Transfers were made by syringe and cannula under argon pressure. Anion samples were collected in septum capped, flame-dried, and argon-purged NMR tubes. The anion concentration was 0.4–0.5 M. Anion volume ranged from 2.5 to 5 mL.

Lithium Anions with n-BuLi. For 5 mL of 0.4 M anion, 2.5 mmol of n-BuLi was added to the reaction vessel through a septum-fitted access port. The hexane was removed under vacuum. An equivalent amount of previously distilled TMEDA was optionally added at this time. The heterocyclic compound (2 mmol) was added and the reaction flask cooled to −18 °C with an ice/salt bath. Freshly distilled THF containing Me$_4$Si was added slowly.

Lithium Anions with LDA. For 5 mL of 0.5 M anion, 2.75 mmol of n-BuLi was added to the reaction flask followed by 2.85 mmol of diisopropylamine. After addition of 2.5 mmol of het-erocyclic compound, the reaction mixture turned solid and became liquid at room temperature after 10 min. Hexane was evacuated with stirring and the flask cooled to −18 °C with an ice/salt bath followed by slow addition of freshly distilled THF (~1% Me$_4$Si).

Sodium Anions with Sodium Dimsyl. A 2 M sodium dimsyl stock solution was prepared in the following manner: 25 mmol of NaH (50% oil dispersion) was placed in a three-necked reaction flask and washed three times with 5 mL of petroleum ether. A magnet stirrer and 12.5 mL of purified Me$_2$SO were introduced into the flask, and the mixture was heated to 75 °C under nitrogen for 35–40 min. The sodium dimsyl prepared with heating began to deteriorate after a few days. A more stable stock solution could be prepared by allowing the reaction mixture described above to sit at room temperature for 3 days. The resulting sodium dimsyl was clear straw-colored and resulted in nearly 100% anion formation when used directly. The sodium anion was made in an NMR tube. For 0.5 mL of a 0.5 M ^{1}H NMR sample, 335 μL of purified Me$_2$SO and 125 μL of 2 M sodium dimsyl stock solution were added to 40 μL of heterocyclic compound. ^{13}C NMR samples were usually 5 times these amounts in a 10-mm NMR tube.

Sodium Anions with Sodium α-Methylstyrene Tetramer. For 15 mL of 0.5 M anion, 3 mmol (0.0897 g) of sodium was weighed into a reaction flask. An amount (4.5 mL) of freshly distilled THF (~1% Me$_4$Si) and 0.32 mL (0.2954 g, 2.5 mmol) of α-methylstyrene were added. The dark red solution was magnetically stirred 2–3 h. The reaction flask was cooled with an ice bath and 0.40 mL (0.423 g, 2.5 mmol) of the heterocyclic compound was added. The anion mixture was allowed to warm to room temperature with stirring (1–2 h).

Potassium Anions with Potassium *tert*-Butoxide. For 2.5 mL of 0.5 M anion, 1.38 mmol (0.155 g) of KO-*t*-Bu was placed in a reaction flask. Then 1.25 mmol of heterocyclic compound and 2 mL of petroleum ether were added. The flask was cooled to −18 °C with an ice/salt bath followed by addition of 1.38 mmol of n-BuLi with stirring. After 3–4 h, the hexane and petroleum ether were removed. Finally 2 mL of freshly distilled THF (~1% Me$_4$Si) were slowly added, and the solution was allowed to warm to room temperature with stirring.

Potassium Anions with Potassium Diphenylmethane. The potassium anion of 3-benzylpyridine was alternately prepared by a competitive reaction with potassium diphenylmethane. The latter anion was prepared by using KO-*t*-Bu as described above and then an equivalent amount of 3-benzylpyridine was added at −18 °C. After warming to room temperature, the anion sample was transferred to a 5-mm NMR tube.

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Table I. 300-MHz Proton Chemical Shifts of 2-Benzylpyridine Anions

cation	T, °C	H_α	C_1	H_2	H_3	H_4	H_5	H_6	$C_{1'}$	$N_{2'}$	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$
Li+/THF	60	4.47		7.02	6.80	6.22	6.80	7.02		N	7.23	5.33	6.47	6.37
Na+/THF	60	4.52		7.32	6.83	6.20	6.83	7.32		N	7.49	5.44	6.50	6.15
Li+/THF	rt[c]	4.47			6.79	6.19	6.79			N	7.20	5.31	6.49	
Na+/THF	rt	4.49		7.37	6.81	6.17	6.81	7.37		N	7.49	5.42	6.48	6.04
Na+/Me2SO	rt[a]	4.28		7.22	6.56	5.90	6.56	7.22		N	7.38	5.25	6.30	5.72
K+/THF	rt	4.46		7.38	6.78	6.12	6.78	7.38		N	7.59	5.42	6.46	5.99
Li+/THF	-60	(4.48)[b]		6.80	6.80	6.17	6.80	6.80		N	7.21	5.29	(6.55)	(6.69)
		(4.44)											(6.32)	(5.92)

[a] EM-360 NMR. [b] Parentheses refer to E and Z forms, respectively. [c] rt = room temperature.

Table II. 75.4-MHz Carbon-13 Chemical Shifts of 2-Benzylpyridine Anions

| T, °C	cation	C_α	C_1	C_2	C_3	C_4	C_5	C_6	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$
60	Li+/THF	83.7	145.7	120.2	128.9	114.6	128.9	120.2	159.0	N	148.2	101.6	133.0	115.3
60	Na+/THF	82.3	145.6	119.3	127.4	113.4	127.4	119.3	160.7	N	148.9	102.1	132.1	117.4
60	K+/THF	83.0		120.0	128.7	112.9	128.7	120.0		N	149.0	102.4	131.9	117.6
rt[d]	Li+/THF	84.6	145.6	120.6	128.5	114.3	128.5	120.6	158.5	N	148.4	100.9	133.0	112.0[a]
rt	K+/THF	83.0	145.7	119.8	128.7	112.7	128.7	119.8	160.2	N	149.0	102.2	131.6	117.9
rt	Na+/THF	82.5		119.1	127.4	113.2	127.4	119.1		N	148.8	102.0	131.9	118.3
rt	Na+/Me2SO	84.0	145.1	119.8	126.7	110.5	126.9	119.8	158.8	N	148.3	100.2	130.1	116.1
-80	Li+/THF	(85.0)[c]	(145.3)	120.4	128.2	(113.2)	128.2	120.4	(157.4)	N	(148.6)	(100.4)	(133.5)	(111.5)
		(86.0)	(146.1)			(113.6)			(158.9)		(148.0)	(100.8)	(130.7)	(119.7)
-80	K+/THF	83.5	145.4	122.6	127.9	112.3	127.9	116.7	159.7	N	148.8	101.8	131.4	117.8
-80	Na+/THF	84.5	145.7	122.5	127.3	112.4	127.3	116.0	159.7	N	148.7	101.0[a]	131.3	118.4
Fraser[b]	Li+	86.3	147.0	121.5	129.2	121.5	129.2	121.5	159.4	N	149.3	101.4	134.0	114.7

[a] Estimated. [b] Reference 13. [c] Parentheses refer to E and Z forms, respectively. [d] rt = room temperature.

Results

The anions of 2-BP, 3-BP, and 4-BP were prepared from the parent heterocycles and appropriate metalating agents (see Experimental Section). Included in the study are the effects of solvent variation, chelating agent, and cation variation. The samples at 0.4–0.5 M were examined by NMR at various temperatures.

NMR Measurements of 2-Benzylpyridine. The ¹H and ¹³C spectra of the lithium salt of 2-BP (0.5 M in THF at 60 °C) are shown in Figure 1. Assignments were made by using two-dimensional (2-D) HOMCOR and HETCOR experiments, as well as by homonuclear decoupling. The resulting ¹H and ¹³C chemical shifts are listed in Tables I and II. As expected the benzylic H_α (4.47 ppm) appears as the most upfield signal of all the anion resonances and shows no coupling in the HOMCOR diagram. We find no evidence of long range (~1 Hz) coupling between H_α–$H_{5'}$ such as was observed by Takahashi[12d] and Hogen-Esch.[14a]

As the temperature is lowered, pattern changes characteristic of dynamic processes are seen. In this system restricted aryl rotation caused by charge delocalization in the pyridyl ring gives rise to E and Z conformational isomers. The proton assignments for the Li salt in Table
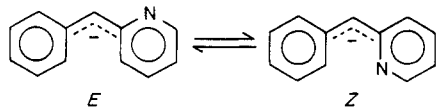
I are made at 60 °C when the E ⇌ Z equilibrium is fast on the NMR time scale and single sets of peaks are found. At -20 °C and below, distinct resonances of unequal proportions are observed for $H_{6'}$, $H_{5'}$, and H_α. The E/Z isomer ratio, although difficult to determine accurately because of peak overlap and base-line distortion, is approximately 2 and appears to be invariant with temperature.

For the phenyl ring, low-temperature investigation reveals an upfield chemical shift change for H_2 and H_6 from 7.02 to 6.80 ppm in the temperature region -60 to -20 °C but no clearly defined peaks of the two isomeric forms. None of the remaining phenyl protons showed dynamic behavior or temperature dependence greater than 0.05 ppm. This spectral change in pattern for the phenyl ring
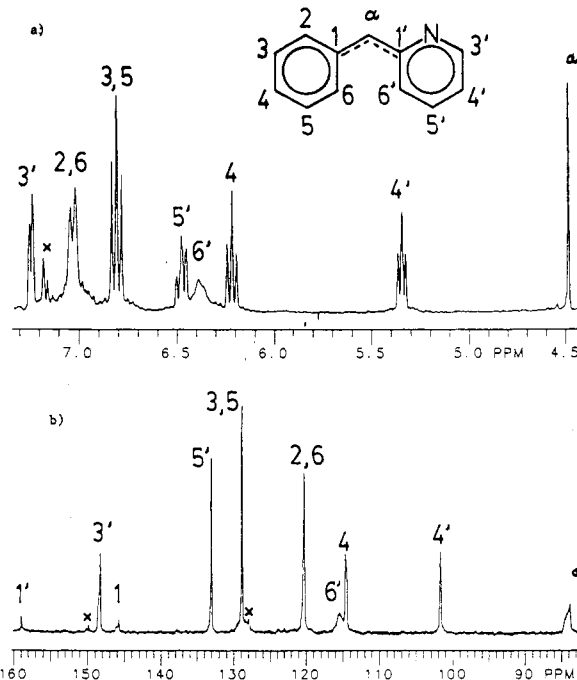

Figure 1. (a) 300-MHz proton NMR spectrum of lithium 2-benzylpyridine, 0.5 M in THF at 60 °C. (b) 75.4-MHz carbon-13 NMR spectrum of lithium 2-benzylpyridine, 0.5 M in THF at 60 °C.

is unusual. The high-temperature ortho signal is not observed at room temperature, but we know from the ¹³C spectra (vide infra) that rotation of the phenyl ring is always fast on the NMR time scale. Of direct interest $H_{6'}$ shows a similar broadening. There is evidence that the process involves a shift of cation position with an increase of steric effect at the positions most likely to be affected, namely, $H_{2,6}$ and $H_{6'}$. This point will be further developed after consideration of cation variation.

Assignments for the ¹³C NMR spectra (Table II) were confirmed with 2-D HETCOR experiments and by comparison with data from diphenylmethyl[9c] and 2-ethylpyridine[14a] anions. At 60 °C in the spectrum of Li2-BP

Table III. 300-MHz Proton Chemical Shifts of 3-Benzylpyridine Anions

cation	T, °C	H_α	C_1	H_2	H_3	H_4	H_5	H_6	$C_{1'}$	$H_{2'}$	$N_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$
Li$^+$/THF	60	4.43		6.73	6.73	6.02	6.73	6.73		7.50	N	6.37	6.40	6.70
Na$^+$/THF	60	4.35		6.73	6.74	5.99	6.74	6.73		7.60	N	6.62	6.43	6.77
Li$^+$/THF	rt[b]	4.44		6.73	6.73	6.01	6.73	6.73		7.50	N	6.41	6.41	6.73
Na$^+$/THF	rt	4.37		6.70	6.71	5.95	6.71	6.70		7.57	N	6.56	6.40	6.74
Na$^+$/Me$_2$SO	rt[a]	4.12		6.46	6.50	5.80	6.50	6.46		7.50	N	6.42	6.31	6.61
K$^+$/THF	rt	4.38		6.77	6.77	5.97	6.77	6.77		7.71	N	6.69	6.53	6.69

[a] EM-360 NMR.   [b] rt = room temperature.

the signals have nearly averaged; however, even at this temperature, $C_{6'}$ is only somewhat differentiated from the base line. The $C_{6'}$ (115.3 ppm) assignment is made from a 60 °C spectrum of Li2-BP in THF with TMEDA added. Spectra of the anion without TMEDA show overlap with the C_4 signal.

The dynamic process noted in the ^{1}H studies is elaborated in the ^{13}C NMR in a higher temperature range due to the greater range of chemical shifts for ^{13}C. At -20 °C and below pyridyl ring rotation is slow on the NMR time scale and the spectra display sets of isomer peaks. An E/Z ratio of 3 is estimated and appears to be temperature-independent, although the average value calculated from ^{13}C spectra differs somewhat from that calculated from ^{1}H spectra. Isomer ratios reported by Hogen-Esch[14a] for salts of 2-ethylpyridine were temperature-invariant and free of NOE complications.

At room temperature some line broadening of C_2 and C_6 is observed and may be related to aggregation phenomena rather than phenyl rotation processes since slow rotation of the phenyl ring signals is not attained at temperatures as low as -80 °C. Phenyl ring coalescence of the Li salt is not achieved even at -80 °C, at which point the anion is near precipitation. From estimates of $\Delta\nu$ and T_c, a limit of $\Delta G^\ddagger$ is given in Table IX.

Dynamic changes and isomer peaks are observed in the ^{13}C spectra for Li2-BP for all but the phenyl ring ortho and meta carbons. While it was not possible to obtain the required data for a full line shape analysis because of overlapping peaks, temperature-dependent shifts, and unequal isomer populations, the value of T_c could be estimated to provide a qualitative approximation of the rate. The value is listed in Table IX. Other than the pattern changes discussed below, the effect of temperature on ^{13}C chemical shifts of Li2-BP is minor.

Effect of Cation and Solvent. The effect of cation and solvent was investigated with the Na and K salts of 2-BP in THF and the Na salt in Me$_2$SO. A HETCOR experiment was used for the Na2-BP assignments and the K2-BP chemical shifts are easily assigned.

Cation variation has a small effect with notable exception on the ^{1}H chemical shifts of 2-BP anions (Table I). With larger cation trends of shielding of the phenyl ring and deshielding of the pyridyl ring are seen. The α proton shows virtually no effect with cation variation, a trend also observed by Hogen-Esch[14a] for 2-EP anions. Of particular interest is the unexpected deshielding effect on the otho protons H_2 and H_6 of the phenyl ring with increasing cation size. This deshielding is related to cation radius suggestive of a steric effect. For the lithium anion the high-temperature value is similarly deshielded. As described earlier, at lower temperatures this signal appears much further upfield. Thus, at higher temperature the lithium cation position more nearly resembles that of Na and K. Similarly noteworthy is a comparable deshielding trend in the $H_{3'}$ proton which is α to the nitrogen atom in the pyridyl ring. These points will be discussed in a later section.

In the ^{1}H spectra of the K salt of 2-BP, the pyridyl ortho hydrogen, $H_{6'}$, at 5.99 ppm at room temperature remains

unchanged to -60 °C. A similar resonance is found with the Na salt at 6.05 ppm. The position of these resonances is evidence that these salts are predominantly in the Z configurations. For the high-temperature Li salt, a rotationally averaged $H_{6'}$ resonance is found at 6.37 ppm and at low temperature is resolved into isomer peaks at 6.69^E and 5.92^Z ppm in the ratio of 2:1.

Carbon-13 chemical shifts with cation change are reported in Table II. Using $C_{6'}$ as the primary indicator, the Z form is assigned as the major isomer in the Na and K salts of 2-BP due to its deshielded positions.[14a] The E/Z isomer ratios for Li, Na, and K are respectively 2–3, 0.2, and <0.1. These results of cation variation agree directionally with those of Hogen-Esch[14a] who reported an increase in Z isomer as the cation size increased, although in the present system much less E isomer is found for the 2-BP anions.

Two results are noted with change in ^{1}H chemical shift for Na2-BP as the solvent changes from THF to the more cation solvating Me$_2$SO. First, change in solvent for the same cation has a much larger effect than the change in cation for the same solvent. Second, the change in solvent from THF to Me$_2$SO reflects a shielding effect at all the positions in the anion. This effect is least at the ortho protons in the phenyl ring, which may be sterically deshielded. Overall, the effects on ^{13}C chemical shifts with solvent change are compressed and less regular.

NMR Measurements of 3-Benzylpyridine Anions. The ^{1}H and ^{13}C NMR spectra of the Li salt of 3-BP (0.5 M in THF, 60 °C) are shown in Figure 2. The resulting ^{1}H and ^{13}C chemical shifts are listed in Tables III and IV. For the ^{1}H spectra only H_α and H_4 are readily assigned from the 1D plot. The HOMCOR and HETCOR experiments were particularly valuable in proton resonance assignments for overlapping and completely masked signals in the 1D ^{1}H spectrum.

The effect of temperature variation on the ^{1}H chemical shifts reveals a slight shielding trend in the pyridyl ring in the range of 60 to 25 °C with no other substantial effects. As the temperature is further decreased to -50 °C, pattern changes are observed. Assignments and spectral interpretation are somewhat difficult due to apparent signal depression and an increasingly rolling base line. Never-

E   *Z*
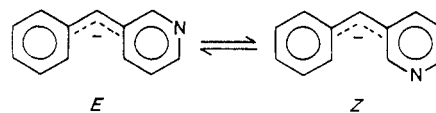
theless, certain features are unambiguous. The peak for H_α broadens and resharpens as two peaks which are assigned to the E and Z forms. The signals for $H_{2'}$ and $H_{6'}$ also undergo pattern changes, but the signals of Z isomers in both cases are never clearly differentiated. This process is likely a rotational process in the pyridyl ring and is further substantiated by the ^{13}C DNMR study.

For the ^{13}C spectra at 60 °C the 1D and HETCOR experiments provide straightforward assignments for all carbons with the exception of $C_{2'}$ and $C_{6'}$. In the 60 °C spectrum the signals for $C_{2'}$ and $C_{6'}$ are only beginning to

Table IV. 75.4-MHz Carbon-13 Chemical Shifts of 3-Benzylpyridine Anions

T, °C	cation	C_α	C_1	C_2	C_3	C_4	C_5	C_6	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$
60	Li⁺/THF	80.2	146.7	119.7	128.1	111.2	128.1	119.7	142.5	141.2	N	124.8	122.7	118.1
60	Na⁺/THF	76.7	146.5	118.7	128.4	110.6	128.4	118.7	142.6	142.7	N	125.5	124.5	117.8
60	K⁺/THF	77.0	145.9	118.0	128.8	110.2	128.0	118.0	142.0	143.0	N	124.6	123.6	118.0
40	Na⁺/Me₂SO	77.7	145.3	117.3	127.7	108.4	127.7	117.3	140.8	142.3	N	125.6	123.6	115.7
rt[e]	Li⁺/THF	80.0	146.5	119.5	128.1	111.1	128.1	119.5	142.1	144.9	N	124.9	122.4	114.2
rt	Na⁺/THF	78.0	146.5	118.8	128.2	110.2	128.2	118.8	142.3	b	N	125.5	124.4	b
rt	Na⁺/Me₂SO[a]	77.6	145.1	117.1	126.6	108.2	127.6	117.1	140.6	142.4	N	125.4	123.3	115.6
rt	K⁺/THF	77.2	145.9	117.9	128.8	109.8	128.8	117.9	141.9	143.1	N	124.4	123.6	117.5
−60	Li⁺/THF	80.3	146.3	b	128.2	110.6	128.2	b	141.8	(145.0)[d] (133.9)	N	125.4	122.6	114.4
−60	Na⁺/THF	79.5	146.4	123.1	128.5	109.2	128.5	114.0	141.8	(145.9) (135.4)	N	124.4	124.0	(123.2) (113.9)
−60	K⁺/THF	78.5	146.2	122.8	128.9	109.2	128.9	113.6	141.7	(145.7) (135.2)	.N	124.5	124.0	(125.2) (114.2)
Fraser[c]	Li⁺	80.8	147.4	120.2	128.8	111.6	128.8	120.2		143.0	N		123.5	125.5

[a] Bruker WH-90 NMR. [b] No detectable signal. [c] Reference 13. [d] Parentheses refer to E and Z forms, respectively. [e] rt = room temperature.
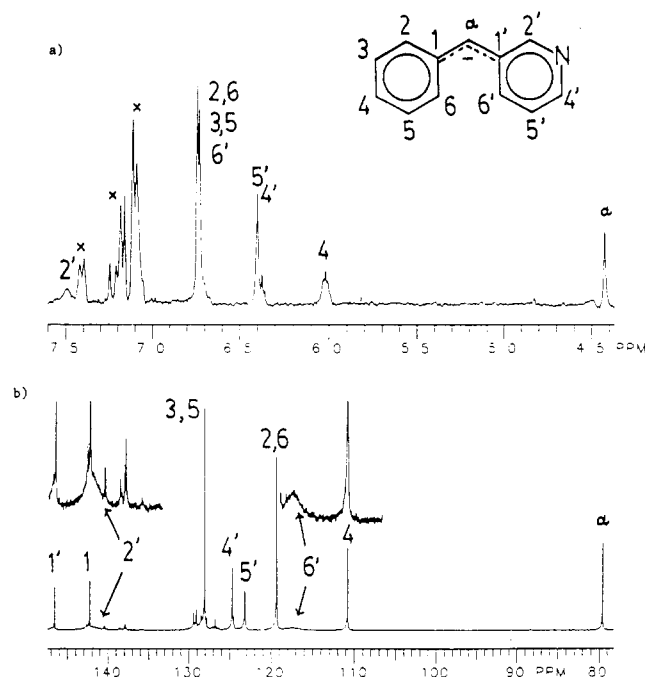

Figure 2. (a) 300-MHz proton NMR spectrum of lithium 3-benzylpyridine, 0.5 M in THF at 60 °C. (b) 75.4-MHz carbon-13 NMR spectrum of lithium 3-benzylpyridine, 0.5 M in THF at 60 °C.

be differentiated from the base line. This observation is field-dependent. The spectra at the lower field strength of 22.6 MHz reveals sharp resonances for $C_{2'}$ and $C_{6'}$. Moreover, the chemical shift values are those expected from the rotationally averaged signals of E and Z forms.

At −60 °C rotation of both aryl rings about the central methine carbon axis is slowed on the NMR time scale. The ortho carbons $C_{2'}$ and $C_{6'}$ in the pyridyl ring each have two signals of unequal height at −60 °C, and these are used as monitors of the E/Z ratio which is ~2:1. The two signals for $C_{6'}$ are at 114.4^E and 125.9^Z ppm and those for $C_{2'}$ are at 145.0^E and 133.9^Z ppm. More closely spaced isomer peaks are also seen for $C_{5'}$ at 122.6^E and 123.9^Z ppm.

As the temperature is lowered from 60 °C to room temperature, changes in the pyridyl ring resonances are observed. At room temperature peaks are seen for the more populated E isomeric form of $C_{6'}$, $C_{2'}$, and $C_{5'}$. As the temperature is lowered further to 0 °C, Z isomer peaks for $C_{6'}$, $C_{2'}$, and $C_{5'}$ are seen. Pattern changes for the phenyl ring in the same temperature range reveal differences in the ¹³C DNMR of this ring. At 0 °C the $C_{2,6}$ signal has

substantially collapsed and disappears into the base line at −50 °C. We were not able to observe distinct signals for C_2 and C_6 at the limiting low temperature (−80 °C). Estimates for the rotational barriers of the pyridyl and phenyl ring are presented in Table IX. Other than the changes due to dynamic behavior as discussed above, ¹³C chemical shifts of Li3-BP show little temperature-dependence (Table IV).

For the 60 °C ¹H spectrum of Na3-BP (0.5 M in THF), assignments are made by consideration of the HOMCOR diagram and by deuterium NMR of an anion deuterated at the 2' and 4' positions (αNd3-BP). In fact the $H_{4'}$ and $H_{5'}$ signals are nearly overlapped in the lithium 1D and 2D spectra, but the Na3-BP HOMCOR diagram shows these two peaks to be clearly separated at 6.62 ppm ($H_{4'}$) and 6.43 ppm ($H_{5'}$) for the sodium compound. Proton chemical shifts of the Na anion in THF differ slightly from the Li anion with small shielding and deshielding effects <0.1 ppm. The temperature study reveals similarities to the lithium anion with the appearance of isomers Z forms for H_α at 4.56^E and 4.36^Z ppm below −20 °C. An E/Z isomer ratio of 5 is estimated.

For the ¹³C NMR results with change to Na cation (Table IV), the greatest change in shift is observed at C_α which is shielded by 3.4 ppm. Phenyl ring ortho and para carbons are shielded and there is deshielding in the pyridyl ring with, surprisingly, the meta position ($C_{5'}$) most affected (1.8 ppm). At −60 °C there is a deshielding at C_α (2.8 ppm) and shielding at the phenyl para (C_4) carbon (1.4 ppm). In the intervening temperatures the phenyl ring undergoes the characteristic dynamic changes associated with slow aryl rotation. The value for $\Delta G^\ddagger$ is given in Table IX.

The case for the pyridyl ring is somewhat different. As the temperature is lowered from 60 °C, the peaks assigned to $C_{2'}$ and $C_{6'}$ broaden and disappear into the base line at room temperature. However, these peaks do not begin to emerge from the base line at different positions until about −5 °C. This is an unusually large temperature range for only a rotational process. Possibly the disappearance of the NMR signal at or just above room temperature is caused by an additional relaxation process (e.g., aggregation exchange) taking place on the NMR time scale. At lower temperatures the behavior is less complex and by comparison of the spectral patterns at the lower temperature regions with uncomplicated systems (LiDPM) an estimate of $\Delta G^\ddagger$ is given in Table IX.

The effect on chemical shifts of a change of solvent from THF to Me₂SO for the same cation (Tables III and IV) reveals a shielding trend at all positions in ¹H shifts up to

Table V. 300-MHz Proton Chemical Shifts of 4-Benzylpyridine Anions (ppm Downfield from Me₄Si)

T, °C	cation	H_α	C_1	H_2	H_3	H_4	H_5	H_6	$C_{1'}$	$H_{2'}$	$H_{3'}$	$N_{4'}$	$H_{5'}$	$H_{6'}$
60	Li⁺/THF	4.59		6.95	6.84	6.29	6.84	6.95		5.76	6.80	N	6.97	6.46
60	K⁺/THF	4.57		7.0	6.9	6.36	6.9	7.0		5.87	6.9	N	7.0	6.51
rt[b]	Li⁺/THF	4.58		6.93	6.83	6.28	6.83	6.93		5.76	6.79	N	6.96	6.45
rt	Na⁺/THF	4.58		6.94	6.80	6.25	6.80	6.94		5.82	6.85	N	7.10	6.51
rt	K⁺/THF	4.58		7.00	6.92	6.34	6.92	7.00		5.88	6.9	N	7.0	6.62
rt	Na⁺/Me₂SO[a]	4.27		6.78	6.70	6.12	6.70	6.78		5.69	7.00	N	7.17	6.28

[a] Bruker 90-MHz NMR. [b] rt = room temperature.

Table VI. 75.4-MHz Carbon-13 Chemical Shifts of 4-Benzylpyridine Anions (ppm Downfield from Me₄Si)

T, °C	cation	C_α	C_1	C_2	C_3	C_4	C_5	C_6	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$
60	Li⁺/THF	88.4	144.3	122.9	128.2	115.4	128.2	122.9	146.5	115.7	144.0	N	146.6	106.9
60	K⁺/THF	86.1	144.1	122.4	128.7	116.0	128.7	122.4	145.6	115.4	146.0	N	148.7	106.3
rt[b]	Li⁺/THF	88.0	144.1	122.5	128.0	115.1	128.0	122.5	146.2	115.5	143.8	N	146.5	106.6
rt	Na⁺/THF	86.3	144.6	122.1	127.9	114.3	127.9	122.1	146.3	115.6	145.0	N	147.6	106.8
rt	K⁺/THF	85.9	144.2	122.1	128.6	115.5	128.6	122.1	145.7	115.5	146.0	N	148.6	106.4
rt	Na⁺/Me₂SO	83.8	144.0	120.1	127.6	112.5	127.6	120.1	147.6	114.6	144.0	N	145.0	105.9
-80	Li⁺/THF	87.7	143.8	122.2	128.1	114.9	128.1	122.2	145.9	115.6	144.0	N	146.6	106.6
Fraser[a]	Li⁺	88.6	146.9	123.3	128.7	107.4	128.7	123.3	144.5	116.2	147.2	N	144.5	115.5

[a] Reference 13. [b] rt = room temperature.

0.25 ppm and ¹³C shifts up to 2.0 ppm, however, with some small differences in shielding pattern.

A room-temperature ¹H spectrum of K3-BP (0.5 M in THF) shows considerable broadening. The best resolution is seen at 0 °C and assignments are straightforward. At -50 °C the appearance of two α peaks at 4.55^E and 4.37^Z ppm is evidence of E and Z isomers in the ratio of ~5:1. Additionally, E isomer peaks for $H_{2'}$ at 7.61 ppm and $H_{5'}$ at 6.55 ppm are visible. A study of the intervening temperatures gives evidence of a dynamic change occurring between -20 and -30 °C and the value of $\Delta G^\ddagger$ is given in Table IX.

Carbon-13 chemical shifts for the K anion at 60 °C, are very similar to those for the Na anion. At the limiting low temperature of -60 °C the C_2 and C_6 resonances are separate, though broadened, peaks at 122.8 and 113.6 ppm, respectively. The predominant E isomer peaks of $C_{6'}$ and $C_{2'}$ are seen at 114.2 and 145.7 ppm, respectively, and the smaller Z isomers can be assigned. For the phenyl ring, the pattern observed in the intervening temperatures closely follows that of KDPM. Coalescence temperature is estimated at -10 °C with an estimated value for $\Delta G^\ddagger$ of 11.5 kcal/mol. This value for the rotational barrier is very similar to those calculated for the Li and K anions of DPM which are 11.3 and 11.7 kcal/mol, respectively. For the pyridyl ring the rotational process involving C_α and $C_{6'}$ is complicated by an additional dynamic process occurring in the vicinity of room temperature. Nevertheless, the lower temperature portions are straightforward and the values for $\Delta G^\ddagger$ are given in Table IX.

NMR Measurements of 4-Benzylpyridine Anions. Proton and carbon-13 NMR spectra of the Li salt of 4-benzylpyridine (0.5 M in THF) are shown in Figure 3. An anion partially deuterated at the 3' and 5' positions (αNd-4-BP) was prepared and used to confirm ¹H chemical shift assignments shown in Table V. Assignments are also guided by a 2D HETCOR experiment in which unambiguous ¹³C assignments, vide infra, lead to proton identification.

Additionally a HOM2DJ experiment proved useful for obtaining coupling constants. The upfield resonances of a doublet of doublets is assigned to the ortho pyridyl protons $H_{2'}$ (5.72 ppm) and $H_{6'}$ (6.79 ppm) with $J_{\text{ortho}} = 6.8$ Hz and $J_{\text{meta}} = 2.8$ Hz. Further evidence of the identity of these two protons came from the Li salt of αNd-4-BP. The ¹H NMR spectra of this deuterated anion show that these resonances have a pattern with the expected smaller
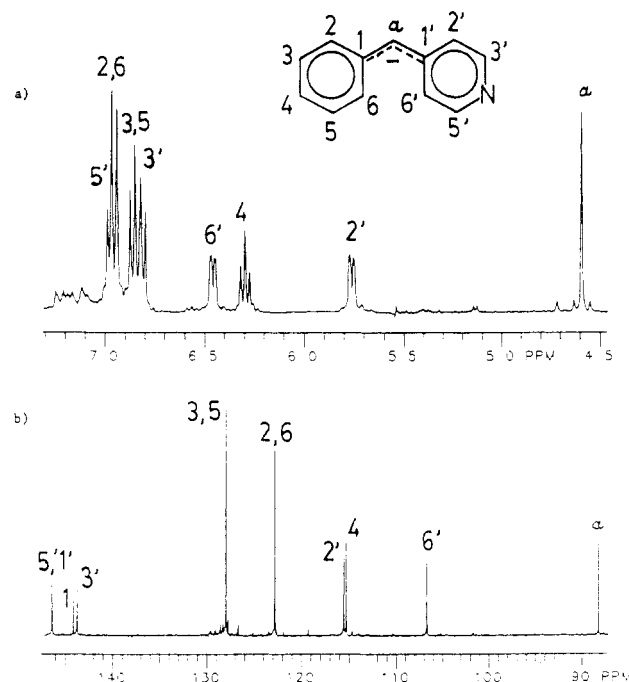

Figure 3. (a) 300-MHz proton NMR spectrum of lithium 4-benzylpyridine, 0.5 M in THF at 60 °C. (b) 75.4-MHz carbon-13 NMR spectrum of lithium 4-benzylpyridine, 0.5 M in THF at 60 °C.

coupling constants. Distinct resonances for the inner and outer ortho positions in the nitrogen-containing ring is evidence that aryl ring rotation is slow on the NMR time scale at room temperature. In contrast, the phenyl ring protons H_2H_6 and H_3H_5 appear as averaged signals.

The absence of any pattern changes over the range -80 to +60 °C rule out any dynamic effects on the NMR time scale. Therefore, ¹H NMR data lead to the conclusion that the phenyl ring is undergoing fast rotation and pyridyl ring slow rotation on the NMR time scale at all temperatures investigated. Additionally, the effect of temperature on the ¹H chemical shifts is small (Table V).

Carbon-13 chemical shifts of Li4-BP are listed in Table VI. The assignments were confirmed with the help of the DEPT, 2D HOMCOR and HETCOR experiments, and the αNd-4-BP anion spectra. Carbons with deuteriums attached have slightly different chemical shifts compared to those with hydrogens attached, and this is also true for

Table VII. Calculated π-Electron Densities

anion	C_α	C_4	$C_{2,6}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	total C ring	total N ring
benzylLi[a]	1.616	1.182	2.208						6.267	
rt[d] LiDPM[a]	1.356	1.166	2.200	1.100	1.032 N(b)	1.166	1.032	1.100	6.339	
avg Li3-BP	1.340	1.144	2.178	0.956 N(b)	1.284	1.052	1.065	1.090	6.305	6.389[b]
Li2-EP[c]	1.415			1.332 N(b)	0.890	1.245	1.004	1.147		6.468[b]
avg Li2-BP	1.309	1.124	2.165	1.388	0.903	1.206 N(b)	1.005	1.113	6.270	6.455[b]
rt Li4-BP	1.289	1.116	2.136	1.113	0.915	1.450	0.932	1.170	6.248	6.497[b]

[a] Reference 7a. [b] Estimated as explained in text. [c] Reference 14. [d] rt = room temperature.

other carbons that are neighbors to deuterated carbons.[17] This isotope effect leads to unambiguous identification of the carbons $C_{2'}$ and $C_{6'}$ in the pyridyl ring in the $\alpha N d$-4-BP anion ^{13}C spectrum.

The effect of temperature variation from +60 to −80 °C on ^{13}C NMR behavior revealed an absence of dynamic changes and virtually no chemical shift changes. Absence of distinct ortho (and meta) signals indicates that the phenyl ring is rotating fast of the NMR time scale even at −80 °C, so T_c < −80 °C. Conversely, the pyridyl ring is nonrotating as evidenced by ^{13}C chemical shifts even at 60 °C. Approximate limits of ring rotational barriers are calculated and presented in Table IX.

An investigation of the effect of cation change included the Na salt in both THF and Me$_2$SO and the K salt in THF. The ^{1}H shifts for the Na/THF anion were confirmed by a HETCOR experiment and those for the Na/Me$_2$SO anion were established by homonuclear decoupling. Proton chemical shifts of Li, Na, and K anions in THF (Table V) are very similar.

Results of ^{13}C NMR studies for the various cations with 4-BP in THF are listed in Table V. The largest effect is found at C_α which is shielded by $\sim$2 ppm in changing from the smallest Li cation to the larger Na and K ions. A second effect results in deshielding at the $C_{3'}$ and $C_{5'}$ positions of 1–2 ppm for both larger cations.

Proton shifts are shielded (0.1–0.3 ppm) at all positions except at $H_{5'}$ and $H_{3'}$ by change in solvent from THF to Me$_2$SO. The effect of solvent change from THF to Me$_2$SO for the Na anion on ^{13}C chemical shifts parallel the changes found in ^{1}H chemical shifts with a major difference in that $C_{3'}$ and $C_{5'}$ are shielded, by 1 and 2.6 ppm, respectively, rather than deshielded as in proton spectra. Also, the degree of shielding observed at $C_{6'}$ ($\sim$1 ppm) is less than that observed at $H_{6'}$.

Discussion

Charge Densities. Carbon chemical shifts have been used in a linear shift vs. π-density relationship (eq 1) and

$$\delta = 289.5 - 156.3\rho \qquad (1)$$

for the calculation of π-densities at nonequivalent carbons in delocalized systems.[7,8] While some π-systems containing heteroatoms give correlation with widely differing slopes,[19] in this work with benzylpyridines, good correlation is found with eq 1.

With a nitrogen atom in one of the rings, a redistribution of charge to the nitrogen-containing ring is expected. For a given amount of ring charge the para positions (C_4 and $C_{4'}$) have the highest electron density.[7d] Additionally, the

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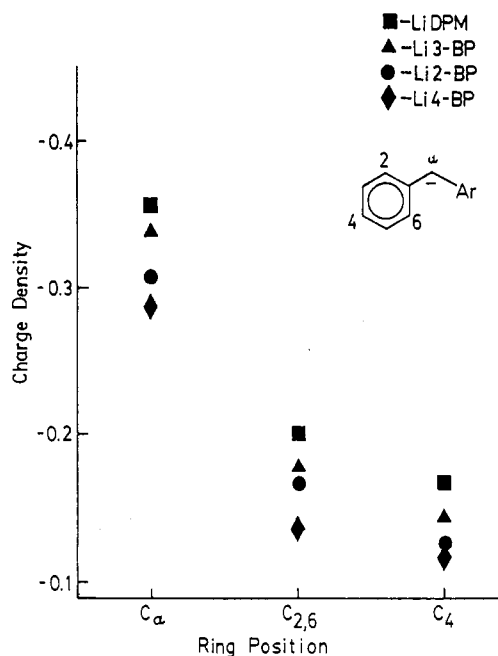

Figure 4. Relationship between charge density in the phenyl rings (calculated as described in text) of lithium anions at select carbon positions.

para position is uncomplicated by hybridization changes and cation effects and thus provides the most direct basis for comparison.[8b] Nevertheless, the benzylic carbon (C_α) is expected to carry significant charge and therefore is highly sensitive to changes in cation, solvent, and temperature so that this position along with the next most sensitive ortho positions (C_2, C_6, $C_{2'}$, and $C_{6'}$) are also used as probes of π-electron densities in the various anions.

Table VII lists the π-electron densities calculated from ^{13}C chemical shifts of the Li anions of 2-, 3-, and 4-benzylpyridines, as well as values for Li salts of toluene,[7a] diphenylmethane,[7a] and 2-ethylpyridine.[14a] The latter anions are included so that comparison can be made between similar carbon and heteroaromatic systems.

The total net negative charge at C_α and in each of the rings graphically depicted in Figure 4 reveals that the phenyl ring and central carbon have less charge in the order DPM > 3-BP > 2-BP > 4-BP. The difference in charge is redistributed to the respective nitrogen-containing rings. The charge at nitrogen is obtained indirectly from the difference between the total π-electron charge in DPM anion less the sum of the empirically determined charge at each of the carbon sites for each benzylpyridine anion.

Figure 5 graphically depicts the charge distribution of the various pyridyl rings in comparison to that seen in LiDPM. The greatest effect of charge redistribution is for Li4-BP. As expected, nitrogen charge decreases in the order 4' > 2' > 3' and in all cases greatly exceeds compa-
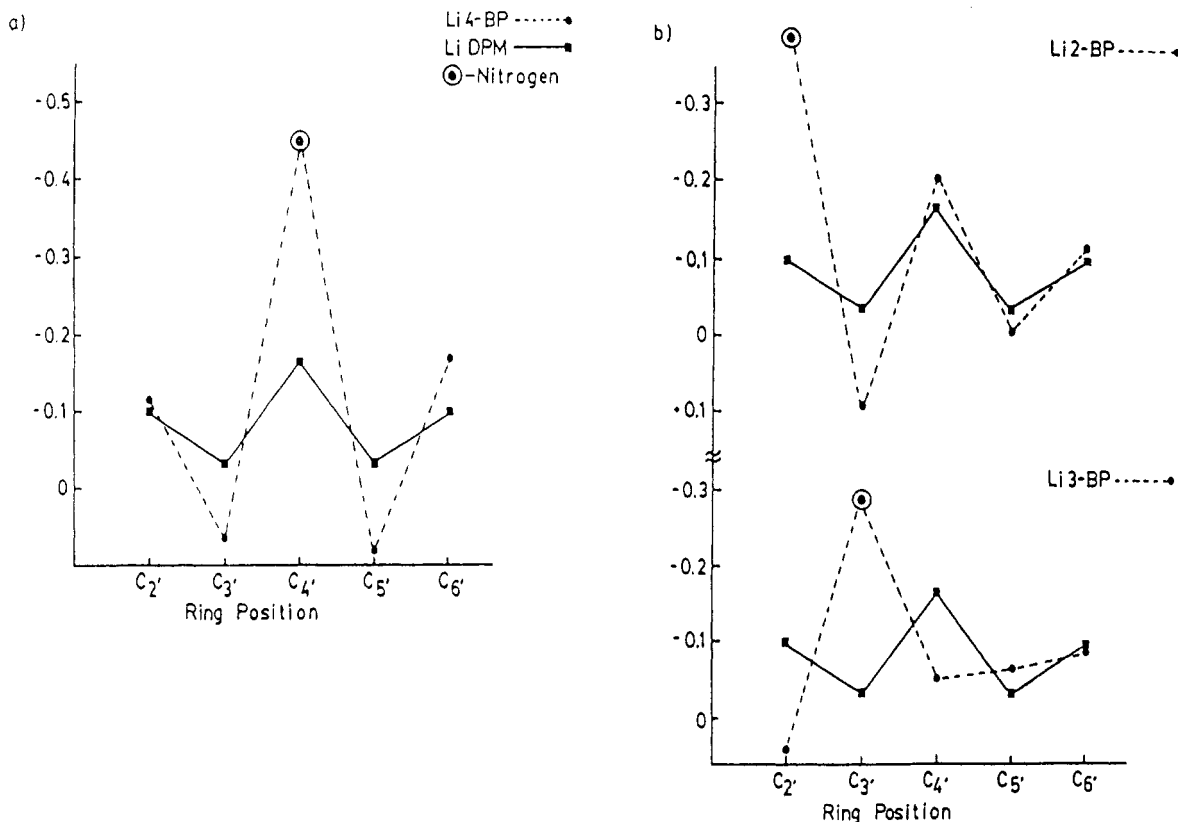
Figure 5. Charge distribution in pyridyl rings relative to comparable positions in phenyl ring for lithium anions: (a) diphenylmethyl and 4-benzylpyridyl; (b) 2-benzylpyridyl and 3-benzylpyridyl.

rable carbon sites. The charge decrease at C_α parallels the acidity changes. In fact, a plot of pK vs. [13]C chemical shifts of C_α for these and some other diaryl compounds leads to a linear relationship which may prove useful in predicting the pK of other compounds from the ^{13}C chemical shift at C_α.

In addition to charge ^{1}H shifts are sensitive to steric and anisotropic effects.[9b,18] Deviations in the correlation between ^{1}H and ^{13}C shifts highlight these phenomena. For example, in diphenylmethyl anions, the inner ortho protons are deshielded with respect to the outer ortho protons, whereas ^{13}C resonances for the inner ortho carbons are more shielded than the outer ortho carbons.[9d] This is likely an anisotropic deshielding of the inner ortho protons. Steric deshielding is seen in crowded nonplanar anions such as α-methyl-substituted diphenylmethanides and (triphenylmethyl)lithium.[9c]

Figure 6 shows the ^{1}H and ^{13}C chemical shift correlation for Li anions of DPM and 2-, 3-, and 4-BP. The clustering of points along the diagonal indicates the monotonic relationship between ^{1}H and ^{13}C chemical shifts. A slope of 0.05 is found for all α, para and meta positions close to the anticipated slope of ~0.06.[7a] Points that fall above the diagonal are all 2,2' and 6,6' ortho positions (except the 2' position in Li4-BP) for which proton resonances are at lower field compared to their position in ^{13}C spectra. Points that fall below the diagonal are generally associated with positions α to nitrogen. Either the protons are unusually shielded and/or the carbons unusually deshielded by position adjacent to nitrogen.

Redistribution of charge brought about by change in cation, solvent, and temperature relate to the nature of ion pairing. For heteroaromatic systems, coordination to nitrogen in the carbanion adds a factor favoring contact ion pairs. Previous investigations on analogous systems of alkali salts of 2-, 3-, and 4-pyridine-type carbanions were
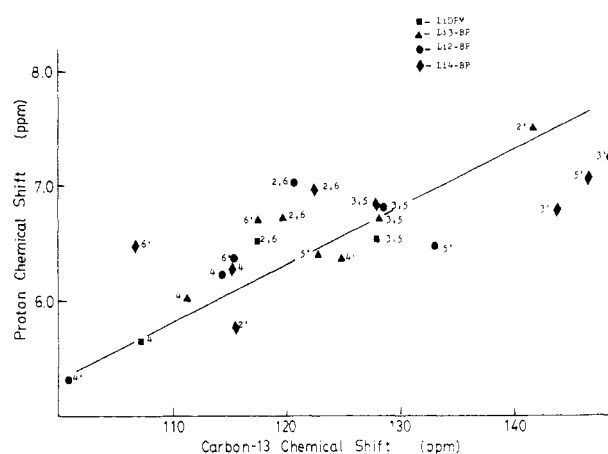

Figure 6. Relationship between proton and carbon-13 chemical shifts for lithium anions.

carried out by Hogen-Esch using UV/vis spectroscopy and conductimetry.[14b] The 2- and 4-pyridyl-substituted analogues exist exclusively as contact ion pairs in THF and DME. In contrast 3-pyridyl-substituted analogues were concluded to be similar to the phenyl analogues that are described as mixtures of tight and loose ion pairs. Subsequently, Na 2-EP was characterized as a contact ion pair.[14a] Thus, precedence exists for anions containing 2- and 4-pyridyl substituents to be tight ion pairs; however, 3-pyridyl-substituted carbanions may exist as solvent-separated ion pairs.

Changes in ion pairing are reflected in such systems as Li and Na DPM by ^{13}C NMR shielding changes at the α-carbon as the temperature, cation, or solvent is varied.[8c] At high temperatures contact ion pairs dominate and at lower temperatures a deshielding effect at C_α results from a larger effective cation size. In contact ion pairs of di-
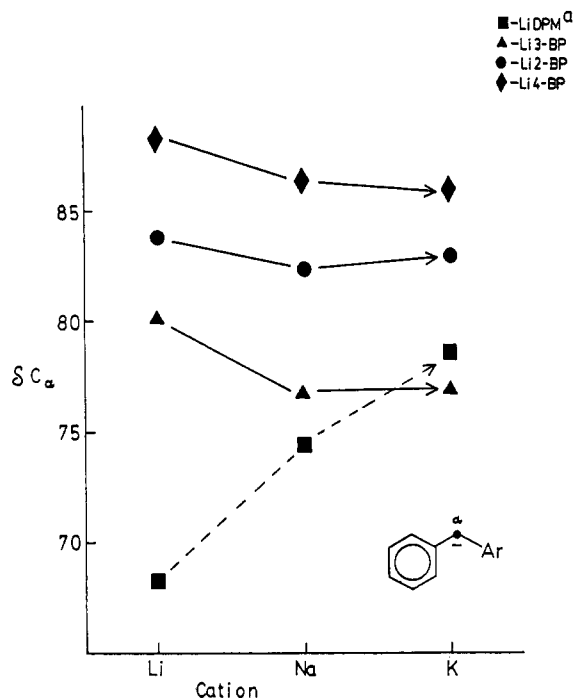
Figure 7. Relationship between δC_α and cation for diaryl anions in THF.

Table IX. Rotational Barriers for Diaryl Compounds[a]

anion/cation	ΔG phenyl ring			ΔG pyridyl ring		
	Li^+	Na^+	K^+	Li^+	Na^+	K^+
2-BP	8[b]	10.7[c]	11.2[c]	14.8[d]		
3-BP	10.2[e]	10.8[f]	11.5[g]	14.5[h]	13[i]	12.5[j]
4-BP	4[k]			19[l]		
DPM	11.3[m]		11.7[n]			

[a] In kcal/mol, 0.4–0.5 M in THF. [b] Estimated from extrapolated coalescence temperatures (T_c) of −90 °C and models for $\Delta\nu$. [c] Determined from T_c's of −30 and −25 °C, respectively, and measured values of $\Delta\nu$. [d] Estimated from T_c of 60 °C and measured value of $\Delta\nu$. [e] Estimated from low-temperature spectra approximation of T_c at −40 °C and estimated value of $\Delta\nu$. [f] Determined from T_c of −25 °C and measured value of $\Delta\nu$. [g] Determined from T_c of −10 °C and measured value of $\Delta\nu$. [h] Estimated from adjusted T_c of 40 °C and measured value of $\Delta\nu$. [i] Determined from adjusted T_c of 10 °C and measured value of $\Delta\nu$. [j] Determined from adjusted T_c of 10 °C and measured values of $\Delta\nu$. [k] Estimated upper limit from $T_c \ll$ −80 °C in ^{13}C DNMR. [l] Estimated lower limit from $T_c \gg$ +60 °C in ^{1}H DNMR. [m] Reference 6a. [n] Determined from T_c of −5 °C and measured value of $\Delta\nu$.

Table VIII. Carbon-13 Chemical Shift Change at C_α and C_p as Function of Temperature and Solvent

anion	temperature[a]		solvent[b]	
	$\Delta\delta C_\alpha$[c]	$\Delta\delta C_p$[c]	$\Delta\delta C_\alpha$[d]	$\Delta\delta C_p$[d]
DPM	4.5	−1.5	5.2	−2.6
2BP	1.6	−1.2	1.5	−2.7
3BP	0.1	−0.6	0.3	−2.0
4BP	−0.7	−0.5	−2.5	−1.8

[a] Temperature changes from −60 to +60 °C for lithium salts in THF. [b] Solvent change from THF to Me$_2$SO for sodium salts. [c] Chemical shift change in ppm brought about by increase in temperature. [d] Chemical shift change in ppm brought about by solvent change from Me$_2$SO to THF.

phenylmethyl and related anions the phenyl rings have greater charge and the α carbons less charge with increasing cation size. The trend of charge at C_α with cation (Figure 7) in BP anions is markedly different, and especially for lithium, compared to DPM systems. However, the para carbon (C_4) of the phenyl rings in all of the anions shows a trend to increasing charge with increasing cation size.

The chemical shift at C_α (Table VIII) in LiDPM is highly temperature-dependent whereas that for the K anion is not. This indicates a change in ion pairing for Li with no such change for K.[8c] Table VIII shows a small temperature dependence for Li4-BP and virtually none for Li3-BP with some temperature dependence for Li2-BP. This suggests no change in the state of ion pairing for 3- and 4-BP and may signal a change in structure for the tight ion pair of 2BP with temperature.

Additional evidence for a single set of tight ion pairs for all BP anions comes from change to a more highly coordinating solvent (Na/THF to Na/Me$_2$SO). A deshielding effect is seen with NaDPM on change from THF to Me$_2$SO but changes of similar magnitude are not seen for BP anions, and 4-BP actually shows a shielding effect (Table VIII). At the same time there is a uniform shielding at the para position in all the phenyl rings.

These cation dependencies suggest that for lithium anions coordination to nitrogen is a major factor and the cation is displaced relative to DPM anion. With larger

cations the center shifts toward the α-carbon causing a shielding increase opposite to that in DPM anions. At the same time delocalized charge is redistributed from the pyridyl ring to the phenyl ring.

A model for LiDPM tight ion pair structure based on crystal structures for related ions of LiTPM[20a] and benzyllithium[20b] places the Li between the central and ortho carbons, with a shortened coordination distance to the central position. Recently a simple hard sphere electrostatic model (HSE) was proposed for the benzyllithium system which predicts two major binding sites.[21] One site agrees with the position determined by X-ray crystallography; in the other site the cation is over the benzene ring.

Anions of 4-BP represent the most extreme case of shifted coordination site to nitrogen. In the proposed structure the cation is over the pyridyl ring and close to the nitrogen. This causes a deshielding effect at C_α, with the smaller Li cation having the largest such effect. Additional evidence for significant cation coordination at nitrogen comes from solvent change for Na4-BP from THF to Me$_2$SO. Solvent change brings an increase of charge at C_α rather than the more typical decrease as cation is removed by solvent, a unique feature for 4-BP anion.

Proposed structures for Li2- and 3-BP include a strong but mitigated role of nitrogen in metal coordination compared to the 4-pyridyl case. In 3-BP anions there is increased charge at the meta nitrogen position, with a smaller but unusual increase in charge seen at the meta 5' position. A model similar to the structures found by Stucky places the cation closer to the nitrogen ring. An alternate model, more like the Bushby model, places the cation over the nitrogen ring unsymmetrically.

The proposed model for Li2BP at low temperature places the cation over the anion plane between C_α and the nitrogen at the ortho position but closer to the ortho nitrogen than in the models mentioned above. That the 6' ortho proton is unusually shielded suggests that the cation may affect anisotropic deshielding. The model is closer to an electrostatically balanced Bushby model[21] with cation position over part of the ring.

With increasing temperature a different type of ion pair is suggested by an increase in shielding at C_α and pyridyl ring H$_{6'}$ and a deshielding of H$_{2,6}$ in the phenyl ring. These

(20) (a) Patterman, S. P.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *92*, 1150. (b) Brooks, J. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7333.

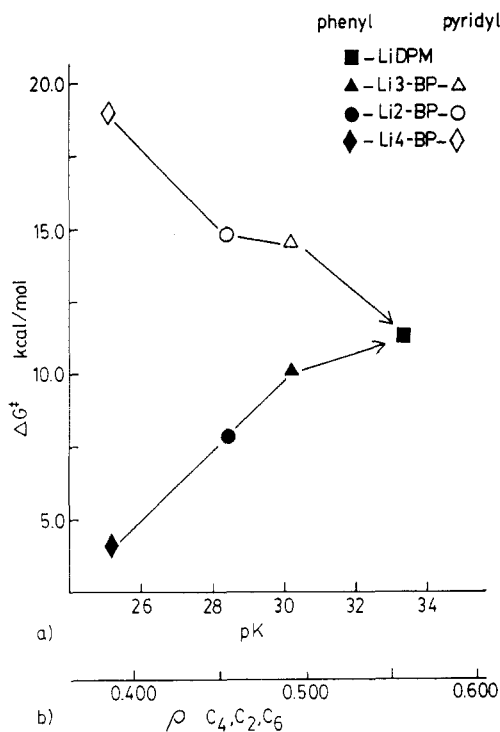(21) Bushby, R. J.; Tytko, M. P. *J. Organomet. Chem.* **1984**, *270*, 265.

Figure 8. Relationship between estimated barriers for phenyl and pyridyl rotations and (a) pK for lithium anions and (b) phenyl ring charge (calculated as in text) for lithium anions.

effects are consonant with an ion pair with cation position closer to the α carbon similar to the DPM anion. From the effects of cation and solvent variation this type of ion pair obtains for Na and K as well.

Precisely determined rates by theoretical line-shape analysis proved impractical in this work due to overlapping peaks, temperature-dependent shifts, and unequal isomer populations. Nevertheless, in many cases a value of T_c could be determined and leads to an estimate of the rotational barrier within 0.5–1.0 kcal/mol. For the phenyl rings this was possible for most combinations of anions and

cations. For the pyridyl rings, the estimation was not as straightforward and in many cases only limits or no values could be obtained. Table IX summarizes the relevant data.

For the phenyl rings (Figure 8) the barrier increases 4-BP < 2-BP < 3-BP < DPM—a similar trend to the comparison of calculated charges. Thus, for Li cation, nitrogen even in the 3-position appears to draw some charge from the phenyl ring.

Only 2- and 3-BP anions are considered for the effect of cation on rotational barrier of the phenyl ring. Results recorded in Table IX show that Li anions are uniquely separated from other cation–anion combinations. On change to Na and K, 2- and 3-BP have similar phenyl ring rotational barriers much like the DPM system when the cation is K. Strong coordination to the nitrogen for the lithium cation as indicated earlier is an attractive explanation.

The estimated $\Delta G^{\ddagger}$ values of the pyridyl rings with the various Li anions (Figure 8) reveals an opposite trend to that seen for the phenyl rings and $\Delta G^{\ddagger}$ increases in the order 4-BP > 2-BP > 3-BP > DPM. Interestingly, rotational barriers for the pyridyl rings of Li2-BP and 3-BP are similar, suggesting that the coordination of cation to the nitrogen is an important factor. With larger cation the pyridyl ring rotational barrier of 3-BP approaches that found for KDPM, and at the same time the phenyl ring rotational barrier increases.

A plot of Li anion $\Delta G^{\ddagger}$ values vs. pK (Figure 8) shows that for the benzylpyridines $\Delta G^{\ddagger}$ of the pyridyl ring increases as that of the phenyl ring decreases in the order 4-BP > 2-BP > 3-BP. Increased anion stability results in increased charge delocalization in the nitrogen-containing ring at the expense of charge delocalization in the phenyl ring, when compared to diphenylmethyl anion. The plot emphasizes the probable close coordination of Li to the nitrogen in each of the anions including 3-BP, which appears to have an unusually high barrier to pyridyl ring rotation.