benzyl halides to changes in medium, as compared with that for the *p*-methylbenzyl halides, is regarded as an indication that activation in the reactions of the former occurs without much stretching of the carbon–halogen bonds and with correspondingly close coordination of the solvent as a nucleophile.[29]

(29) J. J. Frisone and E. R. Thornton, *J. Amer. Chem. Soc.*, **90**, 1211 (1968).

Studies of Solvent Effects on the Nature of Ion Pair Interaction in 9-(2-Hexyl)fluorenyllithium[1a]

M. M. Exner,*[1b] R. Waack, and E. C. Steiner

Contribution from The Dow Chemical Company,
Midland, Michigan 48640. *Received January 8, 1973*

Abstract: The hydrocarbon solubility of 9-(2-hexyl)fluorenyllithium (**1**) permits evaluation of its aggregation and spectral behavior in nonpolar solvents, which is compared with that in polar solvents. Ebulliometry shows **1** to be a dimer in cyclohexane at 25° over the concentration range of 0.01 to 0.1 *m*. A finite equilibrium between monomeric and dimeric ion pairs over the concentration range 0.002 to 0.04 *m* is indicated in THF at 25°. Lithium-7 and proton nmr spectra recorded in polar and nonpolar solvents reveal a regular trend of increasing cation–anion interaction with decreasing solvent polarity. The ^{7}Li chemical shifts cover the largest range and those in hydrocarbon solution are found to be the farthest upfield of ^{7}Li resonances reported to date. The electronic spectrum of **1** in ether solvents has previously been reported and found consistent with the description of contact and solvent-separated ion pairs. An apparently striking departure from the predictions of this description is observed in the electronic spectrum of **1** in hydrocarbon solvents. The band associated with the contact ion pair of **1** occurs in diethyl ether at 358 nm and that associated with the solvent-separated ion pair occurs in tetrahydrofuran at 387 nm. In hydrocarbon solvents, however, this absorption band occurs at 368 nm. Possibilities for this discrepancy are considered. Of note is that **1** is a nonalternant π system; the irregular spectral behavior of perturbed nonalternants is a significant factor for consideration. As an alternative, a sandwich structure for **1** is considered reasonable in those solvents where it is found as a contact ion pair.

Continuing studies of carbon–lithium bonding[2–4] required an organolithium compound which is appreciably soluble in hydrocarbons and whose carbanion is geometrically constrained to planar sp^2 hybridization. Fluorenyllithium,[5,6] although geometrically suitable, does not have the required solubility in hydrocarbons. Examination of the recently investigated[7] 9-(2-hexyl)fluorenyllithium (**1**) showed it to meet the hydrocarbon solubility requirement.[8] This paper deals with information obtained through studies of electronic spectra and lithium-7 and proton magnetic resonance of **1** in hydrocarbon, ether, and mixed hydrocarbon–ether solutions and of colligative properties of **1** in tetrahydrofuran (THF) and cyclohexane.

Intensive investigation of fluorenyl carbanions in ether solvents[5,7] has established contact and solvent-separated ion pair type species. The intent here is to reveal the nature of the ion pair species in hydrocarbon and hydrocarbon–ether mixed solutions. Such data for species that have not contacted ether are lacking. Of note is that **1** is a nonalternant molecule.[9] Other examined systems are odd alternants.[3,4] Although the electronic spectra of the latter type molecules behave in a regular way to steric strain[10] and inductive effects[11] (*i.e.*, local charge density changes), the former do not.[12]

Experimental Section

Glassware and syringes were oven dried at 110° overnight and allowed to cool either under vacuum or under inert gas. Solution transfers were made with gas-tight syringes. All chemical reactions were carried out on a vacuum line under positive argon pressure.[13] Precautions were taken to shield reactions from direct exposure to light. Melting points, obtained on a Thomas Hoover capillary melting point apparatus, are uncorrected.

Materials. 9-Ethylidenefluorene (Aldrich Chemical Co.) was recrystallized from absolute ethanol and freed of residual solvent under vacuum. The recrystallized solid was stored under argon in the dark in a sealed container at −10° until use: mp 102–104° [lit. 102–104,[14a] 104–105° [14b]]; uv max (abs C_2H_5OH) sh 224 (ϵ 39,400), 230 (46,300), sh 236 (30,700), 247 (31,700), 256 (46,300), 272 (13,400), 280 (14,400), 297 (10,400), sh 307 (8,200), 312 (9,700), sh 350 nm ($\sim$25) [lit.[15] 229.5 (ϵ 50,000), 247.0 (33,100), 256.0 (46,800), 270.0 (14,500), 280.0 (15,500), 297.0 (11,800), 311.0 nm

---

(1) (a) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstract ORGN-184; (b) Midland Macromolecular Institute, Midland, Mich. 48640.

(2) L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Amer. Chem. Soc.*, **91**, 1057 (1969).

(3) R. Waack, L. D. McKeever, and M. A. Doran, *Chem. Commun.*, 117 (1969).

(4) L. D. McKeever and R. Waack, *J. Organometal. Chem.*, **28**, 145 (1971).

(5) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

(6) J. A. Dixon, P. A. Gwinner, and D. C. Lini, *ibid.*, **87**, 1379 (1965).

(7) L. L. Chan and J. Smid, *ibid.*, **90**, 4654 (1968).

(8) Analogously, the alkyl substituent in 1,1-diphenylhexyllithium (**2**) induces hydrocarbon solubility, contrasted with the relatively hydrocarbon-insoluble diphenylmethyllithium.[4]

(9) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 45–46.

(10) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 114, 434–448.

(11) R. Waack and M. A. Doran, *J. Phys. Chem.*, **67**, 148 (1963).

(12) J. H. Hammons, *J. Org. Chem.*, **33**, 1123 (1968).

(13) R. Waack, M. A. Doran, and P. E. Stevenson, *J. Amer. Chem. Soc.*, **88**, 2109 (1966).

(14) (a) A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960); (b) D. J. Cram and D. R. Wilson, *J. Amer. Chem. Soc.*, **85**, 1249 (1963).

(15) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, Y. Hershberg, and Y. Sprinzak, *Bull. Soc. Chim. Fr.*, **18**, 702 (1951).

(10.700)]; proton nmr (0.5 M in CCl_4) δ 7.55 (m, 4), 7.20 (m, 4), 6.65 (q, 1, $J = 7.5$ Hz), 2.28 (d, 3, $J = 7.5$ Hz).

n-Butyllithium (Foote Mineral Co.) was obtained as a *ca.* 1.6 M solution in *n*-hexane. All solvents were freshly distilled immediately before use under an atmosphere of nitrogen. Reagent grade diethyl ether was distilled from lithium aluminum hydride. Reagent grade THF was distilled from deep blue lithium benzophenone ketyl. Thiophene-free benzene was distilled first from sodium metal and finally from lithium dispersion. Cyclohexane and *n*-hexane were shaken for a day over concentrated sulfuric acid, distilled with passage of distillate through alumina, and redistilled from lithium dispersion. Purified cyclohexane and hexane were transparent above 215 nm. Hexamethylphosphoric triamide (HMPA) was distilled from triphenylmethylsodium at reduced pressure.

Electronic Spectra. The electronic spectra were examined using the previously described, closed, quartz spectroscopic cell of 2.0-mm pathlength with 1.90–1.94-mm spacers.[16] The cell was modified with a 1-mm bore, solid stopcock between the syringe cap port and the cell flask. Spectra were obtained at room temperature (22–24°) on a recording Cary-14 spectrophotometer equipped with a 0 to 2 absorbance slide wire.

9-(2-Hexyl)fluorenyllithium (1). A weighed amount of 9-ethylidenefluorene (*ca.* 0.0010 g, 0.000052 mol) was dissolved in 10 ml of dry solvent in the closed spectroscopic cell. After recording the electronic spectrum of the parent olefin, the calculated equimolar amount of 1.6 M *n*-butyllithium in *n*-hexane was added. The electronic spectrum of the yellow to deep red solution of **1** was recorded. Formation of **1** at room temperature was immediate in diethyl ether and THF, very fast in benzene, but slow in *n*-hexane and cyclohexane. In the last two solvents, 1 hr was required for the reaction to reach completion. Fractional equivalents of *n*-butyllithium were added until the band intensity was unaffected by further additions. The spectra obtained in diethyl ether and THF were identical with those reported by Chan and Smid.[7] The absorption maxima and approximate molar extinction coefficients are listed in Table III.

Nuclear Magnetic Resonance. Proton magnetic resonance spectra were recorded on Varian A-60 and Varian HA-100 spectrometers.[17a] Lithium-7 magnetic resonance spectra were examined on the spectrometer of Baker and Burd.[18]

9-(2-Hexyl)fluorenyllithium (1). An approximately 0.2 M solution of **1** in hydrocarbon was prepared by the addition of an equimolar amount of 1.6 M *n*-butyllithium in *n*-hexane to a cyclohexane solution of 9-ethylidenefluorene. The solution turned red immediately and was stirred at room temperature for 1–2 hr. For studies in benzene, ether, and HMPA solvents, the cyclohexane was frozen and removed at *ca.* 0° under vacuum. Dry solvent was added to the residual red solid to give a solution of *ca.* 0.4–0.5 M concentration. The solution was transferred under argon to an nmr tube, which was evacuated and sealed. The preparation of **1** for study in *n*-hexane and cyclohexane was carried out directly in those solvents. The product remained in solution as formed, but, when it was precipitated by chilling to −10°, it did not redissolve. Consequently the spectra in these solvents were recorded on saturated solutions of *ca.* 0.1–0.2 M concentration. All preparations normally resulted in residual amounts of unreacted 9-ethylidenefluorene.

Colligative Studies. Ebulliometric studies were carried out according to the experimental practice reported by Steiner and coworkers.[19] The solvent–solution temperature difference in the ebulliometer was evaluated with a 30-junction thermopile.[19] Voltages were read with a Keithley meter and continuously recorded. Temperature differences after addition of substrate were plotted *vs.* total solution concentration. Triphenylmethane was used as the calibration standard.

9-(2-Hexyl)fluorenyllithium (1). For colligative measurements in THF, **1** was prepared in *ca.* 0.5 M concentration by the dropwise addition at room temperature and with stirring of 1 equiv of 1.6 M *n*-butyllithium to a solution of 9-ethylidenefluorene in cyclohexane containing 2 equiv of THF. A two-phase reaction mixture resulted: a lower, deep red layer, rich in THF, and an upper, red layer, rich in hydrocarbon solvent. After 1 hr reaction time the upper layer was decanted by syringe and the lower layer was washed with a small volume of cyclohexane to remove unreacted starting materials. The washing solution was drawn off by syringe, and the remaining solvent was evaporated into a cold trap at −78° by overnight standing at room temperature under high vacuum. A solution of **1** in THF (0.4 M) was prepared and loaded into a micrometer syringe (capacity of 2.5 ml) in a drybox. Additions of **1** to the ebulliometer were made as a THF solution.

For measurements in cyclohexane, **1** was prepared in an analogous manner, by the addition of *n*-butyllithium in *n*-hexane in 10% molar excess to a mixture of 9-ethylidenefluorene in cyclohexane. Color formation was immediate, and the resultant red solution was allowed to stir at room temperature overnight. Dry Ice chilling, followed by centrifugation, separated **1** as a red solid. The reaction solution was drawn off by syringe and the solid was washed once with *n*-hexane. Centrifugation and decantation followed by solvent evaporation into a cold trap under high vacuum at room temperature overnight yielded **1** as an intensely red powder. The powder was pressed into pellets in a drybox; each pellet was weighed as prepared. An estimated minimum yield of **1** based on the weighed pellets was 65%. Additions of **1** to the ebulliometer were made directly using a pellet technique. Dissolution of each pellet required 3 to 4 hr. Six additions were made.

Isolation of 9-(2-Hexyl)fluorene. Hydrolysis of the 9-(2-hexyl)-fluorenyllithium prepared in THF for colligative measurements afforded a yellow oil. Column chromatography on silica gel yielded as the major component 9-(2-hexyl)fluorene on elution with 10% v/v ethyl acetate–hexane. It was further purified by preparative vpc (10% OV-1 on Chromosorb 6, column dimension 2 ft × 0.25 in., at 200°) to give a slightly yellow oil which did not crystallize even after standing for 6 months under refrigeration: uv max (*n*-hexane) sh 222 (ϵ 27,750), 229 (11,350), sh 250 (15,650), sh 257 (23,300), sh 260 (24,800), 263 (26,600), 265 (25.200), 267 (26,000), sh 274 (16,700), sh 280 (11,800), 291 (7,800), sh 295 (6,200), 302 nm (11,500); nmr (CCl_4) δ 7.60 (m, 2), 7.20 (m, 6), 376 (d, 1, $J = 3$ Hz), 2.16 (m, 1), 1.30 (m, 6), 0.83 (m, 3), 0.53 (d, 3, $J = 7$ Hz); ir (CCl_4), 3050 (aromatic CH), 2950 and 2870 (aliphatic CH), 1450 cm^{-1} (aromatic C=C); high resolution mass spectrum[17b] (CEC 21-110B, batch inlet, 200°) molecular ion 250.1729 (calculated for $C_{19}H_{22}$, 250.1721), strong peaks *m/e* 85 (2-hexyl) and *m/e* 57 (*n*-butyl).

Results

Nuclear Magnetic Resonance Spectrum. The lithium-7 magnetic resonance chemical shifts are listed in Table I. Chemical shifts are given relative to external 0.5 M lithium bromide in THF and relative to *n*-butyllithium measured independently in the same solvent

Table I. Solvent Dependence of ^{7}Li Magnetic Resonance Chemical Shift of 9-(2-Hexyl)fluorenyllithium

Solvent	Chemical shift from LiBr[a]	*n*-BuLi[b]	Dielectric const, 25°
HMPA	1.2		35
THF[c]	1.9	2.7	7.5
Et_2O	8.3	10.0	4.3
Benzene	13.3	14.6	2.28
Cyclohexane	13.1	14.8	2.02
Cyclohexane + 2 equiv THF[d]	7.95	9.0	*e*
Cyclohexane + 4 equiv Et_2O[d]	8.8	10.0	*e*

[a] Relative to external 0.5 M LiBr in THF. [b] Measured independently in the indicated solvent (0.5 M). [c] The $\delta_{^7Li}$ value in THF is 1.9 for $(C_6H_5)_3CLi$ (R. Waack, M. A. Doran, E. B. Baker, and G. Olah, *J. Amer. Chem. Soc.*, **88**, 1272 (1966)), 2.2 for $LiB(C_6H_5)_4$, and 2.21 for 1,1-diphenylhexyllithium relative to *n*-butyllithium.[4] [d] Based on dissolved organolithium compound. [e] Inestimable in a meaningful way from gross dielectric constant calculations because of the intimate association of the majority of the ether molecules with the lithium cation of the organometal.

---

(16) R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, **85**, 1615 (1963).

(17) The spectra were recorded through the cooperation of: (a) W. C. Meyer, R. G. Martin, and J. P. Heeschen; and (b) L. Shadoff of The Dow Chemical Company.

(18) E. B. Baker and L. W. Burd, *Rev. Sci. Instrum.*, **28**, 313 (1957); **34**, 238 (1963).

(19) E. C. Steiner, R. O. Trucks, J. D. Starkey, and J. H. Exner, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. POLY-018.

Table II. Aromatic Proton Magnetic Spectrum of 9-(2-Hexyl)fluorenyllithium, 60 MHz

Solvent	Doublet[a] $H_{4,5}$ δ, ppm	Doublet[a] $H_{4,5}$ J, Hz	Doublet[a] $H_{1,8}$ δ, ppm	Doublet[a] $H_{1,8}$ J, Hz	Triplet[a] $H_{2,7}$ δ, ppm	Triplet[a] $H_{2,7}$ J, Hz	Triplet[a] $H_{3,6}$ δ, ppm	Triplet[a] $H_{3,6}$ J, Hz	Charge density[b] on position 3,6
Cyclohexane	8.39	6	Three multiplets ~7.6, 7.1, ~6.7						
Benzene-d_6	7.80	8.0	7.52	8.0	6.70	7	6.40	7	0.083
Cyclohexane + 4 equiv Et_2O[c]	7.92	8.0	7.30	7.5	6.94	7–8	6.60	7.5	0.055
Diethyl ether	8.04	7.7	7.59	8.2	7.00	~8	6.67	~8	0.048
Cyclohexane + 2 equiv THF[c]	7.92	7.5	7.48	8.5	6.90	7–8	6.55	7–8	0.060
THF	7.88	8	7.40	8	6.82	7.5	6.33	7.5	0.082
HMPA	7.88	7.5	7.33	8	6.73	7.0	6.28	7.5	0.083

[a] Based on first-order analysis of spectrum with coupling constants taken from observed splittings. [b] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 2846 (1960). [c] Relative to dissolved organolithium compound.

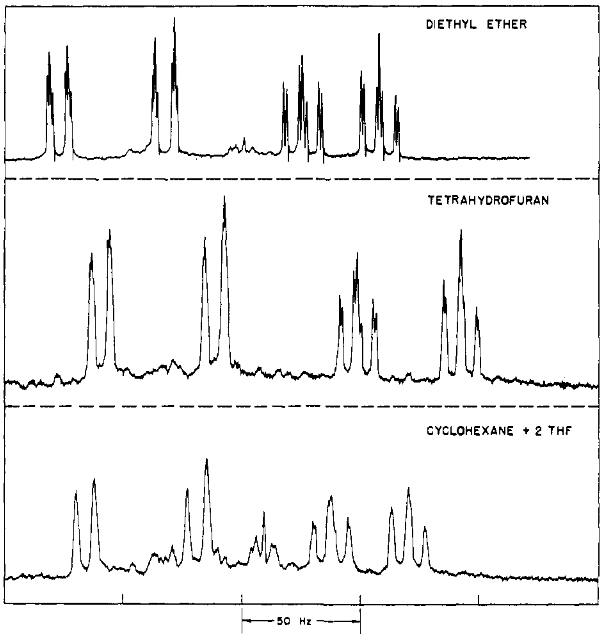

Figure 1. The 100-MHz nuclear magnetic resonance spectrum of the aromatic protons of 9-(2-hexyl)fluorenyllithium in diethyl ether, tetrahydrofuran, and cyclohexane containing 2 molar equiv of THF relative to organolithium concentration (*ca.* 0.5 *M*).

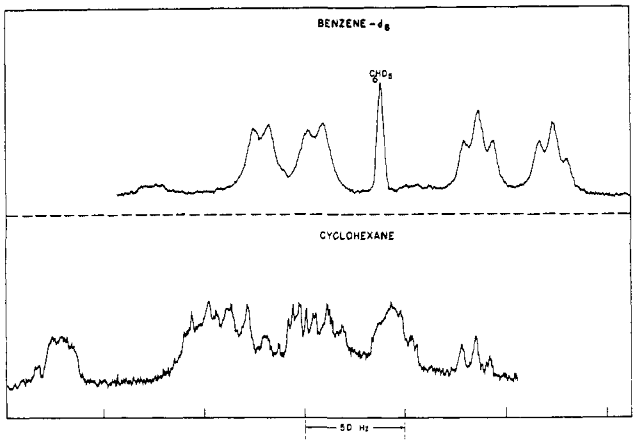

Figure 2. The 100-MHz nuclear magnetic resonance spectrum of the aromatic protons of 9-(2-hexyl)fluorenyllithium in benzene-d_6 (*ca.* 0.5 *M*) and cyclohexane (*ca.* 0.2 *M*).

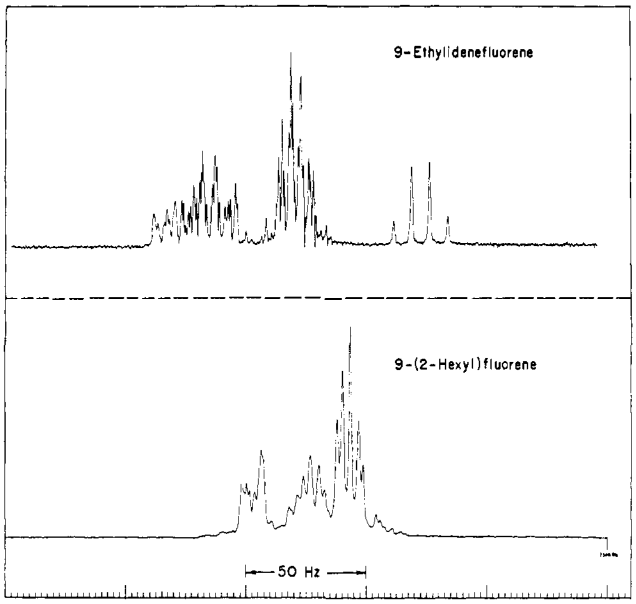

Figure 3. The 100-MHz nuclear magnetic resonance spectrum of the aromatic protons of 9-ethylidenefluorene and 9-(2-hexyl)fluorene (0.5 *M*, CCl_4).

in those cases where the solvent does not react with *n*-butyllithium. There is an overall trend of upfield shift with decreasing solvating ability of these solvents, which for **1** roughly parallels their dielectric constants. (This parallel is apparently coincidental, other factors such as steric bulk and chelating properties having been cancelled out for **1** in this particular series.[7]) The chemical shifts in hydrocarbon solvent are the largest upfield shifts yet reported.

The lithium-7 nmr absorptions in the polar solvents HMPA and THF appear at low field and at similar chemical shifts indicating that the lithium cation in each case is comparably located with respect to the aromatic fluorenyl ring system. The similarity in chemical shifts in this instance is notable, because of the quite different solvating properties of HMPA and THF for the closely related fluorenyllithium.[7] It suggests for **1** a limiting minimum cation–anion ion pair interaction in HMPA and THF. Analogously, in benzene and in cyclohexane, where strong specific cation–solvent interactions are expected to be absent, the upfield and nearly equivalent lithium chemical shifts reflect a similar location and shielding of the lithium cation by the magnetically anisotropic ring system and suggest, for **1** in hydrocarbons, a maximum cation–anion ion pair interaction.

Table III. Electronic Spectrum of 9-(2-Hexyl)fluorenyllithium

Solvent and/or added ether	Ultraviolet absorption maxima and extinction coefficients											
	λ_{max}	$\epsilon \times 10^{-4}$	λ_{max}	$\epsilon \times 10^{-4}$	λ_{max}	$\epsilon \times 10^{-4}$	λ_{max}	$\epsilon \times 10^{-4}$	λ_{max}	$\epsilon \times 10^{-4}$	λ_{max}	$\epsilon \times 10^{-4}$
n-Hexane (1 equiv BuLi)	207	2.22	Sh 250	~3.0	275	4.21	Sh 297	1.5	Sh 305	1.2	Sh 310	1.0
Cyclohexane												
1 equiv BuLi	206	2.33	Sh 248	1.5	275	>3.6	Sh 300	0.7			Sh 310	0.5
5 equiv BuLi	207	2.31	Sh 250	2.2	274	4.51	299	2.11			Sh 310	1.55
50 equiv BuLi	Blank out		Blank out		~265	5.65	300	1.75			Sh 310	1.59
Benzene (5 equiv BuLi)	Blank out		Blank out		Blank out		Sh 300	2.58				
Diethyl ether (2 equiv BuLi)	205	3.2	Sh 251	2.32	274	4.33	298	2.71	Sh 305	2.57		
Tetrahydrofuran												
0.0063 *M*, 4 equiv BuLi	Sh 208	3;0	253	1.85	292	4.24					310	2.96
0.023 *M*, 1 equiv BuLi												
0.067 *M*, 1 equiv BuLi												
n-Hexane (1 equiv BuLi)												
1 equiv THF												
2 equiv THF												
Cyclohexane												
+ 4 equiv Et_2O	207	~3.0	Sh 250	1.6	271/275	3.4	292	1.45	300	1.45	Sh 310	0.73
+ 1–20 equiv Et_2O (see Figure 5)												
+ 10 equiv THF			Sh 250	2.28	274	4.37	298	2.85	Sh 395	2.72		
+ 0.5–50 equiv THF (see Figure 6)												
Benzene (5 equiv BuLi)												
+ 2 equiv THF	Blank out		Blank out		Blank out		300	2.95				
+ 4 equiv THF	Blank out		Blank out		Blank out		300	3.00				

The lithium-7 chemical shifts of **1** in cyclohexane–diethyl ether and cyclohexane–THF are close to that in diethyl ether indicating again that the ion pair interaction is similar in these three solvent systems. Although it is possible that the lithium chemical shift found in the cyclohexane–THF mixture could be an average value resulting from rapid exchange between ~50% THF-like species and ~50% cyclohexane-type species, this is not likely for two reasons. First, exchange is not frozen out even at −20°. Second, the electronic spectrum at low concentrations of **1** in this mixed solvent shows no evidence for the coexistence of two distinct species.

The 60-MHz proton magnetic resonance data for the aromatic moiety of **1** in ether and hydrocarbon solvents are shown in Table II and Figures 1 and 2. Figure 3 illustrates the aromatic regions of the spectra of 9-ethylidenefluorene and 9-(2-hexyl)fluorene. The increased proton chemical shift spread of the aromatic protons of **1** and the upfield shift from that of 9-(2-hexyl)fluorene show that negative charge density is distributed on the ring carbons.[20] In THF the aromatic protons are a sharp, first-order spectrum. In diethyl ether and in benzene the spectrum is analogous, but compressed, in agreement with less delocalized charge density. In THF, diethyl ether, and benzene-d_6, the spectrum of **1** is well resolved at 100 MHz into a doublet, doublet, triplet, triplet with increasing field strength as shown in Figures 1 and 2. The assignment of the coupling and chemical shift pattern is straightforward. Relative electron densities determined from Hückel molecular orbital calculations are in accord with the proton assignments. Recent detailed analysis by Cox concurs with these assignments.[21] In cyclohexane the splitting patterns are more complex and assignment of the spectrum is less apparent. 9-Ethylidenefluorene appears to be a minor contaminant. The appearance in benzene and cyclohexane of an ill-defined multiplet at approximately 50 Hz downfield from the doublet assigned to the aromatic 4,5 protons is unexpected. It is reminiscent of the behavior found for the ortho protons of phenyllithium and pyridine.[22]

Table II also lists the calculated charge density on the position para to the 9 carbon. An overall decrease in charge density with decreasing solvent polarity is evident. Charge density values in THF and HMPA are essentially identical with each other, as are the values in diethyl ether and the two mixed solvent systems. This is consistent with the lithium-7 nmr findings. The apparent increase in charge density in benzene is attributable to specific anisotropic effects of benzene. The overall spread of chemical shift values for the aromatic protons does not change substantially with solvent, which is in contrast with the behavior found in the odd-alternant organolithium systems.[4]

The aliphatic protons of **1** were observed in benzene-d_6 and THF-d_8 solvents. At 100 MHz the chemical shift and splitting patterns were well resolved. Progressive shifts to higher field with increasing remoteness from the 9 position of the fluorenyl ring were observed for the alkyl side chain protons.

---

(20) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963).

(21) R. H. Cox, *J. Phys. Chem.*, 73, 2649 (1969).

(22) J. A. Ladd, *Spectrochim. Acta*, 22, 1157 (1966).

Contact and/or solvent-separated ion						Visible absorption maxima and extinction coefficients							
λ_{max}	$\epsilon \times 10^{-3}$	λ_{max}	$\epsilon \times 10^{-3}$	λ_{max}	$\epsilon \times 10^{-3}$	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
		368	6.0	Sh 390	2.0	Sh 470	400	488	500	523	470	568	150
		370	6.8	Sh 390	2.3	Sh 470	460	492	630	524	680	568	280
		367	8.0			Sh 470	730	487	800	521	600	568	100
		366	8.0			Sh 450	700	472	900	Sh 520	500	568	90
		368	7.9	Sh 380	5.6	Sh 465	740	487	850	Sh 520	600	568	45
						Sh 430	450						
357	11.0			Sh 380	1.4	461	1100	Sh 488	800			Sh 555	40
						Sh 440	950						
						Sh 410	500						
		Sh 375	11.2	387	16.5	Sh 455	540	482	900	515	1200	555	860
		Sh 375	7.0	387	9.4	450	800	482	980	515	1100	555	940
		Sh 375	8.1	387	10.5	450	810	482	1000	515	1200	555	960
358	6.0	367	3.0			462	600	488	500	Sh 523	200	Sh 568	30
						Sh 440	440						
357	7.4	None				460	700	488	500	None		Sh 568	10
						Sh 440	510						
						Sh 410	310						
350	~4.0	365	~4.0			448	~660	476	~680	522	~420	568	~100
						Sh 420	550						
357	13.0	None				461	1230	Sh 488	870			Sh 555	20
						Sh 440	1000						
						Sh 410	570						
		361	10.0	Sh 380	3.2	463	1100	Sh 483	900	Sh 520	340	568	30
						Sh 440	850						
		360	11.4	Sh 385	1.5	464	1100	Sh 490	800			568	30
						Sh 440	900						

Electronic Spectrum. The electronic spectrum of **1** is complex, as is that of fluorenyllithium.[5,7] The spectral data are summarized in Table III, and the spectra recorded in three different solvents are shown in Figure 4. The visible and ultraviolet regions of the spectrum of **1** consist of multiple overlapping bands, which may arise from more than one electronic transition or may be vibrational states of a single electronic transition. The multiple bands shift with changes in solvent in a manner which is difficult to interpret. Therefore, the maxima are reported as experimental observations only, without attempting to correct for the influence of overlap on the "true" maxima.[23]

The absorption band located between the complex absorptions in the visible and ultraviolet portions of the spectrum of both fluorenyllithium and 9-(2-hexyl)-fluorenyllithium is considered sensitive to ion pair–solvent interaction.[5,7] For **1**, this band occurs in ether solvents as a well-defined single absorption in the 350- to 390-nm region. The absorption maximum occurring at the short wavelength end of this region (in dioxane and diethyl ether) is assigned to the contact ion pair, whereas the maximum occurring at the long wavelength end of this region (in THF and HMPA) is assigned to the solvent-separated ion pair.[7]

Focusing attention on this band, the absorption maximum for **1** appears at 357 nm (ϵ 11,000) with a shoulder at 380 nm ($\epsilon_{apparent}$ 1400) in diethyl ether and at 387 nm (ϵ 16,000) with a shoulder at 375 nm ($\epsilon_{apparent}$ 1000) in THF, in agreement with the published absorption maxima.[7] In cyclohexane, *n*-hexane, and benzene, this band occurs at 368 nm (ϵ 6000–8000). The position of this band in hydrocarbon is unaltered either by extreme dilution or by the presence of a large excess (50 molar equiv) of *n*-butyllithium. The appearance of this band at a position intermediate between that in diethyl ether (357 nm) and THF (387 nm) is anomalous and unexpected.[5]

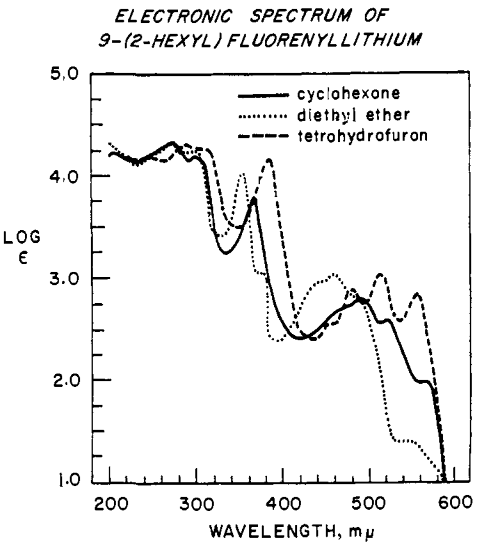

Figure 4. Electronic absorption spectrum of 9-(2-hexyl)fluorenyllithium in cyclohexane (—), diethyl ether (· · ·), and tetrahydrofuran (- - -) at room temperature.

Still further unexpected spectral shifts are observed on addition of small amounts of diethyl ether or THF to **1**

---

(23) B. Roos, *Acta Chem. Scand.*, 18, 2186 (1964).

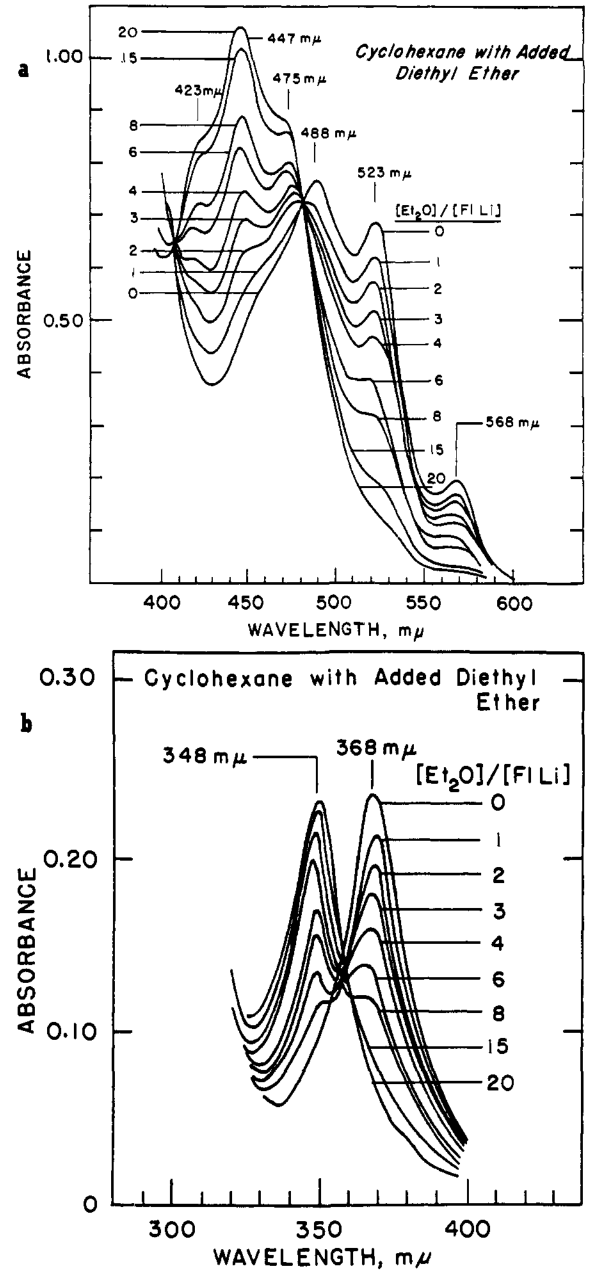

Figure 5. Electronic absorption spectrum of 9-(2-hexyl)fluorenyllithium in cyclohexane with 1 to 20 molar equiv of added diethyl ether at room temperature: (a) visible portion 2.02-mm pathlength; (b) ultraviolet portion 0.074-mm pathlength.

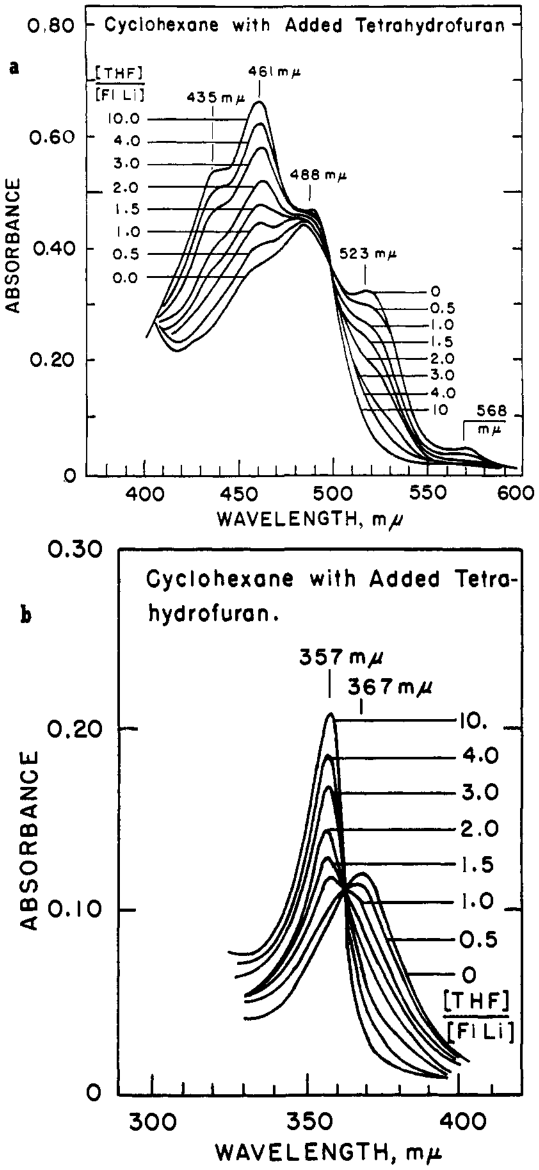

Figure 6. Electronic absorption spectrum of 9-(2-hexyl)fluorenyllithium in cyclohexane with 0.5–10 molar equiv of added THF, at room temperature: (a) visible portion 2.00-mm pathlength; (b) ultraviolet portion 0.060-mm pathlength.

in cyclohexane, Figures 5 and 6. In each case the characteristic peaks of **1** in cyclohexane at 367–368, 488, 520–523, and 568 nm diminish and are replaced by those of the respective ether solvates, isobestic points being observed in both cases. The solvate spectra are very similar to each other in overall appearance, but the THF solvate absorbs at a longer wavelength (about 10 nm) than the diethyl ether solvate. The approximated integrated intensities[10] of the absorption bands in the 345–370-nm region are the same to within about 10%, in spite of the apparently significant differences in their linear intensities (molar extinction coefficients, Table III).

The formation constant for the THF solvate is relatively high since addition of 4 equiv of THF completely eliminates the peaks due to the unsolvated species and further limited THF addition has little effect. The formation constant for the diethyl ether solvate is relatively low, and a 20-fold excess of diethyl ether must be added to eliminate absorptions of the unsolvated species. In both instances, further extensive addition of THF or diethyl ether results in the transformation of the spectrum to that in pure THF or diethyl ether, respectively.

The diethyl ether case may be analyzed more closely assuming dissolvate formation. Figure 7 shows a plot of the height of the 523-nm peak of the unsolvated species relative to an estimated base line for the solvated species. The resulting curve cannot be fit satisfactorily by either equilibrium model i or ii

$$A + B \overset{K_1}{\rightleftharpoons} AB \qquad \text{(i)}$$

$$A + 2B \overset{K_2'}{\rightleftharpoons} AB_2 \qquad \text{(ii)}$$

where A = the 9-(2-hexyl)fluorenyllithium and B = ether. However, it can be fit quite well with model iii using $K_1 = 15\ M^{-1}$ and $K_2 = 22\ M^{-1}$.

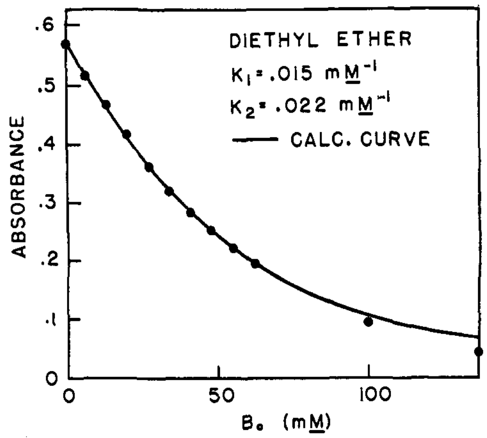

Figure 7. Plot of the height of the 523-nm peak in the visible spectrum of 9-(2-hexyl)fluorenyllithium in cyclohexane *vs.* the concentration of added diethyl ether (B_0). The curved line is calculated using $K_1 = 0.015\ \text{m}M^{-1}$ and $K_2 = 0.022\ \text{m}M^{-1}$.

$$\begin{aligned} \text{A} + \text{B} &\overset{K_1}{\rightleftharpoons} \text{AB} \\ \text{AB} + \text{B} &\overset{K_2}{\rightleftharpoons} \text{AB}_2 \end{aligned} \qquad \text{(iii)}$$

A better analysis could be made if the model took into account the dimeric nature of **1**. (See the following section.) Thus, it would be expected that the first

$$\begin{aligned} \text{A}_2 + \text{B} &\rightleftharpoons \text{A}_2\text{B} \\ \text{A}_2\text{B} + \text{B} &\rightleftharpoons \text{A}_2\text{B}_2 \\ \text{A}_2\text{B}_2 + \text{B} &\rightleftharpoons \text{A}_2\text{B}_3 \\ \text{A}_2\text{B}_3 + \text{B} &\rightleftharpoons \text{A}_2\text{B}_4 \end{aligned}$$

diethyl ether molecule would add with relative difficulty. This is indicated in the simpler model since $K_2 \cong K_1$.

The THF case may similarly be analyzed. Figure 8 shows a plot of the height of the same peak (in this instance appearing at 520 nm) relative to an estimated base line for the solvated species. The curve is fit with model iii using $K_1 \leqslant 10\ M^{-1}$ and $K_1K_2 = 100{,}000\ M^{-2}$. It is hard to estimate K_1 and K_2 separately because of the difference between them. K_1K_2 is the same as the constant K_2' for the disolvation equilibrium ii.

The unusual behavior of the electronic spectrum provided impetus for examining the aggregation state of **1** in THF and cyclohexane.

Aggregation Studies. Ebulliometric studies of **1** in THF at 25° indicate that there is a finite equilibrium between monomeric and dimeric ion pairs over the concentration range of 0.002–0.040 *m*. This is shown in Figure 9 where the boiling point elevation (in terms of thermopile output) is shown as a function of concentration for **1** and for triphenylmethane. The latter is assumed to be monomeric, and the average state of aggregation, *N*, of **1** at any concentration is the ratio of the output for triphenylmethane to that for **1**. As may be seen in Table IV, *N* varies with concentration and may be accounted for by assuming a dimerization equilibrium constant of about 240 m^{-1}. Even at the lowest concentration a substantial fraction of **1** is dimeric in THF.

Similar studies using cyclohexane as the solvent show a different behavior. At 25° and over a concentration range of 0.01–0.1 *m* the data yield a constant value of 1.8 for *N*. This is anomalous since a nonintegral value of *N* implies the presence of more than one species. If these species are the monomer and dimer in equilibrium, then *N* should vary with concentration, as it does in the THF system. Clearly, this is not the case as may be seen in Figure 10, and another explanation is required. Note that the last point is erroneous due to incomplete dissolution of **1** at that concentration. The best interpretation of the data appears to be that an impurity of low molecular weight is present in the sample of **1** used and that **1** actually exists as a dimer over the entire concentration range.

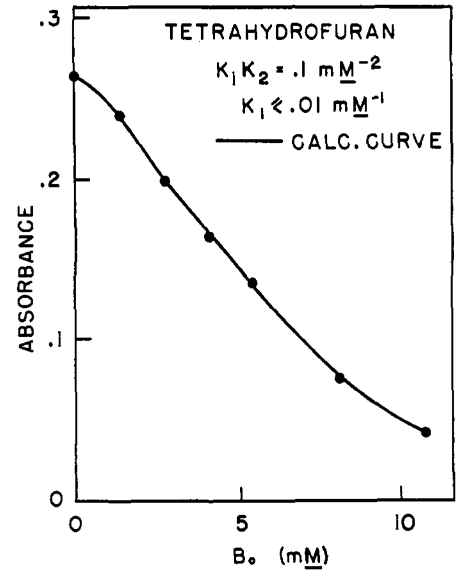

Figure 8. Plot of the height of the 520-nm peak in the visible spectrum of 9-(2-hexyl)fluorenyllithium *vs.* the concentration of added THF (B_0). The curved line is calculated using $K_1 \leqslant 0.01\ \text{m}M^{-1}$ and $K_1K_2 = 0.1\ \text{m}M^{-2}$.

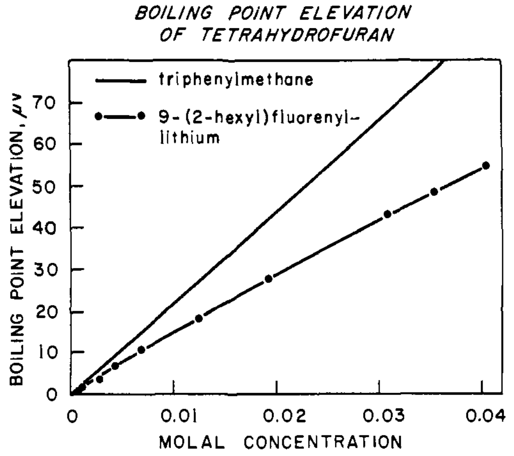

Figure 9. The boiling point elevation of tetrahydrofuran by 9-(2-hexyl)fluorenyllithium (•—•) and triphenylmethane (—) at 25°.

Table IV. Aggregation State of 9-(2-Hexyl)fluorenyllithium in THF at 25°

Concn, *m*	Av deg of aggregation, *N*	Fraction as dimer
0.004	1.39	~0.5
0.010	1.46	~0.6
0.030	1.58	~0.7
0.040	1.63	~0.8

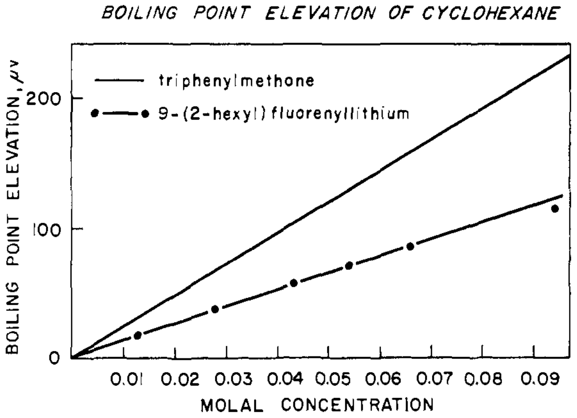

Figure 10. The boiling point elevation of cyclohexane by 9-(2-hexyl)fluorenyllithium (·—·) and triphenylmethane (—) at 25°.

Discussion

The relationship between solvent-dependent spectral behavior and solvent-dependent aggregation in organoalkali metal compounds remains to date largely unexplored. The effects of aggregation on spectral behavior have recently been questioned.[24,25] In the case of 9-(2-hexyl)fluorenyllithium ebulliometry has established solvent-dependent dimerization. There are indications that the solvent-dependent spectral properties of **1** may, to some extent, be contingent on this aggregation behavior.

Dimers of **1** are formed exclusively in cyclohexane at 25°. No measurable amount of dissociation of dimer into monomer is detectable. In THF at 25° an equilibrium between dimer and monomeric **1** is established, with the equilibrium lying toward the side of the dimer. Based on the aggregation data, we conclude that the nmr and optical spectra of **1** are of the dimer in cyclohexane and of a mixture of monomer and dimer in THF. Specifically in THF, the monomer–dimer mixture is composed of at least half dimer at the relatively low concentrations used for the electronic spectra and of at least three-fourths dimer at the higher concentrations employed for the nmr measurements. Colligative data are unavailable for **1** in benzene, diethyl ether, and the cyclohexane–ether mixtures. However, based on the observed aggregation of **1** in cyclohexane and in THF, it is probable that **1** is largely dimeric in each of these solvents. Therefore, dimer is present in substantial, if not predominant, amounts in each of the spectra of **1** recorded in this study. A possible exception might be the spectrum of **1** in HMPA.[7]

The lithium-7 and proton nmr spectra examine the electronic environment of respectively the lithium cation and the alkyl-substituted fluorenyl anion of **1**.[4,6,26] The same overall dependence of cation–anion interaction on solvent polarity emerges from each of these nmr methods. An increase in solvent polarity leads to increased cation–solvent interaction with concurrent diminished cation–anion interaction. The nearly identical lithium-7 chemical shifts for **1** in benzene and cyclohexane are the largest upfield yet reported and suggest that the lithium cation may have reached a limiting *maximum* cation–anion ion pair interaction in hydrocarbons. This behavior is in contrast to that reported for the structural analogue, 1,1-diphenylhexyllithium in hydrocarbons where a significant upfield displacement of lithium-7 chemical shift was noted in cyclohexane over that in benzene.[4] The nearly identical lithium-7 and proton chemical shifts shown by **1** in THF and HMPA, respectively, suggest that in higher polarity solvents the lithium cation may have attained a limiting *minimum* cation–anion interaction. This behavior is in contrast to that reported for fluorenyllithium where the lithium-7 chemical shift underwent downfield displacement in HMPA over that in THF.[26] An intermediate level of cation–anion interaction is indicated for **1** by the nmr data in the low polarity solvents diethyl ether and the cylohexane–ether mixtures.

The nmr data in general reveal the same trends with regard to solvent dependence of cation–anion association which have previously been observed with related organolithiums.[4,26] The lithium cation of the ion pair is poorly solvated in hydrocarbon solvents with the cation–anion interaction at a maximum. As the Lewis base character of the solvent increases, interaction of the cation with the solvent is favored with a corresponding reduction of its interaction with the carbanion.

Two thermodynamically distinguishable ion pair species which coexist in equilibrium have been identified for 9-(2-hexyl)fluorenyllithium, namely contact and solvent-separated ion pairs.[7] Extensive measurements on the absorption spectra of these ion pairs have indicated that the contact ion pair absorbs at a shorter wavelength than the solvent-separated ion pair. The same behavior is observed in unsubstituted fluorenyl alkali metal compounds.[5] In addition, a bathochromic shift in the absorption maximum of the contact ion pair alone was noted with either an increase in the radius of the alkali metal counterion and/or an increase in solvent polarity.[5] These bathochromic shifts are interpreted as reflecting the dual effects of increasing interionic distance and charge delocalization which bring about reduction in the energy of the electronic transition of the aromatic ring system.

From the published data on 9-(2-hexyl)fluorenyllithium,[7] it is evident that **1** is almost completely in the form of its contact ion pair in diethyl ether achieving complete conversion to the solvent-separated ion pair only in the presence of highly coordinating solvents such as THF and HMPA. Presumably then, contact ion pairs predominate in the low polarity solvents cyclohexane, hexane, benzene, and the cyclohexane–ether mixtures.

A solvent-dependent absorption maximum has been singled out as representative of the contact ion pair and the solvent-separated ion pair for 9-(2-hexyl)fluorenyllithium.[7] This solvent-dependent absorption maximum appears for the contact ion pair at 357 nm in diethyl ether and for the solvent-separated ion pair at 387 nm.[7] Reasonably, the absorption maximum for the contact ion pair should occur at the same, or possibly shorter, wavelength in cyclohexane, hexane, and benzene than in diethyl ether, *i.e.*, ≤ 357 nm.[5,7,11] Instead, the absorption maximum, occurring at 368 nm in hydrocarbons, appears at a significantly longer wavelength and at a

---

(24) J. F. Garst, "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 580.

(25) Y. Okamoto and Y. Yuki, *J. Organometal. Chem.*, **32**, 1 (1971).

(26) R. H. Cox, H. W. Terry, Jr., and L. W. Harrison, *J. Amer. Chem. Soc.*, **93**, 3297 (1971).

position *intermediate* between that for the contact and solvent-separated ion pairs. Whereas typically the addition of small amounts of solvating ethers to hydrocarbon solutions of charge-delocalized organolithiums leads to bathochromic shifts,[13] hypsochromic shifts are observed in the case of **1**. These observations lead to the antithetical situation that the transition energy for **1** is lower in hydrocarbons than in diethyl ether, although higher than in THF. The calculated differences in these transition energies are $E_{(\text{ether})} - E_{(\text{cyclohexane})} = 2.5$ kcal mol^{-1} and $E_{(\text{cyclohexane})} - E_{(\text{THF})} = 3.7$ kcal mol^{-1}. A superficial interpretation of these shifts would suggest that there is greater cation–anion interaction in diethyl ether than in hydrocarbon solvents. Clearly this interpretation contradicts the nmr results, and some other explanation is required.

The first explanation which may be considered centers around solvent effects on the electronic spectra of molecules in general. The classical behavior of light induced dipole changes predicts that the more polar (or polarizable) the solvent the smaller the work required to induce charge separation.[27] Hence, with increased medium polarity longer wavelength absorption is expected, except in certain special cases.[11] In these cases, specific interactions with solvent affect the electronic transition energy of dipolar molecules.[28] In the first case, blue shifts may occur when a solvated dipolar molecule experiences a decrease in dipole in the excited state from that in the ground state. The blue shifts are the result of oriented solvent destabilization of the excited state relative to solvation in the ground state. In the second case, blue shifts may occur under the influence of Franck–Condon solvent orientation strain.[28,29] Providing the equilibrium ground state is sufficiently different from that of the excited state, solvent packing strain could bring about a greater destabilization of the instantaneous excited state in polar than in nonpolar solvents. Both the special case of a decrease in dipole in the excited state and the case of the Franck–Condon solvent orientation strain are inconsistent with the relative absorptions of **1** in diethyl ether and THF. Unless there is a different structure for the dimer of **1** in hydrocarbon and ether solvents, neither of these cases appear to be operative in the electronic spectrum of **1**.

In addition to special solvent effects on excitation, it is possible that the structure of the aromatic hydrocarbon itself is affecting the electronic spectrum in a previously overlooked manner. For instance, 9-(2-hexyl)fluorenyllithium is a nonalternant hydrocarbon whereas 1,1-diphenylhexyllithium (**2**) is an odd alternant hydrocarbon. Increasing the solvent polarity causes a progressive shift to longer wavelength in the single broad absorption maximum of **2** in contrast to the behavior of **1**.[11] Unlike **1**, the addition of THF to a hydrocarbon solution of **2** causes red shifts in accord with reduced cation–anion interaction energies.[13] The difference in spectral behavior between **1** and **2** may be a direct consequence of the fact that **1** is a nonalternant hydrocarbon whereas **2** is an odd alternant hydrocarbon.

The electronic spectrum of alternant molecules is well behaved in that steric interactions causing distortions in the π system which inhibit conjugation always cause blue shifts.[10,30] This behavior is the consequence of the pairing properties of the bonding and antibonding π orbitals in alternant molecules.[9,10] In an odd alternant "carbanion" the electronic transition which is most sensitive to anion–cation interaction is the $\pi \rightarrow \pi^*$ excitation of the electrons of the carbon–lithium bond. These electrons, to the first approximation, occupy a nonbonding molecular orbital.[11] The nonbonding orbital arises from participation in the π system of the carbon atom which is involved in carbon–lithium bonding. Ignoring the effect of excess negative charge on the effective electronegativity of the core carbon atoms (Coulomb integrals), the nonbonding orbital is centrally disposed between the bonding and the antibonding π orbitals. This $\pi \rightarrow \pi^*$ transition is generally strong and occurs at energies of the order of one-half of that of the longest wavelength transition in the hydrocarbon.

In contrast, nonalternant hydrocarbons such as the fluorenyl ring system do not have, symmetrically disposed energywise, complimentary bonding and antibonding π orbitals.[9] Steric distortion of the π system in nonalternant molecules causes both hypsochromic and bathochromic shifts, depending on the part of the π system that is most distorted.[10] Solvent-influenced changes in cation–anion interaction bring about changes in charge distribution in aromatic molecules. These charge distribution changes are formally analogous to perturbations brought about by inductive substituent effects. Inductive substituent effects, and consequently solvent-induced charge distribution effects, are less straightforward in nonalternants than in odd alternants.[12]

Hückel MO calculations indicate the highest filled orbital in fluorenyl anion is bonding ($\sim 0.18\beta$) and the lowest empty orbital is antibonding ($\sim 1.0\beta$); the second filled bonding orbital is $\sim 0.70\beta$. The influence of delocalized negative charge density is to reduce the effective electronegativities of the carbon cores, which will alter the relative positions of the energy levels.[30] The effect of differences in amount and distribution of delocalized charge with solvent (as a result of differences in cation–anion interaction) may be blue or red shifts in nonalternants as in odd alternants.[30] Most important is that the bonding and antibonding orbitals in nonalternants do not pair, as they do in alternants, and this results in different spectral behavior of these systems on perturbation. This effect may then be the source of the different solvent-dependent optical behavior of **1** and **2**.

The foregoing discussion has tacitly assumed that the structure of the dimer of **1** is essentially the same in hydrocarbon as it is in ether solvents, aside from the extent of cation–anion interaction. The experimental data have ruled out the likelihood that the monomer–dimer equilibrium is responsible for the abnormally long wavelength absorption of **1** and for the unusual shifts to short wavelength on addition of ether. The data similarly rule out the probability that either an association or a reaction with butyllithium in the system is responsible for the optical behavior of **1**. However, the data do

---

[27] F. A. Matsen, R. S. Becker, and D. R. Scott, "Techniques of Organic Chemistry," Vol. IX, 2nd ed, W. West, Ed., Interscience, New York, N. Y., 1968, p 322.

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

[29] G. C. Pimentel, *J. Amer. Chem. Soc.*, **79**, 3323 (1957).

[30] R. Waack and M. A. Doran, *ibid.*, **68**, 1148 (1964).

not rule out the possibility of a structure for the dimer which is different in hydrocarbons from that in ethers.

Aggregation is in essence a self-solvation. The preference for either aggregation or more extensive solvent interaction is determined by relative "solvation" energetics. Presuming the absence of strong Li–Li interactions,[31] self-solvation or solvent-solvation should have no special effects on carbon–lithium bonding, other than that of the relative solvation energies. In order for aggregation to influence electronic absorption, independent of its effect on cation–anion interaction, perturbation of the π system of one molecule by a second would be required.[10] In THF, where monomer and dimer are in equilibrium, the single absorption maximum indicates that such a situation is absent. In cyclohexane, however, where monomeric **1** is undetectable, perturbation of the π system of one molecule by its partner in the dimer may take place and would be compatible with the spectral data. A structure for the dimer which would favor π-system perturbation would be one in which the two fluorenyl ring systems form a sandwich embedding the two lithium atoms. This structure would allow the two ring systems to be close enough to interact in the same way as cyclophanes interact causing a shift of the electronic transition[10] to longer wavelength than would be expected for monomeric **1** in hydrocarbons. The solvation brought about by the addition of small amounts of ether solvents would cause an effective insulation of the rings from one another diminishing or eliminating this perturbation of the π system. The remaining close contact between the lithium cation and the fluorenyl anion would be reflected by a shift (or return) in the electronic absorption maxima to shorter wavelength.

The addition of small amounts of diethyl ether or THF to cyclohexane solutions of **1** leads to the formation of disolvates in both cases. It is considered likely that the aggregation of **1** in cyclohexane containing small amounts of diethyl ether or THF, as well as in diethyl ether itself, is similar to, or possibly more extensive than, that in THF;[32,33] consequently these disolvates in cyclohexane are probably dimeric and four ether molecules would be associated with each dimer. Etherated sandwich structures would therefore be found in cyclohexane containing limited amounts of diethyl ether and THF. Experimental data would require an analogous structure to be formed also by **1** in diethyl ether. The nmr and electronic spectral properties of **1** in diethyl ether are nearly identical with those of **1** in cyclohexane containing small amounts of THF. The addition of still larger amounts of THF to the cyclohexane solution of **1** would then lead to further loosening of the etherated sandwich and the formation of a dimer with a staggered conformation. This added solvation leads as well to solvent-separated ion pairs, both monomeric and dimeric in THF. Sandwich structures for fluorenyllithium in ether solvents have been proposed.[34] Nmr evidence has led to the proposal that the lithium cation and ether molecules of fluorenyllithium etherates lie above the plane of the aromatic ring.[6,26] A sandwich structure has been proposed by Hogen-Esch and Smid for difluorenylbarium in ether solvents, and this structure is indicated to be retained even when difluorenylbarium is complexed with cyclic polyethers. The evidence indicated that the crown ether is simply sandwiched between the two fluorenyl rings.[34b] A sandwich structure for the diamagnetic dimer of the phenanthrenequinone dianion of sodium and of magnesium has been proposed.[35] A transannular π–π bonded structure is indicated by its optical spectrum, which shows the dimer absorbing at longer wavelength than the monomeric radical ion.

The alternative, layered (sandwich) structure such as that proposed for fluorenyllithium in ether solvents[34a] is not excluded for **1** by our data. Reasonably, one might expect that if such a layered structure existed for **1**, it would be reflected, especially in hydrocarbon solvent, by degrees of aggregation greater than $N = 2$, *i.e.*, by trimer, tetramer, etc., formation. The ebullioscopic data for **1** in cyclohexane show no evidence of aggregates higher than dimers, even at near saturated solutions. Consequently the spectroscopic as well as the ebullioscopic data appear consistent with a sandwich dimer in which the two fluorenyl rings embed the lithium cations in those solvents where **1** exists as a contact ion pair. A loosened, possibly staggered, dimer structure may exist in solvents where **1** is found as a solvent-separated ion pair.

In summary it is difficult to provide a unique explanation for the electronic absorption of **1** in hydrocarbon solution being of intermediate energy between that in diethyl ether and THF, if the energy of this transition is directly representative of cation–anion interaction energies. The lithium-7 and proton nmr data fully support a picture of decreasing cation–anion interaction with increasing solvent polarity. Irregular behavior is evident only in the optical spectrum. Conclusive evidence for aggregate structure differences being responsible for the electronic spectral behavior is lacking; however, the nmr, optical and aggregation data are in agreement with a sandwich structure for **1** in solvents where it is present as a contact ion pair. Alternatively, the electronic spectral changes of **1** with solvent may be a direct consequence of its nonalternant properties.

Acknowledgment. We are grateful for contributions by L. D. McKeever, W. C. Meyer, R. G. Martin, R. O. Trucks, J. P. Heeschen, L. Shadoff, and E. B. Baker.

---

(31) T. L. Brown, L. M. Seitz, and B. Y. Kimura, *J. Amer. Chem. Soc.*, 90, 3245 (1968).

(32) P. West and R. Waack, *ibid.*, **89**, 4395 (1967).

(33) J. A. Ladd and J. Parker, *J. Organometal. Chem.*, **28**, 1 (1971).

(34) (a) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **89** 2764 (1967); (b) *ibid.*, **91**, 4580 (1969).

(35) T. L. Staples and M. Szwarc, *ibid.*, **92**, 5022 (1970).