nitrogen and silicon which are unlikely when M = C. These interactions should (a) reduce (p–p)π overlap between carbon and nitrogen in structure 3 and thereby increase the energy of the ground state and (b) lower the energy of the transition state (where the (p–d)π overlap should be greater). The combination of these consequences should result in a lower activation energy for *N*-trimethylsilylformamide.

The average values of $\Delta G^{\ddagger}$ for IV and V are 2–3 kcal lower than recent values for dimethylformamide (21.0 kcal/mol)[16] and dimethylacetamide (18.1 kcal/mol),[17] respectively. Substitution of a trimethylsilyl group for a methyl group produces, therefore, a decrease of 2–3 kcal in the free energy of activation. This decrease is probably attributable to (a) the greater size of the trimethylsilyl group relative to a methyl group which would result in destabilization of the ground state and a consequent lowering of the rotational barrier[14,18] and (b) (p–d)π interactions as discussed above.

If the structure of compound VI is that given by representation 1, the rotational barrier would be expected to be somewhat lower than the barrier in V because of the steric and electronic effects wrought by substitution of the *N*-methyl group in V by the trimethylsilyl group. The magnitude of the decrease would almost certainly not be as large as the difference between dimethylformamide and V, however, due to competitive (p–d)π interactions between the nitrogen and both silicons of VI. Thus, the barrier in VI could be predicted as, say, 1–3 kcal/mol lower than that of V. The barrier in VI as judged by $\Delta G^{\ddagger}$ is, in fact, the same as that of V, and consequently no assignment of structure is possible. Only if the experimental barrier were grossly different from the predicted barrier, could even a tentative assignment be made. Clearly, further work on the structure of the bis derivative is necessary.

Acknowledgments. The authors are indebted to the Du Pont Co. and the Camille and Henry Dreyfus Foundation for partial support of this work.

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Acidity of Hydrocarbons. XLII. Effect of Temperature on the Absorption Spectra of Some Lithium and Cesium Salts of Carbanions in Amine Solvents[1]

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Abstract: Fluorenylcesium, indenylcesium, and triphenylmethylcesium in cyclohexylamine (CHA) or in CHA–diethylamine show little effect of temperature on the visible absorption spectra, indicating that these compounds exist primarily as contact ion pairs in these solutions. The spectra of fluorenyllithium and indenyllithium in CHA–Et_2NH are temperature dependent and indicate an equilibrium between contact and solvent-separated ion pairs; these compounds are 95 and 65%, respectively, solvent-separated ion pairs at room temperature. Triphenylmethyllithium has a strongly temperature-dependent spectrum in CHA; deeply colored solutions at room temperature are colorless above 100°. The results are interpreted in terms of an equilibrium between solvent-separated ion pairs and the hydrocarbon; that is, the relative acidity of the hydrocarbon depends on the specific anion or ion-pair nature of its conjugate base. A simple electrostatic treatment is shown to account satisfactorily for the difference between contact ion pair acidity and solvent-separated ion pair acidity for several hydrocarbons with planar anions.

The dual concept of contact and solvent-separated ion pairs in organic chemistry[2] was first extended to carbanion systems by Hogen-Esch and Smid[3] with their important analysis of spectra as a function of temperature. We report the application of their analysis to the effect of temperature on the absorption spectra of some lithium and cesium salts of carbanions in solvents containing cyclohexylamine (CHA). The present study has especial significance because of the large and growing number of quantitative relative acidities determined by our research group for lithium and cesium salts of hydrocarbons in the cyclohexylamine solvent.[4]

The effect of temperature on the absorption spectrum of fluorenyllithium in cyclohexylamine–diethylamine (2:1 molar ratio) is shown in Table I. The use of the mixed solvent allowed measurements at lower temperatures than with CHA alone. The positions of the absorption maxima at 452, 480, and 512 nm and the peak ratio at low temperature resemble closely those

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(1) This research was supported in part by Grant No. GM-12855 of the National Institutes of Health, U. S. Public Health Service, and by a National Institutes of Health Predoctoral Fellowship to J. R. M., 1969–1972.

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Table I. Absorption Spectrum of Fluorenyllithium[a]

Temp, °C	$A_{max}^{452\ nm}$	$A_{max}^{480\ nm}$	$A_{max}^{512\ nm}$	K
−42	0.73	0.95	0.69	
−33	0.69	0.90	0.64	
24	0.66	0.79	0.52	
60	0.62	0.67	0.38	4.50
76	0.62	0.62	0.32	2.28
88	0.62	0.60	0.29	1.65

[a] Solvent is 73% cyclohexylamine–27% diethylamine by weight

reported for the solvent-separated ion pair of fluorenylsodium.[3] The effect of lowering the temperature from 88 to −42° was to increase the absorbance by 138, 58, and 18% at 512, 480, and 452 nm, respectively. A 13% change is associated with the variation of solvent density with temperature[5] which affects the concentration of fluorenyllithium. The total change of 18% at 452 nm is close to that expected from the concentration change alone, but the other absorbance peaks show an additional strong change. Previous conductivity measurements[6] establish an ion pair–free ion dissociation constant of 10^{-10} mol/l. for fluorenyllithium in cyclohexylamine; hence, free ions cannot contribute significantly to these spectral changes. Following Hogen-Esch and Smid, the large changes in absorbance appear to be best interpreted in terms of equilibria involving solvent-separated and contact ion pairs. The increase in absorbance at 512 and 480 nm as the temperature decreases is interpreted as a shift of equilibrium (eq 1)

$$\underset{\text{contact}}{R^-, Li^+} \overset{K}{\rightleftharpoons} \underset{\text{solvent-separated}}{R^-||Li^+} \qquad (1)$$

to the right; that is, the contact ion pair is increasingly converted to the corresponding solvent-separated ion pair. The equilibrium constant in eq 1 can be calculated from the spectral data with the following assumptions. (a) The solvent-separated ion pair has λ_{max}^{nm} at 452, 480, and 512. (b) The absorption maxima of the contact ion pair, which are expected to be at shorter wavelengths,[3] must coincide at 452 and 480 nm with the third peak apparently near 425 nm and manifest only as a broadening of the low wavelength peak. This accidental coincidence accounts for the invariance of the position of λ_{max} with temperature. (c) The extinction coefficients for the contact and solvent-separated ion pairs are assumed to be equal and proportional to solvent density. Treatment of the data with the above assumptions gives K as a function of temperature (Table I), and yields the least-squares values $\Delta H = -8.5$ kcal/mol, $\Delta S = -22.7$ eu. K at room temperature corresponds to 95% solvent-separated ion pair and only 5% contact ion pair. Compared to the corresponding results of Hogen-Esch and Smid,[3] the amine solvent is comparable to THF in solvating Li^+ and is better than dioxane. Note that these results fully confirm the interpretation given by Hogen-Esch and Smid[3] of our early spectra of carbanion salts in CHA.[7]

Indenyllithium has a spectrum with a single absorption maximum which appears at different wavelength as the temperature is varied; for example, λ_{max} is 370 nm at −12° and 355 nm at 75°. Furthermore, this absorption band is broad at 37.8° but is sharper at higher and lower temperatures. These effects indicate that two types of ion pairs coexist in equilibrium, but their spectral bands are too broad and too close to produce distinct absorption peaks; instead, there results a gradual shift of absorption maximum and broadening or sharpening of the band as the temperature is varied. Table II shows these spectral results and the calculated equilibrium constants from some appropriate assumptions corresponding to those made above. The least-squares plot (Figure 1) gives $\Delta H = -8.0$ kcal/mol and $\Delta S = -25.6$ eu. The K at room temperature corresponds to 65% of solvent-separated and 35% of contact ion pairs. Compared to fluorenyl anion, these results demonstrate that indenyl anion has a more concentrated negative charge and therefore forms a relatively more stable contact ion pair.

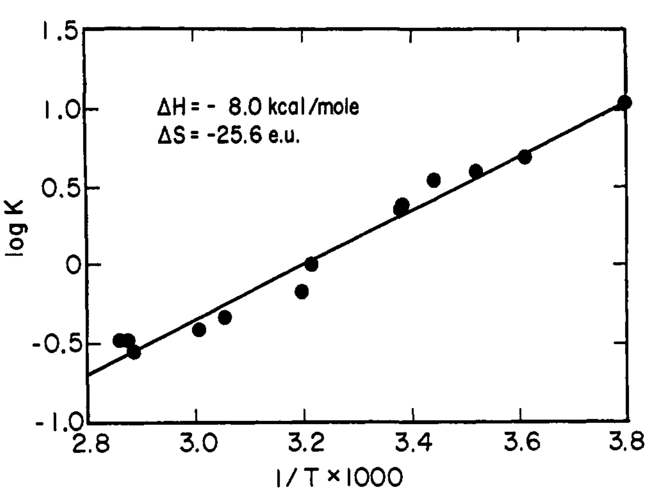

Figure 1. Equilibrium constants for ions pairs, K = [solvent-separated]/[contact], for indenyllithium as a function of temperature; slope, 1.748; intercept, −5.591; correlation coefficient, 0.988; standard deviation, 0.087.

Table II. Absorption Spectrum of Indenyllithium in Cyclohexylamine–Diethylamine[a]

Temp, °C	$A^{340\ nm}$	$A^{370\ nm}$	$A^{400\ nm}$	K
−12.0	0.89	1.31	0.68	
−11.0	0.89	1.32	0.71	
−9.8	0.99	1.29	0.64	11.0
3.7	1.02	1.24	0.585	4.94
10.8	1.035	1.225	0.565	3.98
17.3	1.08	1.18	0.555	3.47
22.6	1.07	1.19	0.505	2.28
22.8	1.09	1.22	0.515	2.12
37.8	1.175	1.01	0.35	1.00
39.4	1.22	1.02	0.30	0.67
54.3	1.275	1.005	0.245	0.46
59.5	1.28	0.955	0.21	0.38
73.5	1.285	0.885	0.16	0.28
74.8	1.28	0.895	0.18	0.33
76.6	1.265	0.900	0.18	0.33

[a] 76% cyclohexylamine–24% diethylamine by weight.

Similar studies with fluorenylcesium in 68% CHA–32% diethylamine, λ_{max}^{nm} 447, 472, and 504, and indenylcesium in 80% CHA–20% diethylamine, λ_{max}^{nm} 470,

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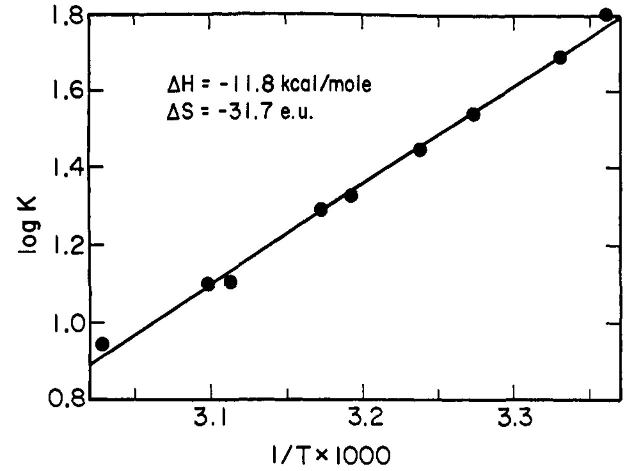

Figure 2. Equilibrium constants, K' = [ion pair]/[hydrocarbon]·[LiCHA], for triphenylmethane as a function of temperature; slope, 2.587; intercept, −6.938; correlation coefficient, 0.998; standard deviation, 0.020.

showed only small changes with temperature attributable primarily to the change in solvent volume. The general form of the spectra does not change but absorbance maxima sharpen at lower temperature; however, the absorbance ratios remain essentially constant throughout the temperature range studied. The observed temperature changes are consistent with a change in vibrational structure of band envelopes with temperature. The interpretation of these results as salts existing almost entirely as contact ion pairs is consistent with the larger ionic radius and smaller solvation demands of cesium cation.

When a mixture of triphenylmethane and lithium cyclohexylamide (LiCHA) in cyclohexylamine in a sealed cell was heated above 100°, the originally red solution became colorless. When cooled again to room temperature, the color was regenerated with no change in the visible spectrum. The cycle could be reproduced repeatedly. It is known that triphenylmethane is not completely converted to its anion with equivalent amounts of LiCHA.[4b,7] The observed thermochromism is interpreted on the basis of the following equilibrium:

$$\mathrm{Ph_3CH} + \underset{\substack{\downarrow\uparrow\\ (\mathrm{LiCHA})_n}}{\mathrm{LiCHA}} \xrightleftharpoons{K'} \mathrm{Ph_3CLi} + \mathrm{CHA} \qquad (2)$$

where n denotes the aggregation number of LiCHA in CHA.[8] If we assume that the ion pair, whatever its nature, has an extinction coefficient equal to that of triphenylmethylcesium, K' is calculated as a function of temperature as shown in Table III. A plot of log K' *vs.* $1/T$ gives an excellent straight line (Figure 2) whose slope and intercept give $\Delta H = -11.8$ kcal/mol, $\Delta S = -31.7$ eu. The constant ΔH (straight line) and the absence of a shift in the position of the absorption maximum throughout the temperature range studied are compatible with the explanation that only one type of ion pair is important for triphenylmethyllithium in CHA. Since monomeric LiCHA is undoubtedly a contact rather than solvent-separated ion pair, the high negative entropy change found for equilibrium 2 demonstrates conclusively that the triphenylmethyllithium involved is a solvent-separated ion pair; that is, the relative stability of triphenylmethyllithium contact ion pair is such that it never appears in the equilibrium. Moreover, the bathochromic shift in the spectrum of triphenylmethyl anion in changing the cation from the larger Cs^+ to the smaller Li^+ is also consistent with the concomitant change from a contact to a solvent-separated ion pair.[3] These results appear to be rather strange when one considers that both fluorenyllithium and indenyllithium have significant amounts of contact ion pair in CHA at room temperature, and that the decreased charge delocalization in triphenylmethyl anion should *inhibit* the separation of the ion pair. However, the twisted rings in triphenylmethyl anion may produce a steric interaction between the tertiary carbanion and the cation that facilitates the separation of the ions and overcomes the charge localization factor. A similar phenomenon has also been observed for 9-*tert*-butylfluorenyllithium which exists entirely as the solvent-separated ion pair over a wide range of temperature.[9]

Table III. Absorption Spectrum of Triphenylmethyllithium in Cyclohexylamine

Temp, °C	$A_{\max}^{492\text{ nm}}$	K' [a]
23.8	1.567	63.0
26.2	1.234	49.1
30.2	0.956	37.8
31.8	0.870	34.5
35.2	0.700	27.9
39.4	0.530	21.0
41.4	0.485	19.28
47.4	0.325	12.70
49.0	0.315	12.52
56.4	0.218	8.75

[a] K' = $[\mathrm{Ph_3CLi}][\mathrm{CHA}]/[\mathrm{Ph_3CH}][\mathrm{LiCHA}]$ with concentrations at the temperature indicated. Monomeric [LiCHA] was calculated from model 2 of ref 8a.

Triphenylmethylcesium behaves much the same as fluorenylcesium and indenylcesium as a function of temperature; this compound also is clearly a contact ion pair.

The above studies of the effect of temperature on lithium and cesium salts of hydrocarbons in CHA confirm our earlier expectations that the lithium salts of delocalized carbanions are largely solvent-separated ion pairs, whereas the cesium salts are contact ion pairs, and give credence to the interpretation of some small differences in relative ion pair acidities in terms of simple electrostatic effects.[4b] The cesium cation in a solvent-separated ion pair is closer to the carbanion than is the lithium in a solvent-separated ion pair; Thus, the cesium is more stabilized by a concentrated anionic charge. The direction of the equilibrium is

$$\mathrm{R^-}\|\mathrm{Li^+} + \text{9-PhFl}^-\mathrm{Cs^+} \xrightleftharpoons{K_{\mathrm{eq}}} \mathrm{R^-Cs^+} + \text{9-PhFl}^-\|\mathrm{Li^+} \qquad (3)$$

apparent from qualitative evaluations of anionic charge distribution[4b] and we now inquire as to the quantitative dependence on simple electrostatic interactions. For

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several carbanions expected to be planar, the charge distribution was calculated using a standard Pariser–Parr–Pople SCF-π method[10] for planar structures with C–C bond distances of 1.40 Å and bond angles of 120 or 108°. The resulting distributions were treated as a collection of point charges not perturbed by the cation. Coulomb's law was used to calculate the electrostatic energy, U, where

$$U = q^+ \sum_{i=1}^{n} q^-_i / r_i$$

and q^+ is a unit positive charge, q^-_i is the ith negative charge and r_i is the distance between q^+ and q^-_i. U was minimized with respect to the coordinates of the cation, subject to the constraint that the distance, d, between the cation and the plane of the anion was constant. An iterative technique was used to locate the coordinates of the cation at the energy minimum and to find the corresponding electrostatic energy. In each of the cases studied, only one minimum was found. The distance, d, was varied between 3.1 and 4.1 Å, but the location of the cation was not very sensitive to the value of d. The total electrostatic energy was, of course, highly sensitive to d, but in an entirely proportional manner; that is, the final correlation was essentially independent of d. Figure 3 shows a comparison of these calculated electrostatic energies for d = 3.1 Å, with the $-\log K_{\mathrm{eq}}$ values for equilibrium 3 as determined from relative pK values

$$-\log K_{\mathrm{eq}} = (\mathrm{p}K_{\mathrm{RH}} - \mathrm{p}K_{9\text{-PhFl}})_{\mathrm{CsCHA}} - (\mathrm{p}K_{\mathrm{RH}} - \mathrm{p}K_{9\text{-PhFl}})_{\mathrm{LiCHA}} \quad (4)$$

These pK values were reported previously.[4b] A small correction (ΔpK = 0.19) was made in the indene point since the lithium salt has now been found (*vide supra*) to be partially contact ion pairs. Thus, the p$K_{(\mathrm{LiCHA})}$ values used in Figure 3 correspond completely to solvent-separated ion pairs.

An excellent linear correlation results. The electrostatic interaction is greatest for the indenyl ion pair, and it has the highest relative acidity toward CsCHA and the contact ion pair. It is noteworthy that the lithium salt of this carbanion is not completely solvent-separated. Conversely, benzanthrenyl anion shows the smallest electrostatic interaction in an ion pair, and it has the highest relative acidity toward LiCHA and the solvent-separated ion pair.

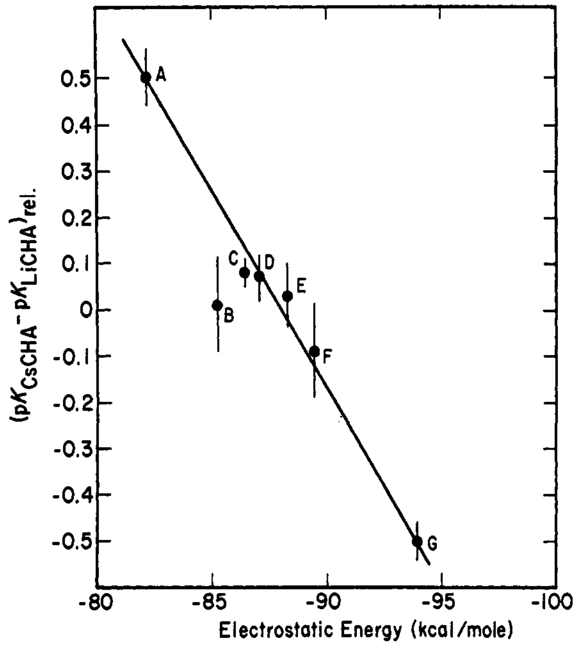

Figure 3. Plot of p$K_{(\mathrm{CsCHA})}$ − p$K_{(\mathrm{LiCHA})}$ from ref 4b for several hydrocarbons *vs.* the calculated ion pair electrostatic energies. Points are A, benzanthrene; B, 2,3-benzofluorene; C, 1,2-benzfluorene; D, 3,4-benzfluorene; E, 4,5-methylenephenanthrene; F, fluorene; G, indene.

Experimental Section

The apparatus and procedures used in the present study were essentially those described in our related studies of spectra and equilibrium acidities of carbanions in cyclohexylamine,[4b,11] except that the apparatus contained a single long-necked Pyrex absorption cell (path length *ca.* 1 mm) so that the cell could be sealed and removed from the vacuum transfer apparatus. The cell was placed in a specially constructed cell holder[12] in a Cary 74 spectrometer. The temperature of the cell was varied by circulating water from a Brinkmann thermostatically controlled bath and the cell temperature was measured by a thermocouple.

Cyclohexylamine, LiCHA, and CsCHA have been discussed in previous papers of this series. Diethylamine was fractionated, bp 55–56°, and dried over its lithium salt before bulb-to-bulb distillation on the vacuum line.

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