# Solvent and Temperature Effects in the Electronic Spectrum of 1,1-Diphenyl-*n*-hexyllithium. Specific Solvent Complexes

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**Abstract:** The unusually large red shift which occurs on adding tetrahydrofuran to 1,1-diphenyl-*n*-hexyllithium in benzene or di-*n*-propyl ether solution is shown to involve the formation of specific complexes with THF. In benzene–THF two etherates are formed. The stoichiometry of the etherates is indicated to be RLi·2THF and RLi·4THF. The first etherate must have a high formation constant, whereas the formation constant of the second etherate is small. In 100% THF, RLi is entirely in the form of the second etherate. The net enthalpy change occurring on formation of the second etherate from the first is −4.6 kcal/mole, and the accompanying entropy change at 22° is −15.6 eu. In hydrocarbon solution excess *n*-$C_4H_9Li$ causes a red shift of the absorption of RLi, indicating cross association, whereas when small amounts of THF are present the spectral changes indicate there is competition between RLi and *n*-$C_4H_9Li$ for the available THF, with the former having the larger solvent affinity. The gross solvent-induced spectral shifts are explained on the basis of the incipient lithium cation acting as a Lewis acid of variable strength depending on its extent of solvation.

The position of the absorption maximum of 1,1-diphenyl-*n*-hexyllithium (hereafter referred to as RLi) was shown to be unusually sensitive to solvent.[1] A change in solvent having a dielectric constant ($\epsilon$) of 7.5 (tetrahydrofuran) to one having $\epsilon$ 1.9 (*n*-hexane) was shown to cause an 86-m$\mu$ shift in the absorption maximum to shorter wavelength. Solvent-induced perturbations of electronic spectra may result from either general solvation phenomena or specific solvation. These two behaviors can be distinguished by observing the effects of a continuous change of solvent mixtures on the spectrum.[2]

It is shown here that the red shift of the absorption maximum caused by the addition of polar ether solvents to RLi in hydrocarbon solution results from the formation of specific etherates with the more polar solvent. An explanation for the gross solvent-induced spectral shifts is given in terms of Lewis acid–Lewis base interaction in which the incipient lithium cation behaves as a Lewis acid[3] of variable strength depending on its extent of solvation. Superimposed on this effect will be the smaller classical solvent effects resulting from solvent polarizability and dipole orientation. Detailed examination of the absorption of RLi in hydrocarbon solution (hexane and benzene) indicates the existence of two distinct species having different absorption maxima.

Solvent sensitivity of the electronic spectrum, analogous to that of the diphenyl and triphenylmethyllithium compounds,[1] has been reported recently for some other organoalkali metal compounds having extensive charge delocalization. Strong red shifts of the absorption maximum with increasingly polar solvents are reported for 9-fluorenyllithium and substituted fluorenyllithiums.[4] Less pronounced shifts are reported to occur with the living anionic polymers of polyisoprenyl, and polybutadienyl, lithium and sodium.[5] The absorption of the radical anion, sodium benzophenone ketyl, also shifts to the red in increasingly polar media.[6,7] A property that these species all have in common is the ability to stabilize the incipient negative charge *via* delocalization over an extensive $\pi$-electron system. Thus, the detailed behavior found for 1,1-diphenyl-*n*-hexyllithium may be representative of these other solvent-sensitive species.

Delocalization of the negative charge, in addition to decreasing the over-all energy of the incipient anion, results in dispersion of the negative charge, which reduces electrostatic attraction between the incipient anion and cation. It might be anticipated that because of electron delocalization in the anion, dispersion of positive charge density *via* cation solvation can have a more pronounced effect on the cation–anion interaction than in the absence of anion delocalization. This implies that the electronic spectra of organoalkali metal molecules not capable of extensive negative charge delocalization should be less sensitive to solvent as is found for benzylic[1] and allylic[5] moieties.

To obtain sufficient information to permit explanation of the unusual solvent sensitivity of the electronic spectrum of 1,1-diphenyl-*n*-hexyllithium, detailed spectral measurements of this species were made in hydrocarbon solutions, in dipolar ether solutions, and in solutions composed of a continuous mixture of these solvents.

## Experimental Section

1,1-Diphenyl-*n*-hexyllithium was prepared from stoichiometric amounts of 1,1-diphenylethylene and *n*-butyllithium in the desired solvent or solvent mixture. The procedure for obtaining electronic spectra of the oxygen and moisture-sensitive organolithium reagents in an argon atmosphere has been described previously.[8] The closed absorption cell[8] was thoroughly evacuated, put under ~6 cm of positive argon pressure, and reagents were added *via* gas-tight syringes.

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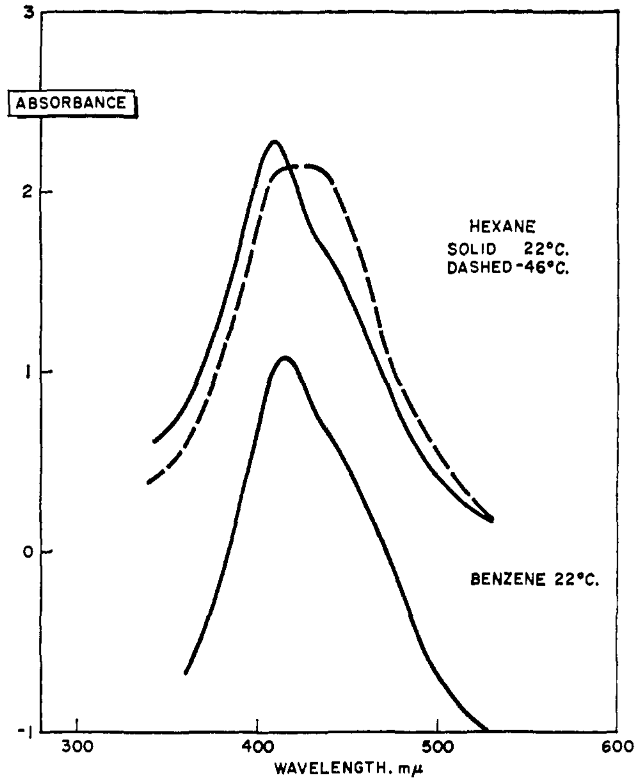

Figure 1. Spectra of 1,1-diphenyl-*n*-hexyllithium in hexane at 22° and −46°; in benzene at 22°.

The addition of *n*-butyllithium to 1,1-diphenylethylene in hydrocarbon solution is very slow[9] requiring several weeks for complete reaction. Thus, experiments in hydrocarbon solution were done in an evacuated sealed absorption apparatus consisting of a quartz cell and a small flask or graduated cylinder connected to opposite arms of a U tube and fitted with a break seal. Within detectable limits the reactions go to 100% conversion. When spectral readings showed no further change in absorbance, this absorption apparatus was attached to the vacuum line *via* the break seal and an adapter comprised of a vacuum stopcock and a port sealed with a rubber syringe cap. After thorough evacuation, the break seal was opened to admit a positive argon atmosphere. Incremental additions of THF (as a solution in hydrocarbon for the small amounts) were made and spectral readings were taken after each addition. An experiment was terminated by adding ethanol or water and the product 1,1-diphenyl-*n*-hexane determined by gas-liquid partition chromatography (glpc). This product constituted >95% of the recovered organic material. Small amounts of higher molecular weight compounds, presumably arising from the decomposition of RLi, were found in the long-term experiments. Similar evacuated absorption apparatuses were used for studies of effect of variable concentration by distilling solvent from one arm to the other, and of the effect of excess *n*-butyllithium on the spectrum of RLi.

Spectral measurements at temperatures other than room temperature (22°) were made using a variable temperature unit consisting of a two-compartmented box with quartz windows.[10] The inner compartment is split into four sections by two baffles and the cell. Temperature control is achieved by a flow of hot or cold nitrogen. The outer compartment remains at room temperature. A thermocouple placed adjacent to the cell just above the light path is connected to a Fenwal regulator which controls the gas flow necessary to maintain the set temperature. Calibration of the thermocouple was done using a Leeds and Northrup potentiometer. The spectra reported are all corrected for the change in volume which accompanies a change in temperature. This correction is ±0.1%/deg. change from room temperature for 100% THF. The spectra were taken on a Cary Model 14 recording spectrophotometer.

Measurements of the vapor composition[11] over benzene-RLi solutions, containing from $10^{-3}$ to $10^{-1}$ *M* THF (and a similar level of hexane as an internal standard), were made using glpc having a flame ionization detector. A 5-ml vapor sample in a gas-tight syringe was used. Good separation of hexane, THF, and benzene were obtained on a 4-ft column of diisodecyl phthalate on Chromosorb at 60°. Relative sensitivity of the instrument (F & M Model 609) to benzene, hexane, and THF was determined to be 1:1:0.5 using liquid samples of mixtures of known composition. The ratio of THF/hexane in the vapor for a given ratio of liquid was found to be independent of the absolute concentration when benzene was in excess. The solution of RLi was made up in a sealed evacuated flask having an attached quartz cell. When spectroscopic measurements showed that the reaction was complete, the flask was connected to the vacuum line *via* a break seal, opened to argon, and aliquots of THF were added, as in the previously described sealed spectroscopic cells. Spectra and vapor composition measurements were made after each addition of solvent.

## Results

To distinguish between a general solvent effect, which depends on the average solvation propensity, or specific solvation involving the formation of solute–solvent complexes, the relation between the position of the absorption maximum and solvent composition of a mixed solvent pair was determined.[2] A general solvation effect is characterized by a progressive shift of the absorption maximum in proportion to the average solvation ability of the mixture. Specific solvation is distinguished by pronounced spectral changes in the presence of only small amounts of the polar solvent. Incremental addition of polar ether to a benzene or hexane solution of RLi results in the absorption maximum shifting to longer wavelengths. There are also informative changes in shape and widths of the absorption curves. The spectral behavior of RLi in hydrocarbon solution is described first followed by the behavior with increasing amounts of THF.

In hydrocarbon solution, hexane ($\lambda_{max}$ 410 mμ) or benzene ($\lambda_{max}$ 415 mμ), the spectrum of RLi is comparatively broad and has a long wavelength shoulder (see Figure 1). In both these solvents decreasing temperatures cause an increase in the long wavelength absorption. At −46° in hexane solution (see Figure 1) the spectrum consists of two approximately equal maxima at 410 and 435 mμ. The breadth of the absorption band and the change with temperature indicates that in hydrocarbon solution the absorption is due to two distinct forms of RLi which are in equilibrium. Even more surprising is that a 100-fold dilution ($1.2 \times 10^{-2}$ *M* to $1.1 \times 10^{-4}$ *M*) caused no change in the shape or position of the absorption curves. Nor is there a change in the apparent molar absorptivity, *i.e.*, the solution conforms to the Beer–Lambert law. Thus, an explanation requires a concentration-independent, but temperature-dependent, equilibrium. Possible species involved in such an equilibrium are discussed later.

The addition of increments of THF to the hydrocarbon solution of RLi causes a most pronounced change in both the position of $\lambda_{max}$ and width of the absorption bands (see Figure 2). When slightly less than 2 equiv of THF relative to RLi is added, the absorption maximum shifts to 450 mμ; the spectrum is a symmetrical absorption envelope and of minimum half-width. This behavior indicates the absorption

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(9) A. G. Evans and D. B. George, *J. Chem. Soc.*, 141 (1962).

(10) We are grateful to Dr. E. A. Eastham, National Research Council of Canada, for showing us the low-temperature unit he was constructing when we visited in Jan 1963. This formed the basis for our unit.

(11) Similar measurements were reported as evidence for the stoichiometry of *n*-butyllithium–diethyl ether complex: Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 3517 (1963).

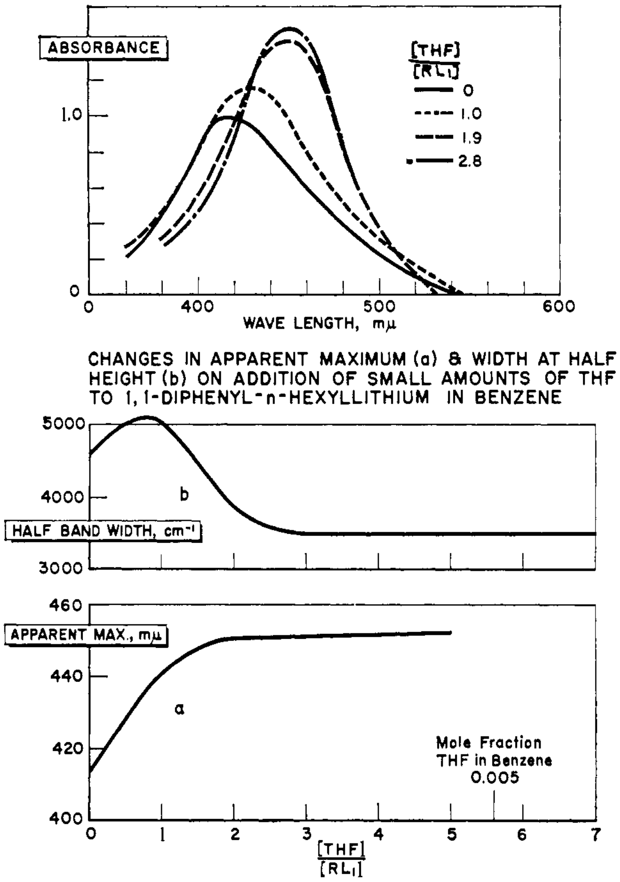

Figure 2. Effect on the spectrum of addition of small amounts of THF to 1,1-diphenyl-*n*-hexyllithium in benzene.

arises from a single species which is suggested to be either an RLi mono- or dietherate having a high formation constant. The evidence, for example the sharp break in Figure 2 when the ratio THF/RLi approaches 2, favors a dietherate. Vapor composition measurements also establish that a specific complex is formed. Figure 3 shows that the relative amount of THF in the vapor over a solution of RLi in benzene to which increments of THF are added increased sharply when the ratio THF/RLi = ~1.8–2.4 The break in the curve is consistent with a dietherate. The average increase in the amount of THF in the vapor after quenching the RLi in three sets of these experiments corresponds to a ratio of THF/RLi = ~1.9–2.2.

Another interesting behavior of RLi in the presence of small amounts of THF is observed with a decrease in temperature. RLi at $1 \times 10^{-2}$ *M* is soluble in *n*-hexane at −80°. When RLi at this concentration is in hexane solution containing 2 to 3 equiv of THF relative to RLi, the RLi etherate comes out of solution as a crystalline precipitate almost quantitatively at −80°. There is no detectable change in position and shape of the spectrum with decreasing temperature. Thus, RLi·2THF complex is indicated to be more polar than "unsolvated" RLi, causing the former to have a lowered solubility in the predominantly nonpolar solvent mixture. At the same RLi concentration and temperature, solutions containing a higher amount of THF are homogeneous. Analysis for THF and 1,1-diphenyl-*n*-hexane by glpc, after washing the crystalline precipitate with dry hexane and quenching, indicated a ratio THF/RLi = ~2. This is additional evidence that the initial RLi–THF complex is a dietherate.

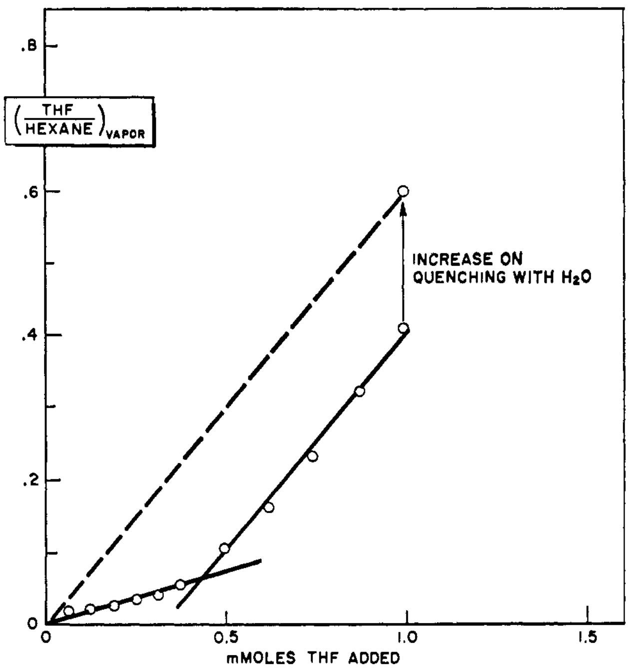

Figure 3. Observed ratio of THF/hexane in vapor *vs.* THF added to 10 ml of benzene–hexane solution containing 0.19 mmole of RLi and 0.44 mmole of hexane (internal standard). In the absence of RLi, (THF/hexane) vapor is linear over the range 0 to 5 mmoles THF added as indicated by the broken line.

Additional increments of THF cause a more gradual red shift of the absorption maximum which approaches the 496-mμ absorption maximum of RLi in 100% THF. The absorption curves in this latter region, *i.e.*, between 450 and 496 mμ, are much broader than those in the presence of small amounts of THF or in 100% THF (see Figure 4, curves A and B). It is shown in Figure 5 that following the abrupt change caused by small amounts of THF, increasing the amount of THF causes a gradual shift of the absorption maximum to longer wavelengths, and the widths of the absorption curves go through a maximum. This behavior indicates that the observed spectrum is a composite absorption resulting from an equilibrium mixture of two distinct species, which are those having absorption maxima at 450 and 496 mμ, and for which the equilibrium constant is small. Evidence that the absorption in this region arises from an equilibrium mixture of these two distinct etherates is obtained from temperature studies. An example is shown in Figure 6 for RLi in an equimolar mixture of THF and hexane. Decreasing temperature causes a shift of absorption to longer wavelength, which is reversible on warming.

The absorption curves shown in Figure 4 for various amounts of THF and Figure 6 at different temperatures were analyzed for the amount of the first etherate (A) and the higher etherate (B). This was done by simultaneous equations using effective absorption coefficients for A and B at 400 and 520 mμ. From a series of absorption curves like those illustrated in Figure 4 (for [RLi] = $1 \times 10^{-2}$), the ratio B/A *vs.* THF concentration is obtained. A plot of the ratio log [B/A] *vs.* log THF will be of slope *n* and of intercept *K* corresponding to the following equilibrium: (1) A +

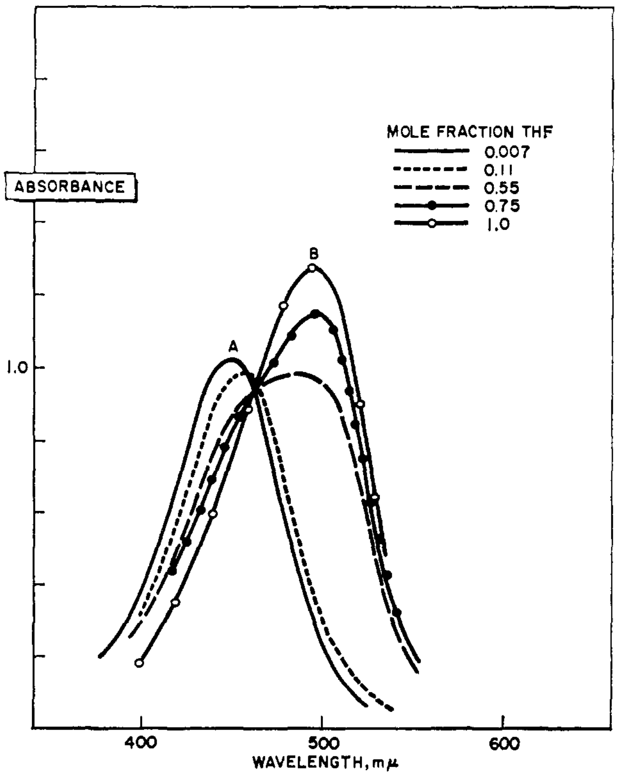

Figure 4. Spectra of 1,1-diphenyl-*n*-hexyllithium in benzene-THF mixtures.

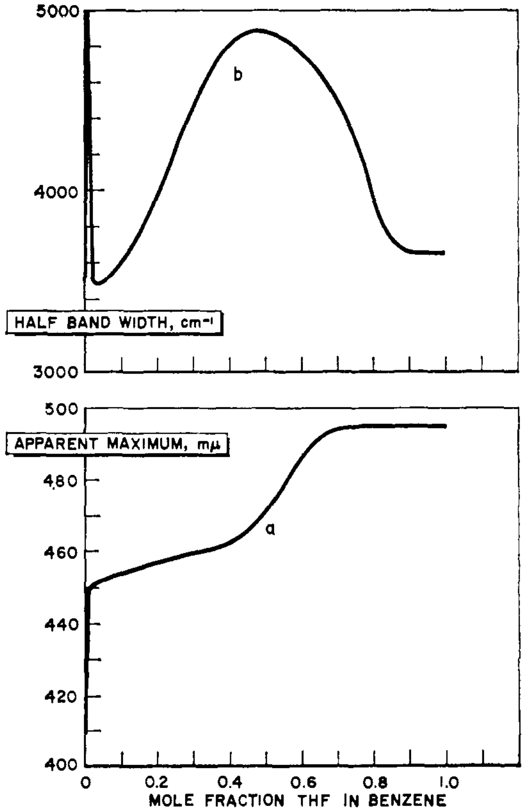

Figure 5. Apparent maxima (a) and widths at half-height (b) from spectra of 1,1-diphenyl-*n*-hexyllithium in the THF-benzene mixtures.

*n*THF $\rightleftharpoons$ B. This plot shown in Figure 7 indicates that *n* is 2 or possibly 3. In view of the usual tetracoordination of $Li^+$ $n = 2$ is probable. Species B is therefore considered to be RLi·4THF. Possibly there may be more than a single equilibrium involved, *i.e.*, conceivably other etherates could exist that have the same or similar absorption spectrum.

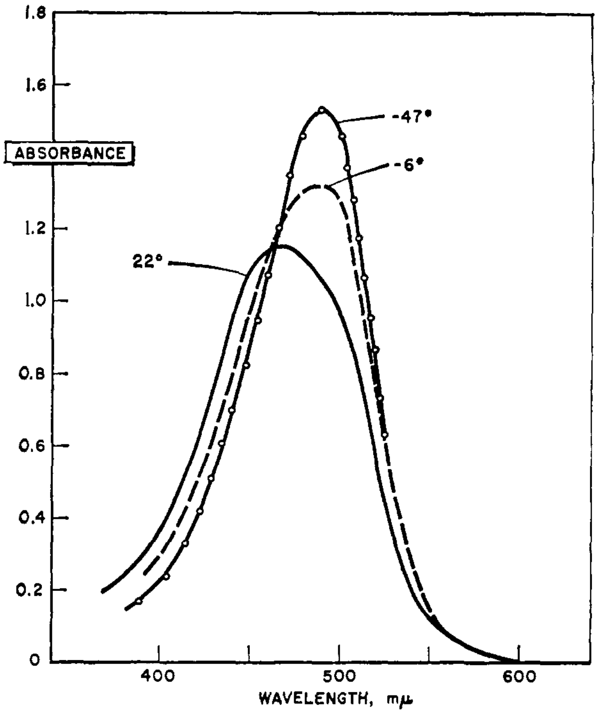

Figure 6. Temperature dependence of the spectrum of 1,1-diphenyl-*n*-hexyllithium in equimolar THF-hexane solution.

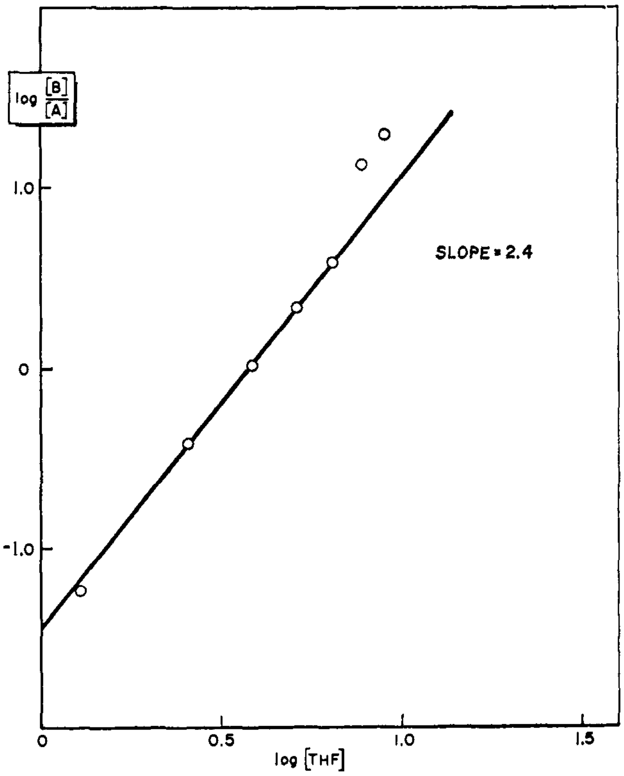

Figure 7. Dependence of the relative amounts of first and second etherates of 1,1-diphenyl-*n*-hexyllithium on THF concentration.

Similar analysis of the temperatures studies of the equilibrium between A and B is also informative. A plot log [B/A] *vs.* 1/*T* shown in Figure 8 is a straight

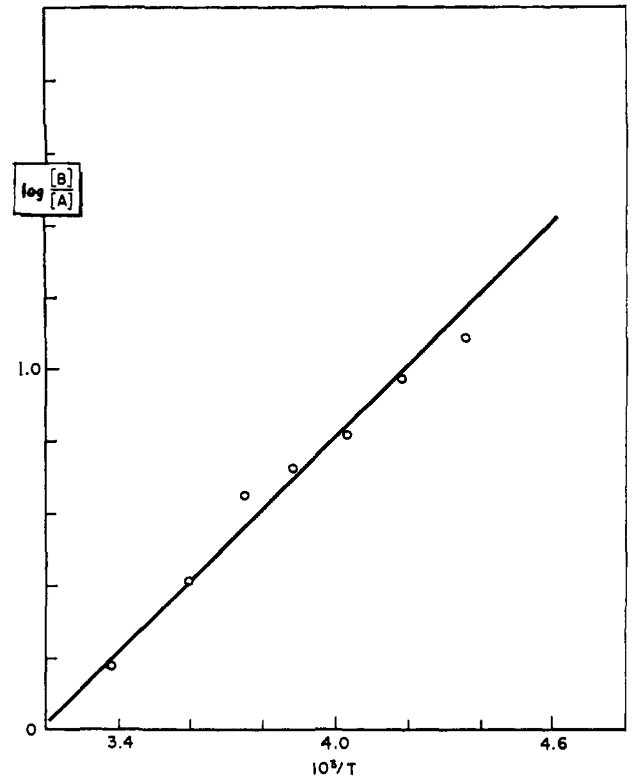

Figure 8. Temperature dependence of the spectrum of 1,1-diphenyl-*n*-hexyllithium in equimolar THF–hexane solution.

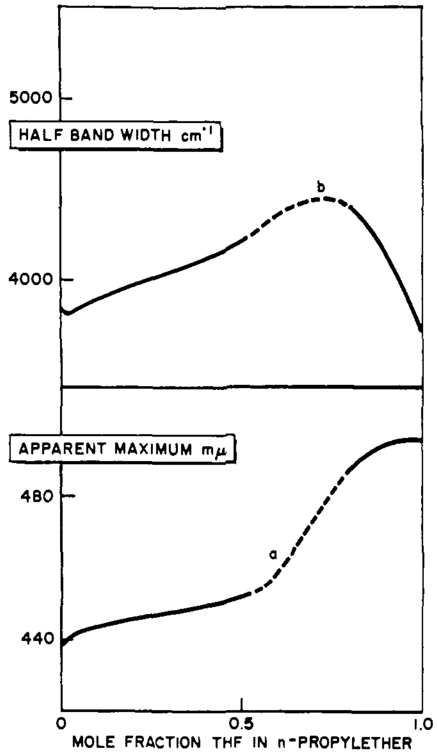

Figure 9. Apparent maxima (a) and widths at half-height (b) from spectra of 1,1-diphenyl-*n*-hexyllithium in the THF–*n*-propyl ether mixtures.

line of slope equivalent to an enthalpy change of −4.6 kcal and an entropy change at 22° of −15.6 eu. Log [B/A] is representative of log $K$ and the plot has the advantage that the slope is independent of the number of THF molecules involved in the equilibrium. The enthalpy change corresponds to a net heat of solvation of species A by THF. The loss of entropy on forming B from A is consistent with a higher organization of THF molecules around the lithium cation in the former species.

In 100% THF the spectrum of RLi is unsymmetrical, having a short wavelength shoulder. The unsymmetrical shape of the curve could be taken as an indication that even in 100% THF an amount of the first etherate is present. However, the spectrum is independent of concentration, and although the position of the equilibrium between A and B is temperature sensitive, the position of $\lambda_{max}$ in 100% THF does not change over the range 25 to −50°. Decreasing temperature causes an over-all narrowing of the spectrum, but the total area under the absorption curve when corrected for volume changes remains constant. These results establish that none of the first etherate is present, and is evidence that in 100% THF, RLi exists as a single species, presumably RLi·4THF.

The changes in the spectrum of RLi in dipropyl ether or dibutyl ether on addition of aliquots of THF are similar to those described for the hydrocarbon–THF solvent system (see Figure 9). The over-all changes, however, are much smaller because the absorption maximum in each of these ethers is nearer to that in THF. The shapes of the curves in Figure 9 are analogous to those of Figures 2 and 5 and indicate that there are two distinct THF complexes. The change caused by small amounts of THF is not as abrupt as it is when the second solvent is a hydrocarbon, indicating that these other ethers are more competitive with THF in solvation of the incipient lithium cation.

**Effect of Excess *n*-Butyllithium.** The addition of small amounts of *n*-butyllithium, *i.e.*, ratio of *n*-$C_4H_9$-Li/RLi < 10, to RLi in hydrocarbon solution results in no change in the spectrum, but when the ratio *n*-$C_4H_9$-Li/RLi > 20, the spectrum is changed to a symmetrical band centered at 428 mμ. *n*-Butyllithium is apparently associating with RLi with a consequent change in transition energy and formation of a single RLi species. Decreasing temperature causes no change in the spectrum of RLi in the presence of a large (200-fold) excess *n*-butyllithium. Excess *n*-butyllithium causes no change in the spectrum of RLi in 100% THF.

A most interesting effect of excess *n*-butyllithium occurs when only small amounts (*i.e.*, mole ratio THF/RLi ~2–10) of THF are present, so that RLi is in the form of the first etherate A, *i.e.*, $\lambda_{max}$ 450 mμ. Under these conditions addition of excess *n*-butyllithium causes the absorption maximum of RLi to shift to shorter wavelength. This is probably caused by the *n*-butyllithium participating in competitive solvation with RLi for the available THF. The distribution of THF will depend on the relative solvation propensities of the two organolithium species. A preliminary study has shown that when the molar amount of *n*-butyllithium is less than that of THF there is no effect on the spectrum of RLi. When *n*-butyllithium is ~2 times the quantity of THF, RLi $\lambda_{max}$ is at shorter wavelength, but still most of the RLi exists as etherate. This behavior indicates RLi has a higher solvation affinity than *n*-butyllithium. Because RLi is presumably more ionic than *n*-butyllithium, owing to electron delocalization, a higher solvation affinity would be expected. Also *n*-butyllithium is probably aggregated in this solution since it is aggregated 4–6-fold in benzene and there is evidence for its 3–4-fold association in 100% THF.[12]

**Solvent Basicity.** For a series of two hydrocarbon and four ether solvents the position of maximum absorption of RLi was shown to be approximately linearly related to solvent dielectric constant[1] ($\epsilon$). As previously indicated,[1] however, solvation ability should depend on over-all basicity of the solvent, which is a function of its dipolar nature (as measured by $\epsilon$) and its steric requirements. Thus, for sterically hindered ethers the relationship between solvation ability and $\epsilon$ would not be expected to hold. Ethers having steric interference to coordination of the basic oxygen with the lithium cation are not as good solvents for RLi as would be predicted from their dielectric constants. This is illustrated by the data in Table I. The position of RLi $\lambda_{max}$ in a given solvent would appear to be a good measure of the over-all solvation capabilities of a given solvent toward organolithium compounds. Experiments are planned to test this postulate quantitatively.

**Table I.** Effect of Solvent on the Position of Maximum Absorption in the Electronic Spectrum of 1,1-Diphenyl-*n*-hexyllithium[a]

| Compd | $\lambda_{max}$, m$\mu$ | $\epsilon$ (22°) | $\epsilon$ (effective)[c] |
|---|---|---|---|
| (A) Sterically Hindered Ethers | | | |
| 2,5-Dimethyltetrahydrofuran | 443 | 5.26[b] | 4.1 |
| 2-Methyltetrahydrofuran | 451 | 6.36[b] | 4.7 |
| Tetrahydropyran | 436 | 5.55[b] | 3.7 |
| (B) Amines | | | |
| *n*-Butylamine | 445 | 5.3[d] | |
| N,N-Dimethylaniline | 447 | 4.91[d] | |
| Pyridine | 484 | 12.3[d] | |
| Hexamethylphosphoramide | 485 | 30[e] | |
| (C) Ethers[a] | | | |
| *n*-Propyl ether | 436 | 3.4[d] | 3.7 |

[a] In addition to those reported previously in ref 1. [b] Measured at frequencies $10^3$ and $10^5$ cps and 23°. We are indebted to Paul Woodland of the Polymer Research Lab, Dow Chemical Co., for making these measurements. [c] $\epsilon$ (effective) is the dielectric constant which would correspond to the $\lambda_{max}$ in the absence of steric effects from correlation illustrated in ref 1. [d] A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, Washington, D. C., 1951. [e] J. E. Hofmann, A. Schriesheim, and D. D. Rosenfeld, *J. Am. Chem. Soc.*, **87**, 2523 (1965).

## Discussion

Solvent-induced shifts can arise either through a general solvation effect or *via* specific solvation. For the former behavior the effect of solvent mixtures would depend on the average solvating ability, whereas the latter behavior should depend on microscopic solvation in the vicinity of the solute. The experiments reported here show that in mixed solvents 1,1-diphenyl-*n*-hexyllithium forms specific solvent complexes with the more polar solvent. Starting with a benzene solution of RLi having $\lambda_{max}$ ~415 m$\mu$, the absorption shifts to 450 m$\mu$ with 2 equiv of THF. The abrupt change in spectrum with small amounts of THF indicates that this first etherate has a large formation constant and is probably a dietherate. Increasing the amount of THF in the solvent mixture produces spectra which are believed to be a composite of two species, the first etherate having absorption maximum at 450 and a higher etherate having $\lambda_{max}$ 495 m$\mu$. The equilibrium constant between the first and second etherates is small; from the intercept of Figure 7 it is estimated to be ~$5 \times 10^{-2}$ (l./mole)$^2$. The slope of Figure 7 indicates this higher etherate has two additional molecules of THF and so is probably a tetraetherate. The stoichiometry of the etherates is being investigated further. An isosbestic point required by this equilibrium is evident in Figure 4, although poorly defined. The inexactness of the isosbestic point could indicate more than one higher etherate is formed, but most likely is caused by the substantial change in the medium and to some extent is a consequence of experimental variations. Thus, in 100% THF, RLi is indicated to be primarily a tetraetherate. Small amounts of presumably more weakly bound etherates having the same absorption spectrum cannot be excluded. The temperature studies established that none of the dietherate is present in 100% THF.

Evidence for specific complexes between organolithium compounds and THF has been reported previously. The kinetics of the propagation reaction of styrene polymerization in benzene–THF mixtures were interpreted in terms of polystyryllithium forming a mono- and di-THF complex.[13] For the latter species the tendency to complex was reported to be small, in agreement with the findings for the higher etherate of RLi. Using a viscosity technique it was shown that THF forms a monosolvate with polyisopropyllithium.[14] Because a large excess of THF (~350-fold) was required for a predominance of the polymer chains to form the etherate the tendency to complex must be small. However, the high heat of solvation reported of 18 kcal/mole indicates a strong complex. The resonance-stabilized fluorenyllithium, which is structurally similar to RLi, has been shown by nmr to form an etherate containing three THF molecules.[15]

It is felt unlikely that RLi exists as free ions in THF solution. Addition of LiBr, $LiClO_4$, or $LiBPh_4$ does not affect the spectrum. In the similar system, fluorenyllithium, conductivity measurements establish that only a spectroscopically immeasurable fraction exists as free ions in THF.[16] In accordance with the negative temperature coefficient of the dielectric constant solvation becomes stronger when the temperature is lowered.[17] Accordingly solvation and ion-pair dissociation are favored by lowering the temperature.[16,18,19] The position of the absorption maximum of RLi in 100% THF solution does not change throughout the temperature range 30 to −50°. At the lowest temperature the dielectric constant of THF is increased ~50% from that of 20°.[20] The micro dielectric

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[18] K. H. J. Buschow, J. Dielman, and G. J. Hoijtink, *J. Chem. Phys.*, 42, 1993 (1965).

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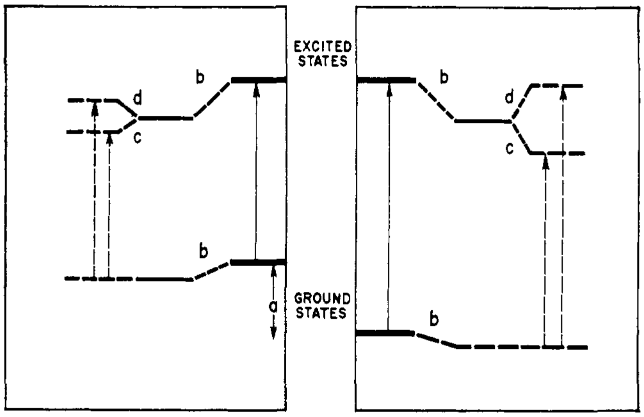
constant (*i.e.*, the effective $\epsilon$ of the solvation shell) would not be expected to show the same temperature dependence as that of the bulk solvent. If the ionic character of the carbon–lithium bond becomes greater with decreasing temperature a red shift in $\lambda_{max}$ should result.[18] Solvents of dielectric constant larger than that of THF, *e.g.*, pyridine, do not shift $\lambda_{max}$ to longer wavelength, in agreement with the effect of decreasing temperature and indicating that in such solvents RLi exists as solvated ion pairs,[16,21] which are bound together by electrostatic attractive forces.[19] Aromatic radical ions, *e.g.*, lithium anthracene or lithium biphenyl, are reported to be entirely in the form of free ions in THF at room temperature.[18] Apparently the energy to be gained by ionization, through enhanced electron delocalization in the free 1,1-diphenyl-*n*-hexyl anion and additional solvation of a free lithium cation, is not sufficient to overcome the resulting loss in electrostatic interaction and coordination energy in the ion pair.

Lithium ion has a vacant 2s and three vacant 2p orbitals. Coordinating ligands would be expected to promote hybridization of these orbitals. Thus, lithium in the dietherate is probably sp$^2$ hybridized, the hybrid orbitals being occupied by the coordinating anion and two THF molecules. One p orbital remains vacant. Lithium in the tetraetherate is probably sp$^3$, having each of the available oribitals occupied by THF molecules.

**Explanation of the Effect of Solvent on the Electronic Transition.** The significance of polarizability of the solvent or orientation of polar solvent molecules by the ground-state dipole of a polar solute to the observed dependence of the spectrum of RLi on solvent were considered in a previous discussion.[1] Although these classical mechanisms[22] for solvent-induced red shifts are no doubt operative to some extent, it is apparent that for the large shifts observed in a spectrum of RLi a more specialized explanation is needed. A straightforward explanation[1] considers that the transition energy depends on the degree of interaction between the incipient carbanion and cation, which in turn is sensitive to the degree of solvation of the potential lithium positive ion.

The carbon–lithium bond electrons of 1,1-diphenyl-*n*-hexyllithium in THF solution are considered to have a predominantly p character[23] and are able to delocalize over the entire $\pi$ system. As a consequence of electron delocalization $R^-$ is an odd alternant ion in which the mobile electron pair of the C–Li bond occupies (to a first approximation) a nonbonding orbital.[24] The first electronic excited state is believed to result from promotion of one of these nonbonding electrons to the lowest antibonding $\pi$ orbital. The extent of electron delocalization will depend on the degree of interaction between the incipient anion and lithium cation.[25] For example, increasing C–Li bond formation may be compared to twisting components of a conjugated $\pi$ system out of plane, which usually causes a hypsochromic shift of $\pi \rightarrow \pi^*$ transitions.[26]



WEAK CATION-ANION DATIVE BONDING, Li CATION STRONGLY SOLVATED.

STRONG CATION·ANION DATIVE BONDING. LACK OF SPECIFIC SOLVATION.

Figure 10. Ground-state–excited-state relationships: a, relative energy of cation–anion interaction; b, stabilization of ground and excited states due to solvent orientation and polarizability; c, nonzero excited-state bond energy; d, Franck–Condon excited-state packing strain.

In bond formation the positive lithium counterion is considered to act as a vacant orbital acceptor of Lewis acid strength dependent on its extent of solvation. Participation of the nonbonding electron pair in C–Li bond formation is considered to lower their energy relative to their state in the free ion where there is optimum delocalization. In the electronic excited state one of the electrons of the C–Li bond is promoted to an antibonding $\pi$ orbital. Dative bonding between anion and cation in the electronic excited state should, therefore, be very weak (it now being a single electron bond); thus, the energy of interaction between the anion and cation in the excited state will be less sensitive to the degree of cation solvation. To a first approximation the excited-state energy is considered to be independent of cation solvation.

The predominant effect of solvents on transition energy is thus suggested to result from the effect of solvent on regulating the Lewis acid strength of the incipient lithium cation, which in turn strongly influences the ground-state energy of RLi primarily by regulating the energy of the nonbonding electron pair. This concept, which has precedent in the explanation given to the shifts caused by H bonding solvents on n $\rightarrow \pi^*$ transitions[2a] and is analogous to that proposed to explain the blue shifts which occur on complexing RLi with stronger Lewis acids, *e.g.*, diethylzinc,[3] is illustrated schematically in Figure 10. For clarity, Figure 10 considers the changes in spectra expected for the extreme extents of carbon–lithium bond formation, *i.e.*, strong dative bonding between anion and cation and free ion pairs in which, owing to strong cation solvation, there is minimal cation–anion dative inter-

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(20) Professor M. Szwarc communicated to us $\epsilon$(THF) $= -1.453 + 2659/T$ for which we are grateful. $\epsilon$(THF) = 7.56 at 22°, 10.5 at $-50°$.

(21) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

(22) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(23) This has been demonstrated by C$^{13}$ nmr measurements for diphenylmethyllithium in THF solution: R. Waack, M. A. Doran, E. B. Baker, and G. Olah, *J. Am. Chem. Soc.*, **88**, 1272 (1966).

(24) H. C. Longuett-Higgins, *J. Chem. Phys.*, **18**, 275 (1950).

(25) This is illustrated by proton nmr studies of RLi in different solvents. In THF electron delocalization results in appreciable charge on the phenyl ring as shown by substantial upfield displacement of the chemical shifts of the *ortho*, *meta*, and *para* protons from those in benzene: R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 4042 (1963). In *n*-hexane solution the upfield displacement of the chemical shifts are small and the ring proton spectra is a squashed multiplet with a maximum upfield displacement of 0.5 ppm. Analysis of this spectrum is underway.

(26) See, for example, M. J. S. Dewar, "Steric Effects in Conjugated Systems," Academic Press Inc., New York, N. Y., 1958, p 46.

action. Transition energies will, to a lesser extent, also be affected by solvent polarizability (most important for nonpolar solvents) and by solvent dipole orientation.[22] Effects of dispersive and dipolar interactions were also considered to be small relative to H-bonding effects on n → π* transitions.[27] The red shift which is reported to occur in the spectrum of the alkali metal benzophenone ketyls with increasing cation size (decreasing cationic field strength) was interpreted as implying that perturbation of the ground state is greater than that of the excited state,[6b,7] in agreement with the ideas proposed here to explain solvent effects.

The difference in transition energy of RLi in different solvents can, permitting the above considerations, be equated to the total relative interaction energy between anion and cation. For example, the relative transition energies of RLi in different solvents are considered to depend mainly on the relative ground-state energies, which in turn depend primarily on the relative magnitude of anion–cation interaction. To a first approximation, however, anion–cation interaction is considered to be negligible in the excited states, so the excited-state energies are taken to be independent of cation solvation. To the extent that bonding between the lithium ion and the anion primarily affects only the energy of the nonbonding electron pair, whereas the perturbation of the other π electrons is minor, the relative cation–anion interaction energy can be identified with the difference in ground-state carbon–lithium bond energies.

There are two phenomena to be considered which could conceivably contribute to weaken the assumption that the excited-state energies are independent of cation solvation. For instance, differences in interaction between anion and cation in the excited state in different solvents, although assuredly much less that in the ground state, may not be insignificant.[27] Because the lithium cation no doubt interacts more strongly with the carbanion in the poorer solvents, the extent of excited-state stabilization by the lithium cation could also be larger in the lower polarity solvents. The second consideration, which would have an opposite effect, is Franck–Condon solvent orientation strain.[22,27] This solvent packing strain[22] could destabilize the instantaneous excited state, providing the equilibrium ground-state configuration is sufficiently different from that of the excited state. The configuration of the excited state would be expected to be most different from that of the ground state in solvents in which cation–anion interaction is the strongest, but these are also the solvents in which solvation energies are the smallest. These two effects should to some extent compensate for one another.

To summarize, in our view the effect of solvents on regulating the ground-state energy is the predominant contributor to the over-all solvent effects. Superimposed on this are effects due to enhanced solvation of the excited state as a consequence of solvent dipole orientation,[1,22] solvent polarizability (expected to be relatively small except in nonpolar solvents), in addition to nonzero excited-state bond energy and excited-state Franck–Condon strain.[27] Similar ideas have been advanced to explain the solvent effects on benzophenone alkali metal ketyls.[6,7] This explanation would also be consistent with the changes observed in the spectra of the alkali metal aromatic radical anions[18] on changing from ion pair to free ion and the small changes in spectra accompanying changes in the cation.[6,28]

**Nature of the Solvated Species.** The recent demonstration[16] of the changes in spectra of fluorenyl alkali metal species with cation and solvent and the explanation in terms of contact ion pairs and solvent-separated pairs is in agreement with the Lewis acid–Lewis base concept offered here. A comparison of the spectral shifts of the longer wavelength transition of fluorenyllithium,[4,16] however, seemingly requires that in addition to affecting the ion state the polarity of the solvent also has a small effect on the transition energy within an ion state. The behavior of RLi in the benzene–THF solvent mixture suggests that in other solvents specific solvates corresponding to discrete interaction energies will be formed. Presumably, then, the solvation ability of a solvent will dictate the type of etherate (*i.e.*, solvate) which is stable, which will fix the gross position of $\lambda_{\max}$. For example, RLi in solvents of dielectric constant ($\epsilon$) $\sim 2 \rightarrow 4$ has transition energy comparable to that of RLi·2THF. On the other hand solvents of $\epsilon > 5$, having no steric interference to solvation, apparently all induce transition energies such that $\lambda_{\max}$ is ~480–495 mμ. This is typical of the second more loosely bound species, *e.g.*, RLi·4THF, which is considered to be a solvent-separated ion pair bound together primarily by electrostatic interaction and as such has only slight anion–cation interaction. The smaller variations of $\lambda_{\max}$ with solvent are a result of differences in donor strength of the solvents (which determines the Lewis acid strength of the solvated cation) and the classical effects of the solvent on the transition energy, *e.g.*, polarizability, orientation, etc. The classical solvent effects are evident even when RLi would be suggested to exist as a solvent-separated ion pair, *e.g.*, RLi $\lambda_{\max}$ in THF and 1,1-dimethoxyethane is 496 mμ whereas in pyridine and hexamethylphosphoramide $\lambda_{\max}$ is 484 mμ. A significant experiment would be to repeat the type of experiments reported here with a solvent mixture of hydrocarbon and a less polar ether which would be expected to demonstrate only one type of solvate.

**Solvation Energy and Coordination Energy.** Considering that solvation changes the energy of interaction between the incipient anion and cation it is possible to differentiate between a net solvation energy (as measured by the exothermicity of solvation) and the over-all energy of interaction between the solvent and the Li cation, which is necessarily a larger quantity. The net enthalpy change for formation of RLi·4THF from RLi·2THF is −4.6 kcal/mole. This compares reasonably with the $\Delta H$ of −6 kcal reported for formation of solvent-separated fluorenylsodium from contact ion pairs in THF solution.[16] Because the extent of solvation of the incipient lithium cation is presumed to influence the strength of the anion–cation interaction the total solvation energy (*i.e.*, the total energy of solvent–cation interaction) will be the net solvation energy ($\Delta H$) plus the energy taken up by the system to reduce the cation–anion interaction, *i.e.*, the solvation energy which is required to decrease the

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(27) G. C. Pimentel, *J. Am. Chem. Soc.*, **79**, 3323 (1957).

(28) M. T. Jones and S. I. Weismann, *ibid.*, **84**, 4269 (1962).

cation–anion interaction and which causes a corresponding increase in energy of the carbon–lithium bond electrons. The transition energies corresponding to the respective absorption maxima are given in Table II. It follows from the previous discussion, assuming to a first approximation that the differences in excited-state energies are small, that the difference in transition energy, $\Delta\Delta E$, corresponds to a change in the energy of interaction (*i.e.*, bond energy) between anion and cation brought about by solvation. Thus the anion–cation interaction energy is ~5.9 kcal/mole less in RLi·4THF than in RLi·2THF and similarly for formation of RLi·2THF from a hydrocarbon-solvated RLi. Because this loss in coordination energy is a consequence of solvation, the total solvation energy will be the energy contributed to raising the ground-state energy of the C–Li bond electrons plus the measured enthalpy of equilibrium 1, or 10.4 kcal for RLi·2THF + 2THF → RLi·4THF. A solvation energy of 18 kcal was reported for the mono-THF complex of polyisoprenyllithium.[14] The $\Delta\Delta E$ between RLi in hexane and RLi·2THF is similar to that between RLi·2THF and RLi·4THF, but because the dietherate apparently has a large formation constant and is presumably a more stable complex it may have a larger $\Delta H$ in accordance with the polyisoprenyllithium mono-THF complex. It has not been possible to obtain $\Delta H$ for formation of RLi·2THF from RLi in benzene because of overlap in the spectrum of these two species.

**Table II.** Transition Energies for RLi

| | $\lambda_{max}$, m$\mu$ | $\Delta E$, kcal | $\Delta\Delta E$ |
|---|---|---|---|
| Hexane | 410 | 69.8 | |
| Benzene | 415 | 68.9 | 5.3 |
| RLi·2THF | 450 | 63.6 | |
| 100% THF (RLi·4THF) | 496 | 57.7 | 5.9 |

**Spectrum in Hydrocarbon Solution.** The spectrum of RLi in hydrocarbon solution (either benzene or hexane) and the changes in this spectrum with temperature indicate the existence of two species in equilibrium which have different absorption properties. The lack of concentration dependence rules out the most obvious explanation for the two species, that of a monomer–dimer equilibrium. A monomer–aggregate equilibrium would not be very concentration dependent for a large enough aggregate, but seems unlikely for steric reasons. Another possibility would be that RLi is in equilibrium with its triple ions[29] which might be expected to absorb at longer wavelength and be favored by lower temperature. For instance if RLi in hydrocarbon solution is predominantly dimeric, equilibrium with its triple ion pairs would be concentration independent. If RLi species absorbing at 415 m$\mu$ is monomeric, the equilibrium, to be concentration independent, would have to be with free triple ions, which seems unlikely. The nature of the RLi species in hydrocarbon solution is being investigated.

**Cross Association.** The change in the spectrum of RLi in hydrocarbon caused by excess *n*-butyllithium is probably due to cross association. Because a considerable excess of *n*-butyllithium is required before the spectrum is affected, the propensity toward cross association is indicated to be weak. On the other hand self-association of *n*-alkyllithiums, which is well established, is indicated to be strong.[12,30] There is previous evidence for cross association between different organolithium compounds. A decrease in the propogation rate of polyisoprenyllithium in the presence of excess *n*-butyllithium (solvents cyclohexane[31] and *n*-hexane[32]) was suggested to be a consequence of cross association. Viscosity measurements show that self-association of polyisoprenyllithium is decreased in the presence of *n*-butyllithium.[33,34] Formation of mixed aggregates of ethyllithium and *t*-butyllithium has been reported.[35] When THF is present the behavior of the spectrum of RLi on addition of *n*-butyllithium indicated that solvation of both species by THF is preferred to cross association. Interpretation of the behavior when only a small amount of THF is present, in terms of relative solvation affinities, was discussed in the previous section.

**Explanation for Lack of Solvent Sensitivity of the Spectrum of Organolithium Compounds.** The solvent effect is considered as depending on the degree of interaction between the incipient anion and cation in the ground state which in turn depends on the ability of the solvent to effect this interaction. A large anion can accommodate excess charge density by electron delocalization throughout the $\pi$ system and so gain stability. Organolithium compounds for which such stabilization is less effective might not be expected to show pronounced solvent effects.

The capability for electron delocalization over an extensive $\pi$ system seems to be prerequisite for a pronounced solvent effect in the spectrum of odd alternant anions. Benzylic-type organoalkali metal species show little solvent effects on their absorption spectra.[1,13,36] Allylic species show a somewhat larger solvent sensitivity,[5] but it is small compared to those found for larger $\pi$ systems.[1,7] These solvent effects are within the range of solvent-induced shifts explicable by the more classical[22] explanations. It seems likely that in these smaller $\pi$ systems the solvent cannot compete with the Lewis base strength of the carbanion because there is an insufficient gain in electron delocalization energy accompanying solvation. Hence, even in the more polar solvents a strong donor–acceptor interaction would exist between the incipient carbanion and alkali metal cation, the energy of which would not, relative to the total transition energy, be significantly different in different solvents. Temperature studies of the spectrum of benzyllithium show its absorption maximum is invariant in the range 25 to −50° in THF solution. Other studies of the solvent effects on the transition energies of these less delocalized odd alternant organoalkali metal compounds are continuing.

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(30) J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

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