# Solvation of Alkali Metal Cations of Arylmethyl Anions by Ethereal Solvents

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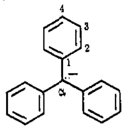
**Abstract:** The ion pair equilibria for triphenylmethyl, fluorenyl, diphenylmethyl, $\alpha$-trimethylsilylbenzyl, and benzyl alkali metal anions dissolved in 2-methyltetrahydrofuran, tetrahydrofuran, and dimethoxyethane have been investigated with variable temperature carbon-13 magnetic resonance. The $\alpha$-carbon chemical shifts for contact ions are very sensitive to cation and are proportional to the reciprocal of the interionic distance. Large $\alpha$-carbon chemical shift changes are observed for the lithium and sodium salts when the change from contact ions at high temperatures to solvent-separated ions at low temperatures is within the experimentally accessible temperature range. The $\alpha$-carbon chemical shifts for lithium and sodium solvent-separated ions are cation independent and comparison of these shifts to the contact shifts of the larger alkali metal carbanions gives an estimate of the interionic distance in the solvent-separated state. Little or no temperature-dependent chemical shift change is observed for the potassium, rubidium, or cesium salts either because they are contact ions at all temperatures or because carbon-13 is insensitive to solvation if it occurs. Entropies and enthalpies of solvation were determined for those salts that undergo approximately 40% of the change from contact to solvent-separated ions within the accessible temperature range.

## Introduction

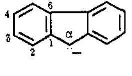
Ultraviolet absorption spectroscopy has been used extensively to characterize the equilibria between contact and solvent-separated ion pairs.[1,2] Fluorenyl salts have been used to determine the thermodynamics of solvation and the effects of cation and solvent on the equilibria.[3-5] Relatively few other carbanions have been studied because of overlap of the ultraviolet maxima (diphenylalkylmethyl[6] and 1,3-diphenylallyl[7,8]). Proton magnetic resonance has also been used to qualitatively study ion-pair equilibria.[4,7,9-16] Shift changes *indirectly* reflect $\pi$-electron density changes and $^1H$ NMR can be used to study a wider variety of carbanion systems (fluorenyl,[4,9,10-17] indenyl,[11,12,17] cyclopentadienyl,[17] triphenylmethyl,[17] 1,3-diphenylallyl,[7,13,18] phenylalkylmethyl,[14,15] and $\alpha$- and $\beta$-naphthylmethyl[15]). However, proton shift changes are quite small and are influenced by factors other than electron density changes, the carbon most sensitive to solvation changes may not be protonated, peak overlap and complex coupling patterns make assignments difficult, and resonances of interest may be obscured by solvent.[17-19] Carbon-13 shifts are a very good empirical measure of $\pi$-electron density differences in charged systems.[20-25] For delocalized carbanions, recent studies have shown that carbon-13 shifts are sensitive to temperature, cation, and solvent.[26-28]

## Results and Discussion

Recently, we reported the solvation properties of the alkali metal salts of diphenylmethane using variable-temperature carbon-13 magnetic resonance.[29] We report here the completed study of triphenylmethyl ($T^-M^+$), fluorenyl ($F^-M^+$), diphenylmethyl ($DPM^-M^+$), $\alpha$-trimethylsilylbenzyl ($TMSB^-M^+$), and benzyl ($B^-M^+$) alkali metal anions in three solvents of different solvating power: 2-methyltetrahydrofuran (MeTHF), tetrahydrofuran (THF), and dimethoxyethane (DME). Chemical shift changes are very large compared to $^1H$ NMR shift changes and complex coupling patterns and solvent interference present no problems. Variable temperature carbon-13 magnetic resonance focuses on the changes in electron density that occur as the carbanion undergoes solvation and may be applied to carbanion systems of widely different structure.



$T^-$



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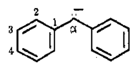
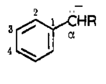


$DPM^-$



$TMSB^-$ ($R = Si(CH_3)_3$)
$B^-$ ($R = H$)

**General Features of Solvation Changes Observed with Variable-Temperature Carbon-13 Magnetic Resonance.** Table I presents carbon-13 chemical shift changes for fluorenyllithium dissolved in MeTHF, typical of the changes observed for the other alkali metal carbanions undergoing solvation. These changes are completely reversible within the accessible temperature range. This temperature range is limited at low temperatures by the solubility of the carbanion salt, precipitation usually occurring between −40 and −50 °C. At high temperatures, good spectra are obtained up to just below the solvent's boiling point for all the alkali metal carbanions in MeTHF and THF, and for the lithium salts except benzyllithium in DME. For the sodium, potassium, rubidium, and cesium salts in DME, reaction of the carbanion with solvent becomes rapid above about 60 °C. For benzyllithium in DME, reaction with solvent becomes rapid above about 30 °C.

As the temperature is increased, the $\alpha$ carbon moves upfield and approaches a constant, shielded chemical shift ($\delta_c$), where the equilibrium favors the contact ion. In the contact ion, the cation resides close to the most electron-rich carbon, C-$\alpha$, and the $\pi$-electron density is strongly polarized toward this carbon.[30-35] In contrast, in the solvent-separated state at low temperatures, the cation is wrapped with solvent and the carbanion responds by spreading the $\pi$-electron density more evenly over the carbanion to give a deshielded chemical shift at C-$\alpha$ ($\delta_s$). The largest chemical shift changes occur at the $\alpha$ carbon for all the alkali metal carbanions studied. For fluorenyllithium, the $\alpha$ carbon moves upfield by 5.5 ppm upon an increase in temperature of 130 °C. This change is compensated by a downfield shift change of the two para carbons of 3.5 ppm. Change in $\pi$-electron density is the major cause of these shift changes.[25] Only minor shift changes are observed at the other carbons (Table I).

Only the lithium and sodium salts undergo appreciable temperature-dependent chemical shift changes. The energy required to convert contact ions into solvent-separated ions is a balance between the coulombic energy needed to separate oppositely charged ions and the energy gained from ion-dipole interaction between the cation and the solvent. The energy needed to separate the cation from the carbanion should decrease as the size of the $\pi$ system increases and the negative charge becomes more disperse. It is generally accepted that the solvating power of the three solvents is in the order DME $\gg$ THF > MeTHF. Dimethoxyethane has two oxygens fa-

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**Table I.** Variable Temperature Carbon-13 Chemical Shifts for Fluorenyllithium in MeTHF[a]

| $t$, °C | $C_\alpha$ | $C_4$ | $C_1$ | $C_2$ | $C_6$ | $C_3$[b] | $C_5$[b] |
|---|---|---|---|---|---|---|---|
| −60 | 82.9 | 107.8 | 137.2 | 116.2 | 122.5 | 119.0 | 118.6 |
| −50 | 82.8 | 107.8 | 137.3 | 116.2 | 122.6 | 119.0 | 118.6 |
| −40 | 82.7 | 107.8 | 137.3 | 116.2 | 122.6 | 119.0 | 118.6 |
| −30 | 82.5 | 107.8 | 137.4 | 116.2 | 122.6 | 119.0 | 118.6 |
| −20 | 82.2 | 107.9 | 137.5 | 116.2 | 122.8 | 119.0 | 118.7 |
| −10 | 81.9 | 108.1 | 137.6 | 116.3 | 122.9 | 119.1 | 118.7 |
| 0 | 81.5 | 108.3 | 137.6 | 116.3 | 123.0 | 119.3 | 118.8 |
| 10 | 80.9 | 108.6 | 137.5 | 116.4 | 123.0 | 119.4 | 118.8 |
| 20 | 80.1 | 109.0 | 137.4 | 116.4 | 123.0 | 119.7 | 119.0 |
| 30 | 79.3 | 109.5 | 137.3 | 116.6 | 123.0 | 119.9 | 119.1 |
| 40 | 78.6 | 109.9 | 137.0 | 116.8 | 122.9 | 120.2 | 119.3 |
| 50 | 78.1 | 110.4 | 136.8 | 116.9 | 122.8 | 120.3 | 119.4 |
| 60 | 77.8 | 110.9 | 136.5 | 117.1 | 122.6 | 120.7 | 119.6 |
| 70 | 77.4 | 111.3 | 136.3 | 117.2 | 122.5 | 121.0 | 119.7 |

[a] Chemical shifts are *interpolated* values from measurements taken at 8 °C intervals in parts per million downfield from $Me_4Si$ using cyclohexane as an internal shift reference and the relationship $\delta_{Me_4Si} = \delta_{C_6H_{12}} + 27.5$. [b] These chemical shift assignments may be interchanged.

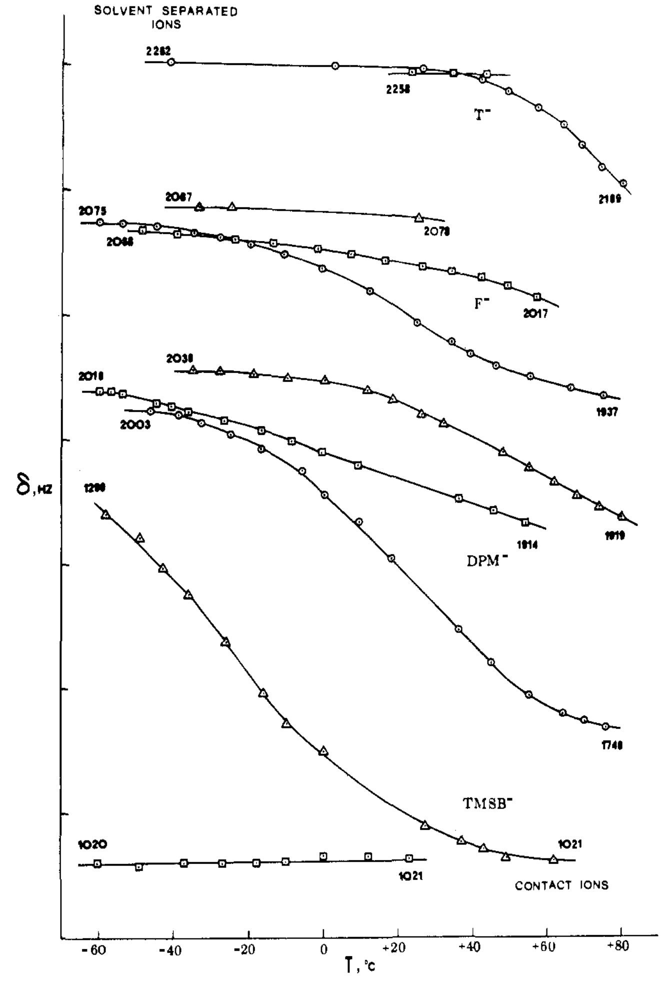

Figure 1. Ion pair equilibrium curves for the lithium salts of T⁻, F⁻, DPM⁻, and TMSB⁻ in MeTHF (⊙), THF (⊡), and DME (△), α-Carbon chemical shifts, plotted on the vertical axis, are in hertz downfield from $Me_4Si$ at 25.0335 MHz with 100 Hz between each division. Chemical shifts at the ends of each curve are the α-carbon chemical shifts at the highest and lowest temperatures.

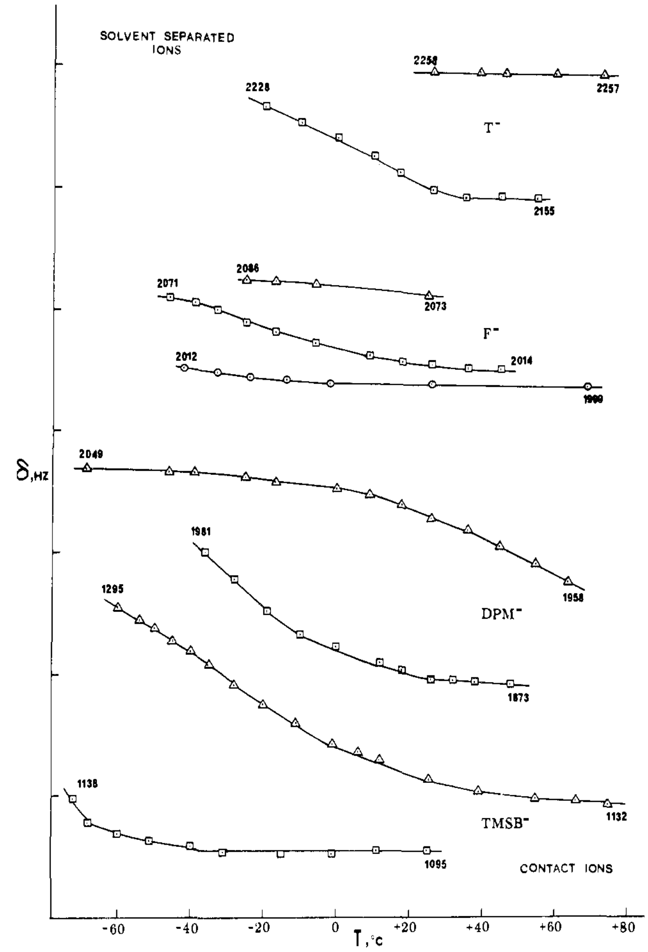

Figure 2. Ion pair equilibrium curves for the sodium salts of T⁻, F⁻, DPM⁻, and TMSB⁻ in MeTHF (⊙), THF (⊡), and DME (△). α-Carbon chemical shifts, plotted on the vertical axis, are in hertz downfield from $Me_4Si$ at 25.0335 MHz with 100 Hz between each division. Chemical shifts at the ends of each curve are the α-carbon chemical shifts at the highest and lowest temperatures.

vorably oriented to coordinate electron pairs with the cation. Tetrahydrofuran is superior to MeTHF because the 2-methyl group sterically crowds the coordination site.

The effect of these two features, size of the carbanion's π system and solvating power, is qualitatively demonstrated by the sigmoidal curves for the lithium salts of T⁻, F⁻, DPM⁻, and TSMB⁻ obtained by plotting the α-carbon chemical shifts against temperature (Figure 1). α-Trimethylsilylbenzyllithium, the smallest π system (8 π electrons, seven carbons), remains a contact ion throughout the temperature range in THF and requires the more powerful solvent, DME, to undergo appreciable solvation. Diphenylmethyllithium and fluorenyllithium (14 π electrons, 13 carbons) are similar in their

**Table II.** α-Carbon Chemical Shifts of Contact Ions ($\delta_c$)[a]

| carbanion | MeTHF $\delta_c$ | THF $\delta_c$ | DME $\delta_c$ | carbanion | MeTHF $\delta_c$ | THF $\delta_c$ | DME $\delta_c$ |
|---|---|---|---|---|---|---|---|
| $T^-Li^+$ | (2706) | (2109) | *b* | $DPM^-Li^+$ | (1682) | (1754) | (1794) |
| $Na^+$ | 2129 | 2155 | *b* | $Na^+$ | 1830 | 1873 | (1897) |
| $K^+$ | 2191 | 2201 | 2248 | $K^+$ | 1958 | 1981 | 1980 |
| $Rb^+$ | 2192 | 2210 | *c* | $Rb^+$ | 1990 | 2000 | 2012 |
| $Cs^+$ | 2206 | 2219 | *c* | $Cs^+$ | 2035 | 2040 | 2035 |
| $F^-Li^+$ | (1914) | (1946) | *c* | $TMSB^-Li^+$ | 1035 | 1021 | 1021 |
| $Na^+$ | 1999 | 2014 | *b* | $Na^+$ | 1087 | 1095 | 1132 |
| $K^+$ | 2073 | 2076 | *c* | $K^+$ | 1362 | 1349 | 1341 |
| $Rb^+$ | 2094 | 2084 | *c* | $Rb^+$ | 1404 | 1394 | *c* |
| $Cs^+$ | *d* | 2111 | *c* | $C_s^+$ | 1462 | 1452 | *c* |

[a] Chemical shifts in hertz downfield from $Me_4Si$ at 25.0335 MHz; shifts in parentheses estimated from plots of contact shifts of larger alkali metal carbanions vs. 1/interionic distance (Figure 3). [b] Contact shifts not attained at 70 °C and insufficient data for potassium, rubidium, and cesium salts to estimate $\delta_c$. [c] Not determined. [d] Cesium salt insoluble even at high temperatures.

**Table III.** α-Carbon Chemical Shifts of Lithium and Sodium Solvent-Separated Ions ($\delta_s$) and Estimated Chemical Shift Changes ($\Delta\delta_c$)[a]

| carbanion | MeTHF | | THF | | DME | |
|---|---|---|---|---|---|---|
| | $\delta$ | $\Delta\delta_e$ | $\delta$ | $\Delta\delta e$ | $\delta$ | $\Delta\delta_c$ |
| $T^-Li^+$ | 2262 | 186 | 2258 | 149 | 2260 | *b* |
| $Na^+$ | *c* | | (2258) | 103 | 2258 | *b* |
| $F^-Li^+$ | 2075 | 161 | 2068 | 122 | 2087 | *b* |
| $Na^+$ | *c* | | (2086) | 72 | 2086 | *b* |
| $DPM^-Li^+$ | 2003 | 321 | 2019 | 265 | 2036 | 242 |
| $Na^+$ | *c* | | (2049) | 176 | 2049 | 152 |
| $TMSB^-Li^+$ | *c* | | *c* | | (1452)[d] | 431 |
| $Na^+$ | *c* | | *c* | | (1452)[d] | 320 |

[a] Chemical shifts in hertz downfield from $Me_4Si$ at 25.0335 MHz; shifts in parentheses estimated by comparing to other solvent-separated shifts (see text). [b] Solvent-separated ions; no appreciable change in solvation within accessible temperature range (Figures 1 and 2). [c] Contact ions; no appreciable change in solvation within accessible temperature range (Figures 1 and 2). [d] Complete solvation not attained even at lowest temperatures; shift estimated by using contact ion shift of cesium salt (see text).

solvation characteristics and both are more easily solvated that $TMSB^-Li^+$. In the poorest solvent, MeTHF, they show almost complete change from contact ions to solvent-separated ions; in THF, the middle portions of the solvation curves are observed; and in the most powerful solvent, DME, only the solvent-separated ends of the curves are seen. Triphenylmethyllithium, the largest system (20 π electrons, 19 carbons), is the most easily solvated and solvation is complete below about 50 °C except in the poorest solvent, MeTHF.

Figure 2 presents the ion pair equilibrium curves for the sodium salts. Qualitatively, sodium and lithium salts are similar but the lithium salts are slightly easier to solvate. For example, neither $TMSB^-Li^+$ nor $TMSB^-Na^+$ is appreciably solvated in THF and they show about the same extent of solvation in DME. Comparing the larger π systems, it is more apparent that the lithium salts solvate more easily. For example, $DPM^-Li^+$ is completely solvated at low temperatures in MeTHF while $DPM^-Na^+$ requires THF to become only partially solvated. Similarly, $T^-Li^+$ becomes completely solvated in MeTHF while $T^-Na^+$ is only partially solvated in the more powerful solvent, THF.

Carbanions of the larger alkali metals were also studied. Solvation is less thermodynamically favorable than for lithium and sodium cations because the energy gain from the ion-dipole interaction between the more diffuse positive field of the larger cations is much smaller. No significant chemical shift changes were observed for the potassium, rubidium, and cesium salts except for slight downfield changes for $DPM^-K^+$ in THF and DME and for $T^-K^+$ in DME and it must be *assumed* that the carbanions of the larger alkali metals are contact ions within the accessible temperature range. However, as will be shown, the absence of downfield chemical shift changes at the α carbons may be due to the insensitivity of carbon-13 magnetic resonance to distinguish between contact and solvent-separated ions of the larger alkali metals.

**Effect of Cation Size. α-Carbon Chemical Shifts of the Contact Ions ($\delta_c$) and the Solvent-Separated Ions ($\delta_s$).** Two very important features emerge when the α-carbon chemical shifts of the contact ions are compared for the same carbanion but for different alkali metal cations. Table II presents observed and estimated $\delta_c$'s for $T^-$, $F^-$, $DPM^-$, and $TMSB^-$. First, $\delta_c$ is very dependent upon cation size. Second, the size of the chemical shift change experienced by the α carbon upon solvation *decreases* as the size of the cation *increases* (Table III, $\Delta\delta_e$). The α-carbon chemical shifts of the contact ions are proportional to the reciprocal of the interionic distance in the contact ion. As the distance between the carbanion and the cation increases, $\delta_c$ becomes more deshielded because the positive fields of the larger cations are less effective in polarizing the π-electron density toward the α carbon. Similarly, the absorption maxima of contact ions undergo bathochromic shifts as the size of the cation increases for fluorenyl salts[1,2,5,36] and alkali metal phenoxides and enolates.[37,38] However, the change is small and the reciprocal of the cation radius is a sufficient measure of interionic distance to obtain good linear relationships. The UV maxima of ketyls and aromatic hydrocarbon anion radicals are also proportional to the size of the cation in the contact ions.[39-41] For these, a distance of 2.0 Å was added to the cation radii to obtain linear plots. Presumably, this 2.0 Å accounts for the contribution of the anion radical to the interionic distance.

The α-carbon chemical shifts of the contact ions also require an estimate of the carbanion's contribution to the interionic distance to be linear and to obtain estimates of the experimentally inaccessible $\delta_c$'s for the lithium salts of $T^-$, $F^-$, and $DPM^-$.[42] If only the reciprocal of the cation radius is plotted against the observed $\delta_c$'s for $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ salts, the least-squares lines predict unreasonably shielded $\delta_c$'s for the lithium salts. For example, the highest field α-carbon chemical shifts for $DPM^-Li^+$ and $F^-Li^+$ in MeTHF at 75 °C are 1749 and 1937 Hz, respectively. Figure 1 clearly shows that these ion pair equilibrium curves have leveled off and only small additional upfield changes are expected. Using only the reciprocal of the cation radius, the least-squares lines predict unreasonably high field values for $\delta_c$:$DPM^-Li^+$, 1537 Hz; $F^-Li^+$, 1837 Hz.

To estimate the interionic distances in the contact ions, the solution radii of these delocalized carbanions are necessary. The best estimates come from conductivity studies and show

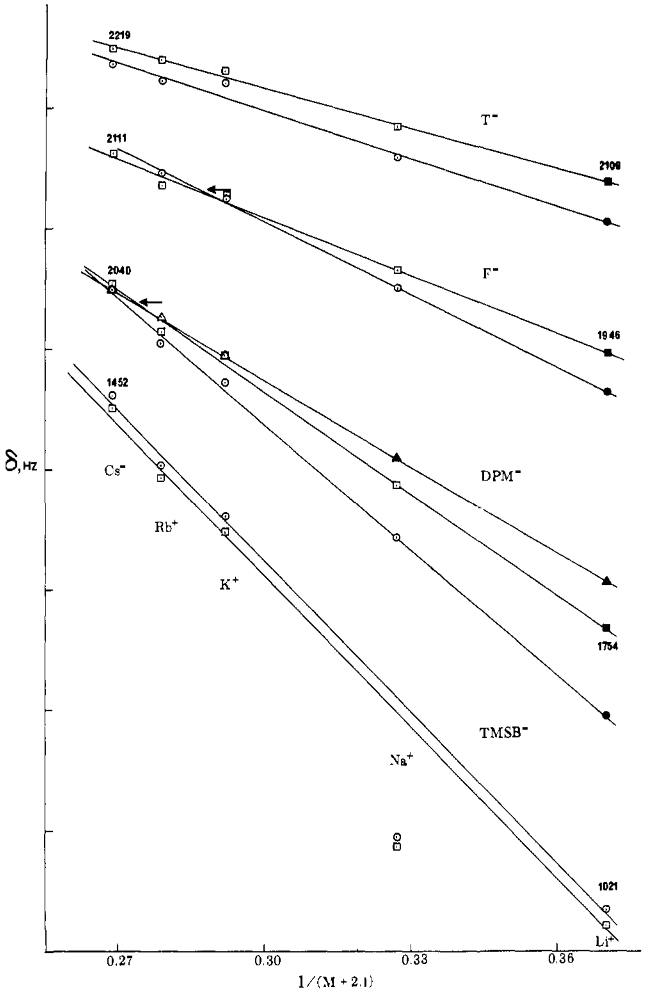

Figure 3. The proportionality between the contact ion $\alpha$-carbon chemical shifts ($\delta_c$) and interionic distances for $T^-$, $F^-$, $DPM^-$, and $TMSB^-$ in MeTHF (⊙), THF (⊡), and DME (△). Solid symbols show *estimated* contact ion shifts. Arrows on the $F^-$ and $DPM^-$ lines indicate approximate position that the horizontal line through the cation-independent lithium and sodium solvent-separated shifts ($\delta_s$) would cross the contact ion lines. For $T^-$, this shift is downfield from the cesium contact shift at 2260 Hz. Chemical shifts at the ends of each set of curves are the contact shifts in THF.

that the radius of fluorenyl carbanion is 2.1 Å.[43] No solution radii have been reported for $T^-$, $DPM^-$, and $TMSB^-$. Therefore, we have used 2.1 Å to approximate the radii of all four carbanions. Figure 3 shows the lines that result when the observed $\delta_c$'s are plotted against the reciprocal of the cation radius plus 2.1 Å. Much better predictions are obtained for the inaccessible $\delta_c$'s of the lithium salts. For the lithium salts that are very close to $\delta_c$ at high temperatures, the predicted values follow: $DPM^-Li^+$, 1682 Hz; $F^-Li^+$, 1914 Hz. These estimated contact shift limits were used in the calculations of the thermodynamics of solvation and are believed to be precise to about ±20 Hz (see Experimental Section). For $TMSB^-Li^+$, all the $\delta_c$'s were experimentally accessible. However, the least-squares lines through the contact shifts for $Cs^+$, $Rb^+$, $K^+$, and $Li^+$ salts show that the sodium contact shifts are much too shielded. The reason(s) for these deviations is not clear.

Despite the crude method used to estimate the carbanion radii, it must be emphasized that the $\alpha$-carbon chemical shifts are *proportional* to the interionic distances in the contact ions. The estimates of carbanion radii do not substantially alter the several qualitative conclusions concerning ion-pair structure that may be based upon this important relationship. First, Figure 3 shows the influence of the external solvent shell on the electron distribution in the carbanion. Second, when $\delta_c$'s of the larger alkali metals are compared to the solvent-separated $\alpha$-carbon chemical shifts ($\delta_s$'s) of the lithium and sodium salts, this comparison gives a qualitative measure of the change in interionic distance that occurs upon solvation. Third, this relationship provides a warning concerning the use of carbon-13 and proton magnetic resonance for the study of the ion-pair equilibria of carbanions of the larger alkali metals.

Figure 3 shows the influence of solvent structure on the $\pi$-electron density at the $\alpha$ carbon for $F^-$ and $DPM^-$ contact ions. The slopes of the lines are shallower for DME than for THF and MeTHF and $\delta_c$ is deshielded in the order DME > THF > MeTHF for lithium and sodium cations. DME disperses the cation's charge more effectively than THF or MeTHF because it has two electron donor sites. Therefore, the $\pi$-electron density is less polarized toward the $\alpha$ carbon and the $\delta_c$'s are more deshielded in DMF. This small effect of the *external* solvent shell acting through the cation's positive field diminishes as the size of the cation increases and is negligible for $K^+$, $Rb^+$, and $Cs^+$ salts. No appreciable solvent effects are seen for the contact ions of either $T^-$ or $TMSB^-$.

As the temperature is lowered, the $\alpha$-carbon chemical shifts approach a constant, deshielded value ($\delta_s$) as the equilibrium becomes dominated by solvent-separated ions. The solvent-separated $\alpha$-carbon chemical shifts were accessible for the lithium salts of $T^-$, $F^-$, and $DPM^-$ in all solvents and for the sodium salts in DME (Table III, Figures 1 and 2). Unlike the large differences for the $\delta_c$'s, the $\delta_s$'s of the lithium and sodium salts of $T^-$ and $F^-$ in DME are cation *independent* and only a small difference is observed for $DPM^-$. This implies that solvated lithium and sodium cations are about the same "size". Further, the effect of solvent upon $\delta_s$ is negligible for $T^-$ and quite small for $F^-$ and $DPM^-$ (Table III). Therefore, we have estimated the inaccessible $\delta_s$'s for the sodium salts of $T^-$, $F^-$, and $DPM^-$ in THF by using the $\delta_s$'s found in DME. These estimates are probably good to about ±10 Hz. No solvent-separated chemical shifts were observed for $TMSB^-$ even in the most powerful solvent, DME. Therefore, we have used the chemical shift of the contact ion of the cesium salt as a crude estimate of the $\delta_s$'s of the lithium and sodium salts.

**Change in Interionic Distance upon Solvation.** If the $\delta_s$'s for the smaller lithium and sodium cations are compared to the $\delta_c$'s of the larger alkali metal cations, one may estimate the change in interionic distance that occurs upon solvation. Extending the horizontal line established by the cation-independent lithium and sodium $\delta_s$'s to the contact ion line gives an estimate of the interionic distance for the solvent-separated lithium and sodium ion pairs (Figure 3, ←). For fluorenyllithium and sodium, the solvent-separated interionic distances are approximately those of fluorenylpotassium contact ion. For diphenylmethyllithium and sodium, the distances are slightly larger and fall between diphenylmethylrubidium and diphenylmethylcesium contact ions.[44] In contrast, $\delta_s$'s for triphenylmethyllithium and sodium (~2260 Hz, all solvents) are more deshielded than $\delta_c$ of the largest alkali metal contact ion, triphenylmethylcesium (2206, 2219 Hz in MeTHF, THF). This trend ($T^- \gg DPM^- > F^-$) shows the effect of carbanion structure on interionic distances in solvent-separated ion pairs. The solvated cation may approach the bridged, planar fluorenyl anion more closely than diphenylmethyl anion in which rotation about the C-$\alpha$-C-1 bond makes the anion bulkier. In solvent-separated triphenylmethyl anions, the distance is even larger because of the steric influence of the three phenyl groups. The size of the chemical shift change at the $\alpha$ carbon depends upon the size of the $\pi$ system and the change in interionic distance upon solvation (Table III, $\Delta\delta_e$:$DPM^- > T^- > F^-$). For the 14-$\pi$-electron systems, $DPM^-$ undergoes a larger change than $F^-$ because of the larger interionic distance required in the solvent-separated ion. For the 20-$\pi$-electron system, $T^-$, one might expect the smallest $\Delta\delta$ because the

**Table IV.** Equilibrium Constants (SS/CI) and Thermodynamics of Solvation[a]

| solvent | equilibrium constants | | | | | | | $\Delta H$, | $\Delta S$, deg · cal/ | |
|---|---|---|---|---|---|---|---|---|---|---|
| carbanion | −25°C | 0 °C | 25 °C | 50 °C | $\Delta t$ | $\Delta\delta_0$ | % | kcal/mol | mol | ref |
| MeTHF | | | | | | | | | | |
| $T^-Li^+$ | SS | SS | SS | 7.41 | 31 | 93 | 50 | −15.5 ± 0.8 | −44 ± 3 | *b* |
| $F^-Li^+$ | >10 | 3.35 | 1.01 | 0.36 | 66 | 138 | 86 | −7.7 ± 1.0 | −26 ± 4 | *c* |
| $DPM^-Li^+$ | >10 | 3.79 | 1.31 | 0.76 | 93 | 254 | 79 | −7.1 ± 0.5 | −23 ± 2 | |
| THF | | | | | | | | | | |
| $T^-Na^+$ | 2.89 | 0.84 | <0.10 | CI | 50 | 73 | 70 | −11.7 ± 0.7 | −44 ± 2 | *d* |
| $F^-Li^+$ | >10 | 6.17 | 3.36 | 1.84 | 50 | 51 | 42 | −4.9 ± 0.3 | −14 ± 2 | *e* |
| $F^-Na^+$ | 1.18 | 0.30 | <0.10 | CI | 57 | 56 | 78 | −7.9 ± 0.9 | −32 ± 3 | *f* |
| $DPM^-Na^+$ | 0.80 | 0.21 | <0.10 | CI | 54 | 108 | 61 | −7.6 ± 0.3 | −31 ± 1 | |
| DME | | | | | | | | | | |
| $DPM^-Li^+$ | SS | >10 | 6.33 | 2.58 | 62 | 117 | 48 | −7.2 ± 0.2 | −20 ± 1 | |
| $DPM^-Na^+$ | >10 | 7.59 | 3.00 | 1.19 | 81 | 91 | 60 | −6.6 ± 0.4 | −20 ± 2 | |
| $TMSB^-Li^+$ | 0.67 | 0.26 | <0.10 | CI | 95 | 278 | 64 | −5.3 ± 0.3 | −23 ± 1 | |
| $TMSB^-Na^+$ | 0.42 | 0.19 | <0.10 | CI | 72 | 163 | 43 | −3.5 ± 0.2 | −16 ± 1 | |

[a] Equilibrium constants are *interpolated* values obtained from ion pair equilibrium curves (Figures 1 and 2); $\Delta\delta_0$ is the observed $\alpha$-carbon chemical shift change used for van't Hoff plots over the temperature range, $\Delta t$; % is the percent conversion within the temperature range, $\Delta t$ $(\Delta\delta_0/\Delta\delta_e)$. [b] Lit.[5c] −11.8 kcal/mol and −32 cal/deg·mol in cyclohexylamine. [c] Lit.[5c] −8.5 kcal/mol and −23 cal/deg·mol. [d] Lit.[17] −8.2 kcal/mol and −28 cal/deg·mol. [e] Lit.[1,2b] −7.5 kcal/mol and −27 cal/deg·mol. [f] Lit.[17] −6.7 kcal/mol and −27 cal/deg·mol; lit.[1,2b] −7.6 kcal/mol and −33 cal/deg·mol.

larger $\pi$ system should be less susceptible to polarization by the cation or the solvated cation. However, this is compensated for by the larger interionic distance required in the solvent-separated ion.

**Solvation of the Larger Alkali Metal Cations.** For the same carbanion, $\Delta\delta$ decreases greatly from lithium to sodium. From Figure 3, one may estimate that *if* a potassium salt were to undergo solvation, the chemical shift change would be quite small (<30 Hz). This observation provides a warning concerning the use of magnetic resonance measurements to study the solvation properties of carbanions of the larger alkali metal cations.[45] The trends established by the lithium and sodium salts and simple thermodynamic arguments allow the conclusion that solvation is much less favorable because the energy gain from ion-dipole interaction between the large cation and solvent is small. Therefore, it is safe to assume that the $K^+$, $Rb^+$, and $Cs^+$ salts are contact ions. However, it is important to recognize that if solvation were to occur for these cations, the change in chemical shift at the most sensitive $\alpha$ carbon might not be observable.

**Ion Pair Equilibrium Constants and Thermodynamics of Solvation.** For carbanions that undergo at least 40% of the conversion from solvent-separated ions to contact ions, van't Hoff plots of the equilibrium constants vs. the reciprocal of the absolute temperature give good straight lines (Table IV, $K = (\delta_0 - \delta_c)/(\delta_s - \delta_0)$ where $\delta_0$ = observed $\alpha$-carbon chemical shift, $\delta_c$ = $\alpha$-carbon contact ion chemical shift, and $\delta_s$ = $\alpha$-carbon solvent-separated ion chemical shift). These thermodynamic values are in close agreement with those of $T^-$ and $F^-$ salts determined by UV[1,2b,5] and $^1H$ NMR[17] measurements except for $F^-Li^+$ in THF. For $F^-$ $Li^+$ in THF, the values are probably low because the solvent-separated limit must be estimated, the chemical shift change is relatively small, and only 42% of the conversion from contact to solvent-separated ions can be observed. The enthalpies of solvation depended upon cation size and are similar for lithium and sodium. With the largest $\pi$ system, $T^-$, and the smallest, $TMSB^-$, the enthalpy's dependence upon carbanion structure is apparent. The exceptionally large enthalpies for trityl salts are due to a combination of two factors. The energy necessary for cation separation is smaller because of the large $\pi$ system and the energy gain from cation solvation is greater because of the large interionic distance. The salts of the smallest carbanion, $TMSB^-Li^+$ and $TMSB^-Na^+$, have enthalpies lower than for $DPM^-$ and $F^-$. This is due to the more concentrated, less polarizable $\pi$ system which increases the energy debt for cation separation.

The large, negative entropies reflect the increased order upon solvation with the "freezing out" of solvent molecules around the cation. These entropies show a solvent dependence similar to that previously reported for fluorenyl salts in THF and DME.[17] Since DME has two coordination sites, fewer molecules of solvent are immobilized than in THF or MeTHF and the entropies are usually smaller in DME. The large entropies for the trityl salts may be associated with the large interionic distances required in the solvent-separated ions.

**Solvation of Benzyl Carbanions.** Variable temperature carbon-13 spectra were obtained for benzyllithium, sodium, potassium, and rubidium. The alkali metal carbanions of $\alpha$-trimethylsilyltoluene were surprisingly stable toward protonation by solvent compared to the benzyl salts. Good spectra were obtained for $TMSB^-M^+$ at high temperatures even in DME, the solvent most sensitive to deprotonation. In contrast, benzyl carbanions could be studied only in MeTHF and THF at ambient temperatures and below. Spectra were obtained for benzyllithium in DME up to 30 °C if the carbanion was prepared at low temperatures. The greater stability of $TMSB^-$ in ethereal solvents is undoubtedly due to the delocalizing influence of the trimethylsilyl group attached to the electron-rich $\alpha$ carbon.[46]

Contact ions dominate at high temperatures as the size of the $\pi$ system decreases (Figures 1 and 2). $TMSB^-Li^+$ and $TMSB^-Na^+$ are primarily contact ions above about 30 °C in all solvents. Therefore, it is safe to assume that the benzyl anions are contact ions at room temperature. Further, it can be predicted that benzyllithium and benzylsodium would undergo very large chemical shift changes upon solvation. An estimate of this change is obtained by comparing the chemical shift of the contact ion of benzyllithium to that of benzylrubidium and assuming that solvated lithium will have about the same "size" as a rubidium cation: 54.6 − 36.5 = 18.1 ppm, 453 Hz. The variable temperature $\alpha$-carbon chemical shifts for benzyl anions are presented in Table V. For benzyllithium in THF and DME, only very small downfield chemical shift changes are observed at low temperatures. Therefore, it may be concluded that very little solvation occurs for benzyllithium or the other benzyl alkali metal anions. For this small carbanion system, the energy of cation separation is comparable to the energy gain upon solvation and solvation is much less thermodynamically favorable.

**Table V.** α-Carbon Chemical Shifts for Benzyl Carbanions[a]

| solvent $t$, °C | THF $Li^+$ $\delta$ | DME $Li^+$ $\delta$ | 25 °C | THF $\delta$ |
|---|---|---|---|---|
| 25 | 915 | 906 | $Na^+$ | 976 |
| 0 | 921 | b | $K^+$ | 1319 |
| −25 | 927 | b | $Rb^+$ | 1366 |
| −50 | 936 | 982 | | |
| $\Delta\delta_0$ | 21 | 76 | | |

[a] Chemical shifts in hertz downfield from $Me_4Si$ at 25.0335 MHz. [b] Not determined.

## Experimental Section

**Materials.** Solvents were refluxed over potassium metal for 24 h, distilled under argon, and then maintained at reflux over sodium–potassium alloy in a solvent still. Lithium sand was available as a 20% dispersion in mineral oil. Sodium and potassium sand were prepared under mineral oil after the removal of the surface oxide coat by heating above the melting points and vigorous shaking as the sample cooled. Mineral oil was removed by several washings with dry solvent. Rubidium and cesium metal were stored in sealed ampules and the ampules broken in the carbanion sample tubes under dry cyclohexane. Hydrocarbon precursors were dried with sodium sand prior to use. Dibenzylmercury was prepared by the reaction of benzylmagnesium chloride with mercuric chloride and recrystallized from ethanol, and he last traces of ethanol were removed under vacuum.

**Bis(trimethylsilylmethyl)mercury ($[Me_3SiCH_2]_2Hg$).** A mixture of bromomethyldimethylchlorosilane and chloromethyldimethylchlorosilane was prepared by the addition of bromine to an excess of trimethylchlorosilane while chlorine was bubbled through the solution and the reaction flask was irradiated with a sunlamp.[47] The reaction mixture was fractionated and the fraction between 95 and 134 °C (740 mm) collected to give a 49% yield based upon bromine. The mixed halosilanes were reacted with methylmagnesium bromide to give a mixture of halomethyltrimethylsilanes boiling between 95 and 120 °C, 80% yield [lit.[48] bp bromo, 115 °C (742 mm); bp chloro, 97 °C (734 mm)]. Bis(trimethylsilylmethyl)mercury was prepared by the addition of mercuric chloride dissolved in THF to the Grignard reagent of the mixed halomethyltrimethylsilanes.[49] Fractional distillation gave bis(trimethylsilylmethyl)mercury, 89% yield, bp 58–62 °C (2 mm) (lit.[50] bp 49–50 °C).

**Bis(benzyldimethylsilylmethyl)mercury ($[PhCH_2SiMe_2CH_2]_2Hg$).** Halomethyldimethylbenzylsilane was prepared by the reaction of benzylmagnesium chloride with the mixed halomethyldimethylchlorosilanes. The Grignard reagent of halomethyldimethylbenzylsilane was added to mercuric chloride to give bis(benzyldimethylsilylmethyl)mercury, 20% yield, mp 49–51 °C. $^1H$ NMR (integrated intensity): $-SiMe_2$, $\delta$ −0.02 (6); $(-CH_2)_2Hg$, −0.28 (2); $PhCH_2-$, 2.03 (2); aryl, 7.13 (5). $^{13}C$ NMR (multiplicity): $-SiMe_2$, $\delta$ 1.02 (4, $^3J_{C-Hg^{199}} = 46$ Hz); $(-CH_2)_2Hg$, 23.8 (3, $^1J_{C-Hg^{199}} = 580$ Hz); $PhCH_2$—, 28.6 (3); aromatic carbons, C-1, 140.7 (1); C-2, 127.7 (2); C-3, 128.1 (2); C-4, 123.7 (2).

**Carbanion Preparations.** Carbanion solutions were prepared in septum-capped, argon-flushed, 12-mL centrifuge tubes. All transfers of solvent and carbanion solutions were made with oven-dried glass syringes. The concentration of the carbanion solutions was varied between 0.2 and 0.7 M. Within this range, no significant chemical shift changes were noted for the same temperature for different concentrations of the same carbanion. Three methods were used to prepare the carbanions: metal reduction of hydrocarbon precursors; metal reduction of organomercurials; and metal reduction of bis(trimethylsilylmethyl)mercury followed by metalation of hydrocarbon precursors.

Direct metal reduction was used to prepare $F^-Li^+$, $F^-Na^+$, and $F^-K^+$. The centrifuge tube containing alkali metal sand (~12 mg-atoms), solvent (8 mL), and fluorene (1–5 mmol) was placed in an ice bath in an ultrasonic bath for approximately 1 h. The ultrasonic bath was particularly valuable in initiating these heterogeneous reductions. Good spectra were not obtained for $F^-Rb^+$ and $F^-Cs^+$ by metal reduction of fluorene, probably owing to the formation of paramagnetic species due to further reduction.

All the alkali metal carbanions of triphenylmethane and diphenylmethane and the rubidium and cesium salts of fluorene were prepared by the metalation of the hydrocarbon precursors with trimethylsilylmethylmetal compounds directly in MeTHF, THF, or DME. Bis(trimethylsilylmethyl)mercury (0.5–2.5 mmol) was syringed into the centrifuge tube containing alkali metal sand (~12 mg-atoms), solvent (8 mL), and hydrocarbon precursor (1-5 mmol). Reduction of the organomercurial was initiated at 0°C in an ultrasonic bath and the carbanions were completely formed in approximately 0.5 h. The potassium, rubidium, and cesium salts of benzyltrimethylsilane, benzylpotassium, and benzylrubidium were prepared in a similar manner except that the reduction of the organomercurial and the metalation of the precursor were carried out heterogeneously in cyclohexane, cyclohexane was removed, and ethereal solvent was added slowly at −78 °C.

The lithium and sodium salts of benzyltrimethylsilane were prepared by metal sand reduction of bis(benzyldimethylsilylmethyl)mercury at 0 °C. In MeTHF, the initially formed benzyldimethylsilylmethyllithium ($PhCH_2SiMe_2CH_2^-Li^+$) could be observed in the carbon-13 spectrum and it was necessary to heat the sample to 50 °C for 1 h to complete the rearrangement to α-trimethylsilylbenzyllithium ($PhCH^-SiMe^3$, $Li^+$). In THF and DME, this rearrangement was rapid and only the α-trimethylsilylbenzyl anion was observed spectroscopically. Benzyllithium and benzylsodium were prepared by the metals and reduction of dibenzylmercury at −30 °C.

**Carbon-13 Measurements.** All carbon-13 spectra were obtained with a JEOL PFT-100/Nicolet 1080 Fourier transform spectrometer with an internal $D_2O$ capillary for locking. At the same temperature, chemical shifts were reproducible to about ±4 Hz. Approximately 1000–3000 average transients were required to obtain satisfactory signal to noise ratios for proton-decoupled spectra. Chemical shifts were referenced to tetramethylsilane and to cyclohexane (689.1 Hz at 25.0335 MHz from $Me_4Si$). It is important not to use solvent resonances as references, particularly the carbon attached directly to the solvent's oxygen. These resonances varied by as much as ±20 Hz and depended upon carbanion, cation, and temperature. Temperature of the carbanion sample was controlled to ±1 °C and was measured before and after each spectral measurement.

**Error Estimates in the Calculation of Thermodynamic Values.** Calculations of thermodynamic values and equilibrium constants were performed for lithium and sodium salts that covered at least 40% of the change from one solvation state to the other and where one of the chemical shift limits was reached at high or low temperature. Calculations were not carried out for the larger alkali metal salts because only very small chemical shift changes were observed (e.g., $DPM^-K^+$, THF, $\Delta\delta = 13$ Hz, $\Delta T = 65$ °C; $DPM^-K^+$, DME, 24 Hz, 80 °C; $T^-K^+$, DME, 17 Hz, 74 °C) and the precision of such calculations is likely to be poor because the range covered if solvation occurs would be small.

The largest contributing factor to the error estimates comes from the estimates of the inaccessible chemical shift limits. The contact ion chemical shift limits were estimated from least-squares plots of the contact limits of the larger alkali metal salts vs. $1/(M + 2.1$ Å) (Figure 3). The errors presented in Table IV for salts with estimated $\delta_c$'s were obtained by varying $\delta_c$ by ±20 Hz ($T^-Li^+$, MeTHF, 2076 ± 20; $F^-Li^+$, MeTHF, 1914 ± 20; $F^-Li^+$, THF, 1946 ± 20; $DPM^-Li^+$, MeTHF, 1682 ± 20; $DPM^-Li^+$, DME, 1794 ± 20; $DPM^-Na^+$, DME 1897 ± 20). Solvent-separated chemical shift limits are less subject to error because they are cation independent. Therefore, for carbanions that required estimated $\delta_s$'s, errors were obtained by varying the estimated limit by ±10 Hz ($T^-Na^+$, THF, 2258 ± 10; $F^-Na^+$, THF, 2086 ± 10; $DPM^-Na^+$, THF, 2049 ± 10). For $TMSB^-$, the $\delta_s$'s were crudely estimated because no solvent-separated limits were accessible. Therefore, error estimates were obtained by varying the estimated limits by ±40 Hz ($TMSB^-Li^+$, DME, 1452 ± 40; $TMSB^-Na^+$, DME, 1452 ± 40). It should be noted that, even though the solvent-separated limits for $TMSB^-$ are crude, the errors are comparable to those for the other carbanions because the error caused by estimating the solvent-separated limit is largely compensated for by the very large change covered by $TMSB^-$ upon solvation.

**Acknowledgment.** Support of this work by the Robert A. Welch Foundation (Grant A331) is gratefully acknowledged. The authors wish to thank the National Science Foundation (GP-32912) for providing funds for the JEOL PFT-100 and Professors Alan Rodgers and Robert Stipanovic for helpful discussions. We would also like to thank Professor Ulf Edlund, Department of Organic Chemistry, University of Umea, for his critical review of this manuscript and for sharing the results of his work on solvation of fluorenyl and indenyl carbanions prior to publication.[51]

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(45) Since the chemical shift changes are much smaller, this warning is likely to be even more important for the use of $^1H$ NMR in solvation studies (ref 17 and 19).

(46) From the carbon-13 spectra of nine different benzyl anions compared to the carbon-13 spectra of benzyl anions with a trimethylsilyl group attached to the electron-rich $\alpha$ carbon, we find that the $\pi$ systems in the trimethylsilyl-substituted carbanions are deshielded by $20.8 \pm 0.8$ ppm. Since a trimethylsilyl deshields carbon by about 6 ppm when it replaces hydrogen, approximately 15 ppm reflects silicon's ability to delocalize electron density through $d\pi$–$p\pi$ bonding. Silicon-29 shifts are shielded by 16–26 ppm in the silyl anions compared to their precursor's.

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