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AGGREGATION AND SOLVATION OF 9-PROPYLFLUORENYLLITHIUM AND OF α,ω-BIS(9-FLUORENYLLITHIUM)POLYMETHYLENES IN TOLUENE

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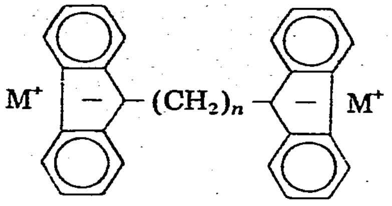
Summary

Bolaform salts of the type $Li^+,Fl^-(CH_2)_nFl^-,Li^+$ (Fl^- = 9-fluorenyl, $n = 2,4$ or 6), when dissolved in toluene, were shown to be present as intramolecular aggregates (λ_m 370 nm) which can be broken up on addition of tetrahydrofuran (THF) or tetrahydropyran (THP) to form solvated tight ion pairs (λ_m 361 nm) and loose ion pairs (λ_m 386 nm). For $n = 6$ the ratio K_1/K_2 of the loose ion pair formation constants for the two terminal ion pairs is close to the statistical factor 4, but for $n = 2$ the ratio is only 0.3. This is attributed to a higher stability of the intramolecular aggregate for this compound. The data for the bolaform salts were compared with those obtained for the one ended salt 9-(n-propyl)-fluorenyllithium. For the latter compound, an equilibrium between the monomeric ion pair (λ_m 353 nm) and the dimeric ion pair aggregate (λ_m 370 nm) was found, the dissociation constant K_d being 2.9×10^{-6} *M*. Addition of THP produces the THP solvated tight ion pair (λ_m 361 nm) and the loose ion pair (λ_m 386 nm).

Introduction

It is well known that properties of ionic species such as their optical spectra or chemical reactivity can be affected by ion pairing or by modifying the structure of ion pairs or their solvation complexes [1]. Such modifications can be brought about by changes in solvent composition, temperature, pressure, additives or other variables. When dealing with ion pairs that are part of a polyelectrolyte chain or a bolaform salt (compounds containing two charges separated by a chain of atoms), intramolecular electrostatic or specific interactions may further influence the behavior of these ion pairs such as their dissociation into free ions, the process of solvent separation into loose ion pairs, or their aggregation. Extensive studies on fluorenyl salts have shown that the optical spectrum of this carbanion provides a sensitive probe for the study of structures of ion pairs and their solvation complexes [1—4]. To gain more insight into intramolecular ion pair interactions we recently synthesized a series of α,ω-bis(9-fluorenyl)-polymethylenes (I) which, by means of a more basic carbanion, can easily be converted into a typical bolaform salt containing two terminal fluorenyl ion pairs, as depicted in structure A [5]. Conductance measurements in tetrahydrofuran revealed that for the cesium salts the first dissociation constant, in comparison to a 9-alkylfluorenyl salt, is enhanced by a factor of 2 to 12 due to formation of a cyclized triple ion, the stability of which is chain length dependent [5]. More recently it was found that the formation of glyme separated ion pairs from the sodium salt of I also differs from that of a normal 9-alkyl-substituted fluorenyl salt [6]. In this case, the glyme separated ion pair formation constants of the two terminal ion pairs increase with chain length by as much as a factor 19, although their ratios remain equal to the statistical factor four except for $n = 2$ in tetrahydropyran. In the latter system the ratio increased to 15, and the formation of an intramolecular ion pair aggregate was invoked to explain this deviation.



(A)

To facilitate the formation of such aggregates and to assess their effect on ion pair solvation we synthesized the lithium salts of I. The aggregation of organolithium compounds in hydrocarbon solvents is well documented [7,8], and while such clusters often break up in more polar media or on addition of cation coordinating ligands, aggregation can still persist in solvents like THF [9] even for delocalized carbanions such as fluorenyl salts [10,11]. In this paper we wish to report the results of spectrophotometric measurements that reveal significant differences between the behavior of the lithium salts of I and that of 9-propylfluorenyllithium, both in hydrocarbon and in ethereal media or their mixtures, differences that can be rationalized in terms of intramolecular ion pair aggregation in the lithium bolaform salts.

Experimental

Materials. The preparation of 9-(propyl)fluorene and of the α,ω-bis(9-fluorenyl)polymethylenes have previously been reported [5]. Spectrograde toluene was dried over calcium hydride and thoroughly degassed. Purification of tetrahydrofuran and tetrahydropyran has been described elsewhere [2].

The lithium salt of 9-(n-propyl)fluorene was prepared under vacuum by treating the hydrocarbon with an equivalent amount of n-butyllithium dissolved in toluene (the heptane present with the BuLi was first removed and replaced by toluene). The reaction, carried out at 50°C, was followed spectrophotometrically,

TABLE 1

ABSORPTION MAXIMA (in nm) AND MOLAR ABSORPTIVITIES[a] OF 9-(n-PROPYL)FLUORENYLLITHIUM AND THE α,ω-BIS(9-FLUORENYLLITHIUM)POLYMETHYLENES IN TOLUENE AND THEIR MIXTURES WITH THF AND THP AT 25°C

Salt	Tight ion pair in toluene						Loose ion pair (excess THF or THP)	
	$<10^{-5}$ M		$\simeq 10^{-2}$ M		Small amount of THF or THP added			
	λ_m	$\epsilon_m \times 10^{-4}$	λ_m	$\epsilon_m \times 10^{-4}$	λ_m	$\epsilon_m \times 10^{-4}$	λ_m	$\epsilon_m \times 10^{-4}$
9-PFl$^-$, Li$^+$	353	1.09	370	0.90	359	1.09	386	1.40
Li$^+$, Fl$^-$(CH$_2$)$_6$Fl$^-$, Li$^+$	368		372	0.90	361	1.13	387	1.40
Li$^+$, Fl$^-$(CH$_2$)$_4$Fl$^-$, Li$^+$	370		372		361		386	
Li$^+$, Fl$^-$(CH$_2$)$_2$Fl$^-$, Li$^+$	370		370	1.10	369[b]	1.10	385[b]	1.40

[a] Absorptivities for bolaform salts refer to individual ion pairs, hence, their values were calculated from equivalent concentrations of ion pairs. [b] In pure THP the main peak is at 369 nm; only a small fraction of ion pairs absorb at 385 nm.

the conversion to the carbanion ($\simeq 10^{-2}$ M) being complete when the optical density had reached a constant value. 1,1-Diphenylhexyllithium was obtained by addition of BuLi to 1,1-diphenylethylene in toluene as described by Waack et al. [12]. This lithium salt was then added to I using a titration procedure previously described [13]. The conversion of I to the lithium bolaform salt is completed when the characteristic hexyl (Ph)$_2$C$^-$ peak appears as a shoulder in the spectrum of the fluorenyllithium bolaform salt. In ethereal solvents the latter salt can also be prepared by treating I with the dimeric dianion of 1,1-diphenylethylene, i.e., Li$^+$, $^-$C(Ph)$_2$CH$_2$CH$_2^-$C(Ph)$_2$, Li$^+$, which can be obtained in THF or THP by treating purified lithium with 1,1-diphenylethylene [14]. A toluene solution of the lithium salt of I can be obtained from its ethereal solution by removing the ether solvent and replacing it by toluene. This must be repeated several times to remove the last traces of THF or THP. The spectrum eventually becomes identical to that of the lithium salts prepared directly in toluene. This is taken as evidence that all THF or THP has been removed.

Experiments were carried out under vacuum in an all glass apparatus and spectra recorded by means of a Cary 14 Spectrophotometer. Effects of ethereal additives on the spectra of the carbanion salts in toluene were carried out at constant salt concentration by using THF or THP solutions containing the same carbanion concentration as that of the toluene solution. Molar absorptivities were determined from the spectra of the individual species (see Table 1) and used in calculating the fractions of the respective ion pairs and their solvation complexes.

Results and discussion

9-(n-Propyl)fluorenyllithium. Concentration and solvent dependent spectra. The wavelengths of the main absorption peak (340—400 nm) for the various systems are recorded in Table 1. In pure toluene the spectrum of PFl$^-$, Li$^+$ (PFl = propylfluorenyl) reveals a concentration-dependent equilibrium between two species absorbing at 353 nm (low concentration) and 370 nm ($>10^{-3}$ M), respectively (see Fig. 1). This suggests the presence of aggregates. Assuming that the 353 nm peak represents the monomeric ion pair, one may write:

$$(\mathrm{PFl^-,Li^+})_n \overset{K_d}{\rightleftharpoons} n\ \mathrm{PFl^-,Li^+} \qquad (1)$$

The aggregation number n and the constant K_d can be obtained from the expression

$$\log A = n \log B - \log K_d/n \qquad (2)$$

where $A = n[\mathrm{PFl^-,Li^+}]_n$ and $B = [\mathrm{PFl^-,Li^+}]$. A plot of log A vs. log B, shown in Fig. 2, yields $n = 2.3$ and $K_d = (2.9 \pm 0.5) \times 10^{-6}$ M at 25°C. The aggregate $(\mathrm{PFl^-,Li^+})_n$ most likely is a dimer, and the deviation from $n = 2$ could have resulted from the uncertainty in determining the exact shape of the monomeric ion pair absorption band.

Support for the dimeric nature of the aggregate comes from ebulliometric data reported by Exner et al. on a similar salt, viz., 9-(2-hexyl)fluorenyllithium, showing that in cyclohexane this lithium salt is a dimer up to 0.1 M concentration [10]. Its absorption maximum, 370 nm in cyclohexane and 368 nm in benzene, corresponds with the high concentration peak of PFl⁻,Li⁺ in toluene. However, high dilution in cyclohexane did not cause their spectrum to change. This

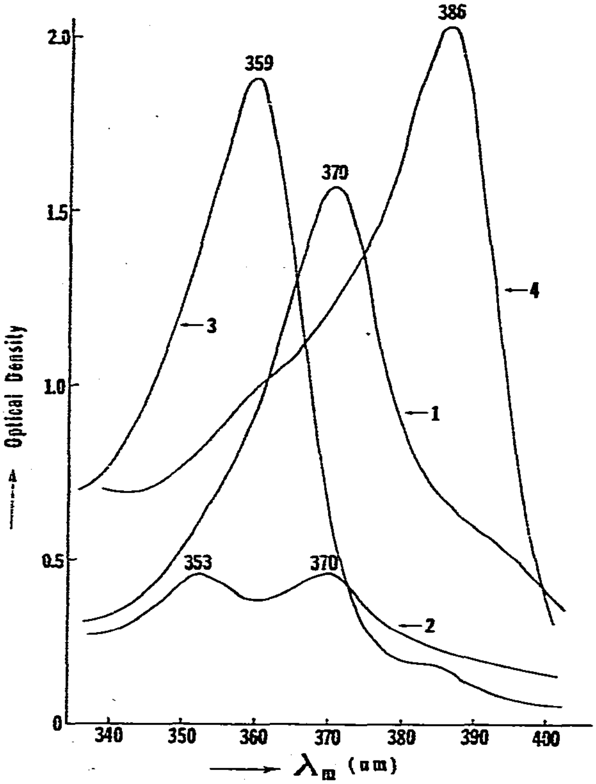


Fig. 1. Optical spectra of 9-(n-propyl)fluorenyllithium; (1) toluene, [PFl⁻, Li⁺] 1.7 × 10^{-3} M; (2) toluene, [PFl⁻, Li⁺] 5.6 × 10^{-6} M; (3) toluene with small amount of THP; (4) pure THP, [PFl⁻, Li⁺] 1.7 × 10^{-3} M.

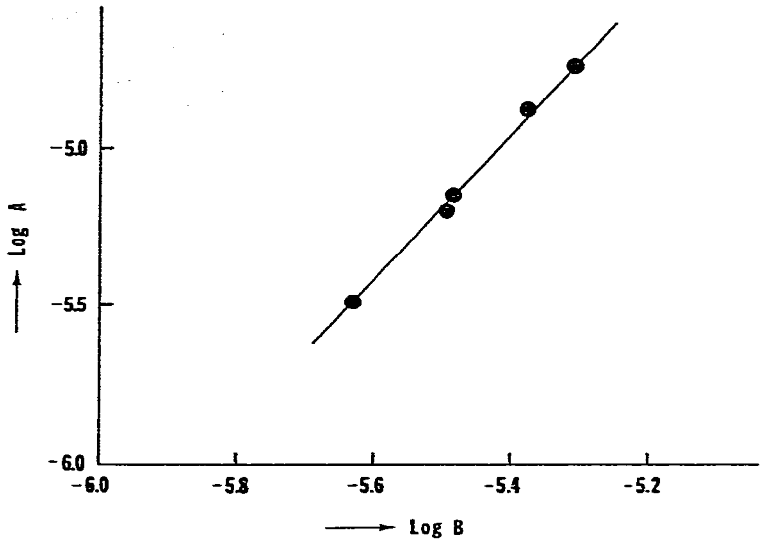


Fig. 2. Aggregates of 9-(n-propyl)fluorenyllithium in toluene at 25°C. $A = n[\text{PFl}^-, \text{Li}^+]_n$; $B = [\text{PFl}^-, \text{Li}^+]$.

may not be surprising since the solvating properties of cyclohexane are considerably poorer than that of toluene, and aggregation constants are likely to be much higher in the former solvent. To our knowledge, the results obtained with PFl^-, Li^+ in toluene constitute the first clear spectrophotometric detection of a monomeric—dimeric ion pair equilibrium for lithium carbanion salts in hydrocarbon solvents, although such equilibria have been known to exist for a long time [15, 16]. Two species were reported to exist in benzene and cyclohexane solutions of diphenylhexyllithium [12], but this equilibrium was found to depend only on temperature, not on concentration. That no shift has been reported for fluorenyllithium itself may not be surprising, since the absence of a bulky 9-alkyl substituent probably yields a much tighter aggregate and, therefore, a lower K_d value.

Our observation of an aggregation equilibrium also clarifies some of the supposedly anomalous spectral shifts observed on addition of ethers [10]. Addition of small quantities of solvents such as THP or THF to organolithium compounds in hydrocarbon media generally produces mono- or di-etherates [1,12, 16—17]. In the case of fluorenyl or other carbanion salts formation of such externally solvated tight ion pairs usually results in a bathochromic spectral shift due to a weakening of the anion—cation interaction, the magnitude of the shift being dependent on the polarity of the additive [1,19—21]. However, Exner et al. reported an anomalous hypsochromic shift from 370 to 360—361 nm on addition of THF to their hexylfluorenyllithium compound in cyclohexane, and to 348 nm on addition of ethyl ether. The same shift is observed in our system when THF or THP is added to PFl^-,Li^+ in toluene at high concentration, but the same spectrum is also obtained when the experiment is carried out with PFl^-, Li^+ at low concentration. In the latter case the spectral shift is a normal bathochromic one, from 353 nm to 359 nm (see Table 1). It is interesting in this respect to note that Hogen Esch and Smid reported for fluorenyllithium in toluene a λ_m of 348 nm [2] while Evans and Rees found in benzene λ_m 357 nm [22].

The latter investigators prepared the salt directly in benzene, while the former authors synthesized their compound in THF, then replacing this solvent with toluene. Clearly, traces of THF remained in their solution and the spectrum was that of a THF solvated tight ion pair, while Evans and Rees were dealing with an ether free aggregate.

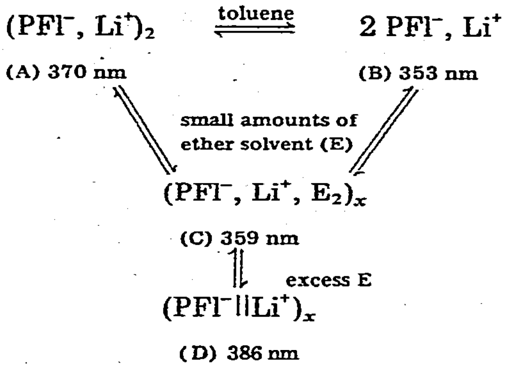
The results of Exner et al. on the hexylfluorenyl salt suggest that the tight ion pairs of PFl^-, Li^+ absorbing at 359 nm are coordinated with two THP or THF molecules. Additional quantities of these ether solvents eventually produce a new absorption band occurring at 386 nm (Table 1). This peak was previously identified as belonging to the loose ion pair of a 9-alkyl-substituted fluorenyl salt, and is essentially independent of solvent and counterion [19]. The equilibrium constant for the reaction (eq. 3) was measured by adding increasing quantities of THP to the salt solution in toluene at constant carbanion concentration. From the relationship of eq. 4 the value for m and K_s can be obtained, where

$$\underset{(359\text{ nm})}{PFl^-, Li^+, 2\,THP} + m\,THP \overset{K_s}{\rightleftharpoons} \underset{(386\text{ nm})}{PFl^-||Li^+} \tag{3}$$

$$\log R = m \log[THP] + \log K_s \tag{4}$$

$R = [PFl^-||Li^+]/[PFl^-, Li^+, 2\,THP]$. A plot of log R vs. log THP is shown in Fig. 3, yielding $n = 2.06$ and $K_s = (1.9 \pm 0.1) \times 10^{-2}\,M^{-2}$. As found for other THP or THF separated lithium carbanion pairs [10,12,19] four THP molecules are coordinated to the Li^+ in the PFl^-, Li^+ ion pair.

To summarize, the various species and absorption maxima for PFl^-, Li^+ are shown in Scheme 1.



SCHEME 1

Species C and D may be either monomeric or dimeric (a hexylfluorenyllithium dimer—monomer equilibrium could be measured in THF between 0.002 and 0.04 M [10]) but aggregation of these solvated tight or loose ion pairs apparently has no effect on the spectrum. Monoetherates of the type PFl^-, Li^+, E could not be detected but may exist at very low carbanion concentration.

The anomalous hypsochromic shift on addition of an ether solvent cannot be attributed to the non-alternant character of the fluorenyl carbanion as suggested by Exner et al. [10], since the shift is normal when the monomeric ion pair is taken as the reference point. The anomaly, therefore, must be found in the dimer

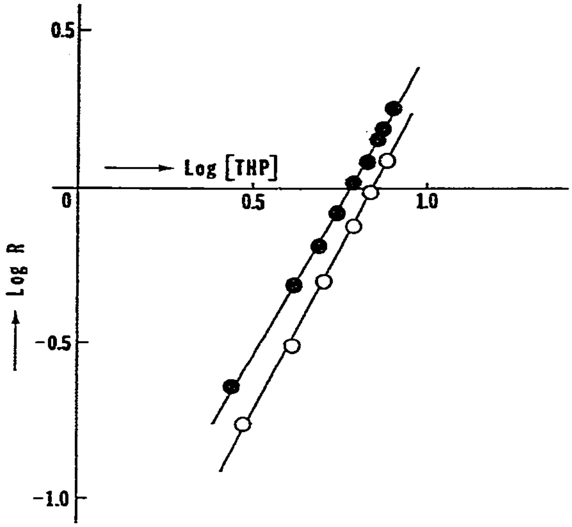


Fig. 3. Formation of loose THP solvated ion pairs in toluene for PFl$^-$, Li$^+$ (○) and for Li$^+$,Fl$^-$(CH$_2$)$_6$Fl$^-$, Li$^+$ (●). *R* represents the ratio of loose to solvated tight ion pairs.

structure of these lithium carbanion salts, and an alternative suggestion by these authors is more attractive. They propose that the 370 nm peak of the dimer results from a mutual pertubation of the π system of the two carbanion rings, which, as shown in other compounds, can cause a bathochromic shift [23]. The dimer was visualized as containing two Li$^+$ cations sandwiched in between the two fluorenyl rings, rather than a stacked structure of the type Fl$^-$, Li$^+$, Fl$^-$, Li$^+$. In the latter case it would be hard to explain why no higher aggregates than dimers are found. Moreover, the spectrum of the dimer of hexylfluorenyllithium in cyclohexane (370 nm) is nearly the same as that in benzene (368 nm). This does not appear to be the case for the monomeric ion pairs. While this ion pair for PFl$^-$, Li$^+$ absorbs at 353 nm in toluene, the 348 nm peak of the ethyl ether complex of hexylfluorenyllithium in cyclohexane [10] suggest that in this solvent the peak of the non-solvated monomeric ion pair, if detectable, would be found at around 345 nm or below. This different behaviour of the monomeric and dimeric ion pairs in the two hydrocarbon solvents is not unexpected since in the proposed dimer structure the two Li$^+$ cations are not exposed to solvent molecules, contrary to that for the cation in the monomeric species.

On addition of an ether, the dimer must undergo a considerable rearrangement in order for the Li$^+$ to interact with one or two ether type molecules. Such a solvate can still be dimeric [10], but its spectrum reveals that π-cloud interactions are now absent. The conversion of the 370 nm dimer to its 360 nm etherate is schematically depicted in Fig. 4, showing a loss of the π-cloud interactions and the exposed Li$^+$ atoms carrying two solvent molecules (indicated by an arrow.)

α,ω-Bis(9-fluorenyllithium)polymethylenes. Formation of intramolecular aggregates. Above 10^{-3} *M* the bolaform salt Li$^+$, Fl$^-$(CH$_2$)$_6$Fl$^-$, Li$^+$ when dissolved in toluene absorbs at 372 nm, the same λ_m as found for the dimeric ion pair (PFl$^-$, Li$^+$)$_2$. However, dilution of the hexane salt below 10^{-5} *M* does not reveal the 353 nm band characteristic for the monomeric PFl$^-$, Li$^+$ ion pair. Only a

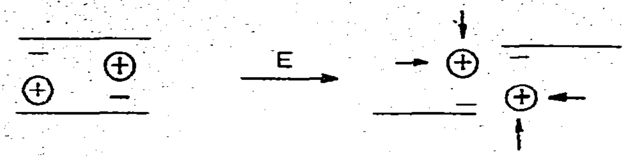


Fig. 4. Schematic representation of the conversion in toluene solution of the 371 nm dimeric aggregate of 9-(n-propyl)fluorenyllithium into the 361 nm dietherate on addition of an ether E. Arrows denote solvating THF or THP molecules.

slight change to 368 nm is observed. The spectra of the butane and ethane salt (see Table 1) between 10^{-2} and 5×10^{-6} M remain unchanged at λ_m 370—372 nm. On the other hand, addition of small quantities of THP or THF again produces a hypsochromic shift to 361 nm characteristic for the etherate complex except for the ethane salt, the spectrum of which remains unchanged at 369 nm.

The concentration independent spectra suggest the presence of an intramolecular aggregate which, in analogy with (PFl$^-$, Li$^+$)$_2$, most likely consists of the two Li$^+$ cations sandwiched in between the fluorenyl moieties [24]. Except for the ethane salt the aggregate easily rearranges to a more open structure with each Li$^+$ complexed to probably two THP or THF molecules as found for other organolithium compounds (exposure to THP or THF vapor is already sufficient to affect the conversion to the etherate).

Excess THF or THP forms the solvated loose ion pair absorbing at 386 nm, but even in pure THP the main absorption band of the ethane salt remains at 369 nm, with a small peak emerging at 385 nm. For PFl$^-$, Li$^+$ and the hexane salt the fraction of loose ion pairs in THP is about 0.9. If the ethane compound is only partially metalated, e.g., 30%, and, therefore, essentially a one-ended carbanion salt of the type HFl(CH$_2$)$_2$Fl$^-$, Li$^+$, the spectrum in THP resembles that of a loose PFl$^-$, Li$^+$ ion pair absorbing at 385 nm. Increasing the degree of metalation causes the ratio of loose to tight ion pairs to decrease until at 100% metalation the fraction of loose ion pairs is less than 0.15. The intramolecular aggregate of the ethane bolaform salt is unusually stable and its structure even in pure THP barely changes.

The study of the fluorenyl bolaform salts has as one of its objectives the determination of effects of neighboring charges (e.g., ion pairs) on the formation of a solvated ion pair complex such as a THP solvated loose ion pair. Two equilibria must be considered which are shown in eq. 5 and 6, where V, W and Y

$$\underset{\text{(V)}}{\mathrm{Li^+, Fl^-(CH_2)_nFl^-, Li^+}} + x\mathrm{THP} \overset{K_1}{\rightleftharpoons} \underset{\text{(W)}}{\mathrm{Li^+, Fl^-(CH_2)_nFl^-||Li^+}} \tag{5}$$

$$\underset{\text{(W)}}{\mathrm{Li^+, Fl^-(CH_2)_nFl^-||Li^+}} + x\mathrm{THP} \overset{K_2}{\rightleftharpoons} \underset{\text{(Y)}}{\mathrm{Li^+||Fl^-(CH_2)_nFl^-||Li^+}} \tag{6}$$

refer to the tight—tight, tight—loose and loose—loose ion pair species, respectively. Most likely the tight ion pair absorbing at 361 nm already contains two externally complexed THP molecules.

When the two ion pair separation processes are independent the ratio K_1/K_2 should be equal to the statistical factor 4. The complex formation constant

$K = K_1/2$ defined by reaction 7 can be determined by plotting log R vs. log [THP], where $R = [Fl^-||Li^+]/[Fl^-, Li^+]$ and is obtaned directly from the spectra.

$$\sim\sim Fl^-, Li^+ + x\ \mathrm{THP} \overset{K}{\rightleftharpoons} \sim\sim Fl^-||Li^+ \qquad (7)$$

Such a plot for the hexane salt is depicted in Fig. 3. The linear relationship yielding $x = 1.96$ and $K = (2.6 \pm 0.2) \times 10^{-2}\ M^{-2}$, implies that the two separation processes are independent, each requiring two THP molecules, the same as found for PFl^-, Li^+. Treated as two separate equilibria gives eq. 8 from which the expres-

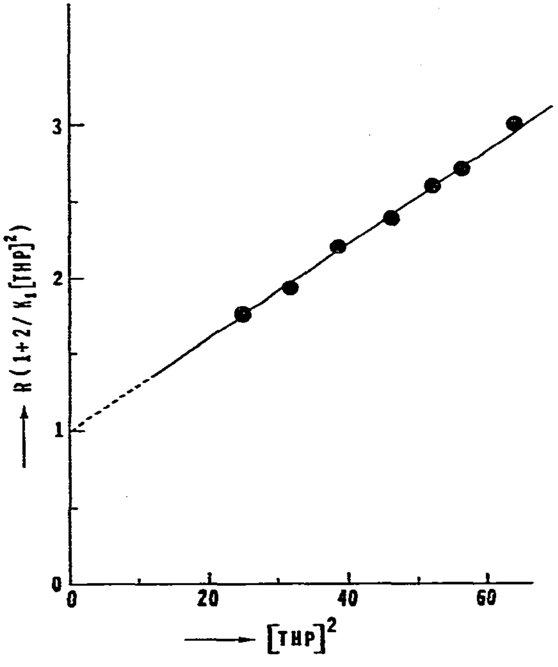
$$R = (W + 2Y)/(W + 2V) \qquad (8)$$

sion 9 can be derived. A rough estimate of K_1 and K_2 can be arrived at by substi-

$$R\{1 + 2/K_1[\mathrm{THP}]^2\} = 1 + 2\,K_2[\mathrm{THP}]^2 \qquad (9)$$

tuting in eq. 9 the R values at two THP concentrations. By successive approximation the exact K_1 and K_2 values for which a plot of $R\{1 + 2/K_1[\mathrm{THP}]^2\}$ vs. $[\mathrm{THP}]^2$ yields a straight line with intercept unity, can be found. Such a plot for the hexane salt in toluene on addition of THP is shown in Fig. 5, and yields $K_1 = 4.7 \times 10^{-2}\ M^{-2}$ and $K_2 = 1.5 \times 10^{-2}\ M^{-2}$, with $K_1/K_2 = 3.1$. The deviation from the statistical factor 4 may be due to experimental error.

The observation of two independent ion pair separation processes for the fluorenyl belaform salts was also made by Collins et al. [6]. In their system glyme-5



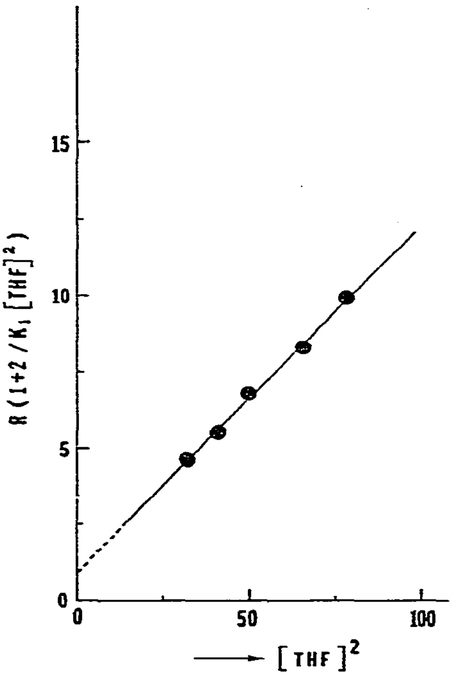


Fig. 5. Determination of the two complex formation constants K_1 and K_2 (equilibria 5 and 6) for THP solvated loose ion pairs of $Li^+, Fl^-(CH_2)_6Fl^-, Li^+$ in toluene.

Fig. 6. Determination of the two complex formation constants K_1 and K_2 (equilibria 5 and 6) for THF solvated loose ion pairs of $Li^+, Fl^-(CH_2)_2Fl^-, Li^+$ in toluene.

was added to the sodium salts dissolved in THF, and for $n = 2, 3, 4$ and 6 the ratio K_1/K_2 was found to vary between 3.5 and 4.3. However, the absolute values of K_1 and K_2 change considerably with the chainlength n, K_1 increasing from 130 M^{-1} for $n = 2$ to $K_1 = 2450\ M^{-1}$ for the hexane salt, the value for 9-propylfluorenyl sodium being 443 M^{-1} (in these processes only one glyme-5 molecule solvates the sodium ion). In our system the value $K_1 = 4.7 \times 10^{-2}\ M^{-2}$ for the hexanelithium salt is about 2.5 times that measured for $\mathrm{PFl^-, Li^+}$.

As noted before, in pure THP bis(fluorenyllithium)ethane contains only a small fraction of loose ion pairs. However, a THF solvated loose ion pair is formed on addition of a sufficient quantity of THF. For the corresponding butane and hexane salts, as well as for $\mathrm{PFl^-, Li^+}$, the spectra in mixtures of toluene and THP generally revealed three simultaneous absorption maxima, the 361 nm band of the open dietherated tight ion pair, the 370 nm peak of the non-solvated aggregate and the 386 nm loose ion pair band. For the ethane salt in THF/toluene mixtures only the 369 and 386 nm band are observed. Experiments similar to those described for the hexane compound were carried out for the ethane salt in THF/toluene mixtures and a plot of eq. 9 for this system is shown in Fig. 6. A straight line is found for $K_1 = 1.8 \times 10^{-2}\ M^{-2}$ and $K_2 = 5.6 \times 10^{-2}\ M^{-2}$, with $K_1/K_2 = 0.32$.

The peculiar behavior of the bis(fluorenyllithium)ethane salt is not limited to the lithium compound. Collins et al. [6] found a ratio of $K_1/K_2 = 15$ for the glyme-5 ion pair separation process of the sodium salt in tetrahydropyran. It was argued that in that system separation of the first $\mathrm{Na^+}$ ion results in the formation of a species $\mathrm{Fl^-, Na^+, Fl^-||Na^+}$, with the second $\mathrm{Na^+}$ trapped in between the two fluorenyl rings, causing the second separation step to the more difficult. This type of structure, which resembles the intramolecular cyclized triple ion formed on dissociation of the cesium bolaform salts in THF [5], also was postulated to exist in 1,2-dimethoxyethane. In that solvent, without glyme-5 present, the ethane sodium salt has a spectrum identical to that of a mixture of equal fractions of tight and loose ion pairs.

The low K_1/K_2 ratio for the lithium salt is probably related to the high stability of the intramolecular aggregate in toluene and even in some ethereal solvents. The absence of a 361 nm peak suggests that the etherated tight ion pair for the ethane salt apparently exists in a form which does not require a rearrangement of the non-solvated aggregate in toluene. It has been argued [6] that in a 9-fluorenylethane aggregate the short ethane chain forces the two fluorenyl rings in a more tilted position. This would make the two $\mathrm{Li^+}$ ions between the rings somewhat more accessible to solvating molecules without the necessity for a drastic conformational change in the aggregate. The first solvent-separation step leads to complete solvation of the $\mathrm{Li^+}$ cation, and to accommodate the solvent molecules the aggregate is likely to change into a more open structure. This apparently requires a considerable amount of energy, but once this is accomplished, the second solvent-separation step proceeds considerably easier. The low K_1/K_2 value, therefore, suggests that species of the type $\mathrm{(THF)_2\ Li^+, Fl^-CH_2CH_2Fl^-||Li^+}$, present after the first separation step, can only make up a small fraction of the total amount of ion pairs present. This may be the reason for not observing the 361 nm band belonging to the solvated tight ion pair. The close proximity of the two ion pairs in the ethane salt apparently does not affect the carbanion spectrum since the loose ion pair of the compound has a spectrum identical to that of PFl$^-$, Li$^+$.

In conclusion, our investigations show that the solvation of α,ω-bis(9-fluorenyllithium)polymethylenes in toluene is chain-length dependent, although the basic structure of the intramolecular aggregate, judging from the nearly identical optical spectra, does not appear to differ much from that of the dimeric ion pair aggregate of the one ended 9-propylfluorenyllithium. It may be of interest to examine the reactivities of these one- and two ended lithium salts in toluene. The former one dissociates on dilution to the monomeric ion pairs which are usually much more reactive than the dimeric species. The bolaform salts remain aggregated even at very low concentration, and, in comparison with PFl$^-$, Li$^+$, may be much less reactive in addition and protonation reactions.

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Notes added in proof:

23 It has been suggested that the dimer spectrum may result from exciton exchange between the two fluorenyl chromophores, and that the bathochromic shift of the aggregate to 370 nm indicates an antiparallel orientation of the two carbanions, as is also proposed in Fig. 4. See T.E. Hogen Esch and M.J. Plodinec, J. Phys. Chem., 80 (1976) 1090.

24 The possibility that the species absorbing at 370—372 nm may be an intermolecular dimer composed of two interacting bolaform lithium molecules, as suggested by one of the referees, can not be entirely excluded.