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SOLVATION OF ION PAIRS OF BARIUM AND STRONTIUM SALTS OF α,ω-BIS(9-FLUORENYL)POLYMETHYLENES IN TETRAHYDROFURAN

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Summary

The conversion of tight ion pairs into loose (solvent separated) ion pairs for strontium and barium salts of the dicarbanions $\text{Fl}^-(\text{CH}_2)_n\text{Fl}^-$ (where Fl^- is 9-fluorenyl and n equals 2, 4 or 6) was studied spectrophotometrically in tetrahydrofuran as a function of temperature, and compared with the behavior of the barium and strontium salt of the monocarbanion 9-n-butylfluorenyl. On cooling to —80°C the barium salts, $\underbrace{\text{Fl}^-, \text{Ba}^{2+}, \text{Fl}^-}$, for n equals 4 and 6 are converted to the mixed tight-loose ion pair $\underbrace{\text{Fl}^- \| \text{Ba}^{2+}, \text{Fl}^-}$ ($\Delta H = -8$ kcal/mol, $\Delta S = -36$ eu). The strontium salts of these two compounds are already fully separated ion pairs below —30°C, i.e., $\underbrace{\text{Fl}^- \| \text{Sr}^{+} \| \text{Fl}^-}$. However, the dicarbanion salt with n equals 2 remains a tight ion pair down to —110°C, at least when barium is the counter ion. With strontium this compound is also difficult to solvate, but at —100°C the tight ion pair slowly converts to a fully solvated loose ion pair complex, a process which is followed by precipitation of the salt. The possible cause of this peculiar behavior is being discussed.

1. Introduction

In solvents of low dielectric constants, ions readily associate to ion pairs, triple ions or higher aggregates. When a molecule is endowed with more than one ionic moiety (e.g., a polyelectrolyte or a bolaform salt where two charges are separated by a chain of atoms), ionic interactions may lead to inter- or intramolecular aggregates, depending on the distance between the ionic groups, their concentration, and other factors. The phenomena are more complex in ion-solvating media, e.g., in ethereal solutions of carbanion salts, where the existence

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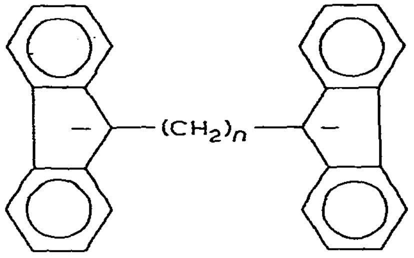
of different kinds of ion pairs has been amply documented [1—4].

The frequent use of species with two carbanionic ends such as in the anionic polymerization of two-ended living polymers [1] prompted us some time ago to study intramolecular interactions in alkali salts of bis(9-fluorenyl)polymethylenes as a function of the nature of the alkali ion, the solvent and the length of the chain separating the two carbanions [5—7]. The compounds, shown below,

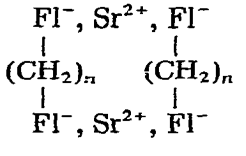


Bis(9-fluorenyl) polymethylenes

(I, n = 2;
II, n = 4;
III, n = 6)

were selected for these studies because the fluorenyl carbanion (Fl^-) is a sensitive spectrophotometric and conductometric probe for determining the solvation state of carbanion pairs [2,8]. The results show that solvents or ligands which interact with alkali cations to form externally solvated ($C^-, M^+\cdots S$) or loose ($C^- \| M^+$) ion pairs decrease the stability of intramolecular aggregates of the type $\underline{Fl^-, M^+, F}l^-$ or $\underline{Fl^-, M^+, F}l^-, M^+$. However, salt I ($n$ = 2) frequently behaves differently, and stable aggregates of the above type do exist in solvents like tetrahydrofuran and 1,2-dimethoxyethane.

The number of possible ionic structures is even larger with alkaline earth cations as the counterions. Spectrophotometric [9—12], conductance [13] and kinetic studies of strontium and barium salts of fluorenyl, cumyl [14] and polystyryl [15—17] have underscored the complexity of these systems. It may be anticipated that alkaline earth salts of I, II or III form intramolecular ion pairs of the type $\underline{Fl^-, M^{2+}, F}l^-$, although intermolecular aggregates such as IV cannot be excluded (15).



$$\begin{array}{ccc} Fl^-, & Sr^{2+}, & Fl^- \\ | & & | \\ (CH_2)_n & & (CH_2)_n \\ | & & | \\ Fl^-, & Sr^{2+}, & Fl^- \end{array}$$

(IV)

The solvation state of the carbanion pairs affects their reactivity and stereochemistry. Barium and strontium salts of I, II and III can again serve as sensitive probes to study changes in the ion pair structure as a result of solvent-cation interactions. The present study deals with such changes as a function of temperature in tetrahydrofuran as solvent. The results, when compared with those obtained for a corresponding monocarbanionic salt, viz., barium or strontium di(9-n-butylfluorenyl) [18], reveal some interesting phenomena, especially for the salts with $n = 2$.

Experimental

1,2-Bis(9-fluorenyl)ethane ($n = 2$) and 1,6-bis(9-fluorenyl)hexane ($n = 6$) were kindly supplied to us by the Union Carbide Corporation, while the synthesis of 1,4-bis(9-fluorenyl)butane ($n = 4$) was reported earlier [5,19]. 9-Butylfluorene was synthesized by adding sodium fluorenyl [8] in THF to an excess of butylbromide. The compound was purified by sublimation and its purity checked by CrC.

The carbanions were obtained by stirring under vacuum at room temperature THF solutions of the respective hydrocarbons on an excess of finely divided barium or strontium. The technique for making reactive surfaces of these two metals has been described elsewhere [20]. The progress of the reaction was monitored spectrophotometrically and was stopped after the optical density reached a constant value. The reactions are essentially quantitative but take a few days to complete. The carbanion solutions were filtered under vacuum through sintered glass, sealed in ampoules and stored in a freezer. Spectra were measured between 40° and —100°C by means of a Beckman Acta V spectrophotometer equipped with a special thermostatted sample compartment.

Results and discussion

Formation of carbanion salts

The formation of the dicarbanionic salts $\underline{\mathrm{Fl}^-, \mathrm{M}^{2+}, \mathrm{Fl}^-}$ could conceivably proceed via the monocarbanionic species $\mathrm{Fl(CH_2)_n\,Fl^-, M^{2+}, Fl^-(CH_2)_n\,Fl}$. In case of incomplete conversion, such species may affect the spectral data for the dicar-

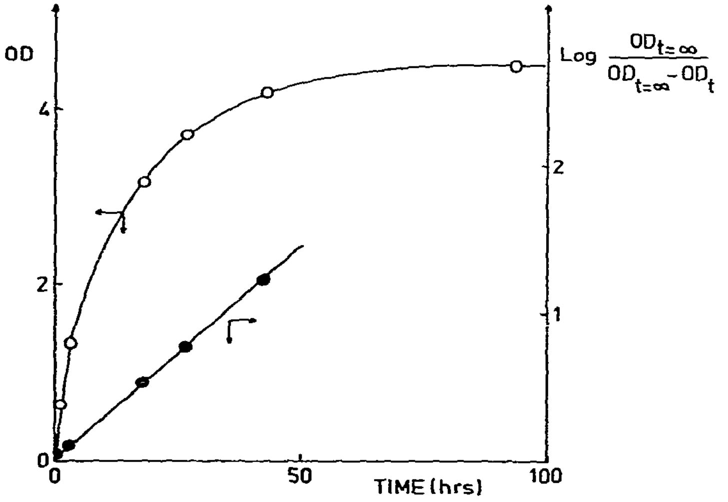


Fig. 1. Formation of barium bis(9-fluorenyl)hexane in THF at 20°C.

banionic salts. To check for their presence, the formation of one of the salts, barium bis(9-fluorenyl)hexane was followed simultaneously by optical spectroscopy and by conductance. The dicarbanion $\underline{\mathrm{Fl^-, M^{2+}, Fl^-}}$ should be non-conducting even at very low concentration, while the conductance of the monocarbanionic salt should resemble that of barium 9-butylfluorenyl.

The results show that during formation of the barium salt of III the conductivity rises to a maximum of only 0.14 μ mho at about 50% conversion where the carbanion concentration reached a value of 1.2×10^{-3} *M*. At 100% conversion the conductivity is down to 0.05 μ mho. Barium 9-butylfluorenyl has a much higher conductivity, in fact, the value 0.14 μ mho is already reached at 10^{-6} *M* [18]. Hence, the conductivity experiment strongly suggests that from the start the difluorenyl hydrocarbon is directly converted into the dicarbanionic salt $\underline{\mathrm{Fl^-, Ba^{2+}, Fl^-}}$. This appears to be confirmed from optical measurements. Figure 1 depicts the kinetic results derived from optical measurements at the 361 nm peak of the tight ion pair of $\underline{\mathrm{Fl^-, Ba^{2+}, Fl^-}}$. The optical density reaches a maximum after about 80 h (prolonged stirring eventually causes the OD to decrease due to slow destruction of the carbanions). A plot of log $\mathrm{OD_\infty}/(\mathrm{OD_\infty} - \mathrm{OD_\lambda})$ versus time is linear up to at least ninety percent conversion. Such a first order dependence on hydrocarbon concentration is in agreement with the proposed direct formation of the dicarbanion.

Optical measurements

At room temperature in THF the barium salts of 9-butylfluorenyl and of I,

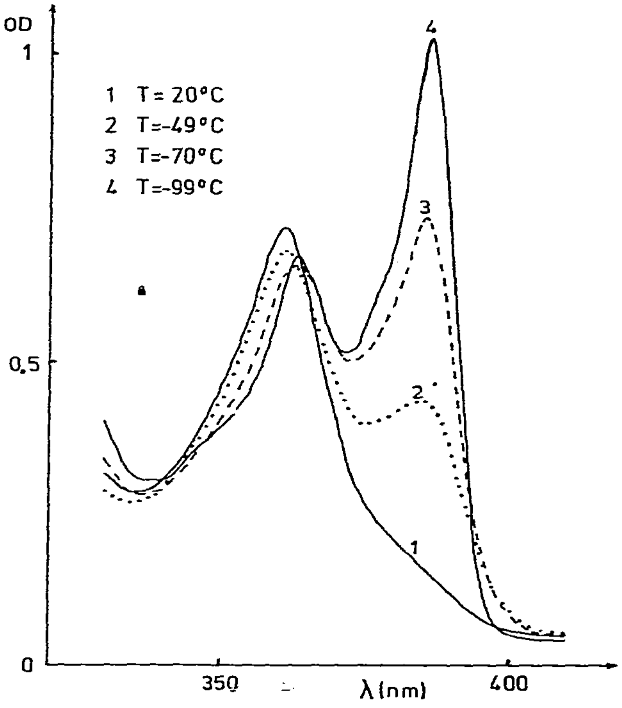


Fig. 2. Spectrum of barium bis(9-fluorenyl)butane in THF between 20 and —99°C. [carbanion] = 2×10^{-4} *M*.

II and III exist exclusively as tight ion pairs, the main absorption band being at λ_m = 361 nm. This maximum is 14 nm higher than the 347 nm maximum of difluorenylbarium [9], the difference being identical to that found between the alkali salts of 9-alkyl-substituted and unsubstituted fluorenyl carbanions [21]. The extinction coefficient is much lower than for the alkali salts, similar to what was observed for barium and strontium difluorenyl [11,13]. For barium bis(9-fluorenyl)hexane, assuming quantitative conversion (Fig. 1), ϵ_m 361 nm was calculated to be 5500 per carbanion. Values of 5250 and 5900 for this salt were obtained by converting it to the lithium salt (exchange with LiCl) and the starting hydrocarbon (with methanol), respectively. The average $\epsilon_m = 5500 \pm 200$ compares with a value of 12 000 found for potassium or cesium fluorenyl [8]. The low extinction coefficients found for the tight ion pairs of divalent salts of fluorenyl have been attributed to hypochroism caused by the close proximity of the two chromophores [9].

Except for the barium salt of I, a new absorption maximum emerges at 387 nm on cooling the barium solutions. The λ_m is identical to that previously recorded for the loose ion pair of alkali 9-alkyl-substituted fluorenyl salts [21]. An example of the temperature-induced spectral changes are shown in Fig. 2 for barium bis(9-fluorenyl)butane. Barium difluorenyl itself does not show a spectral change even down to —100°C [9], but a substituent at the 9-position of fluorenyl is known to facilitate the formation of loose ion pairs. However,

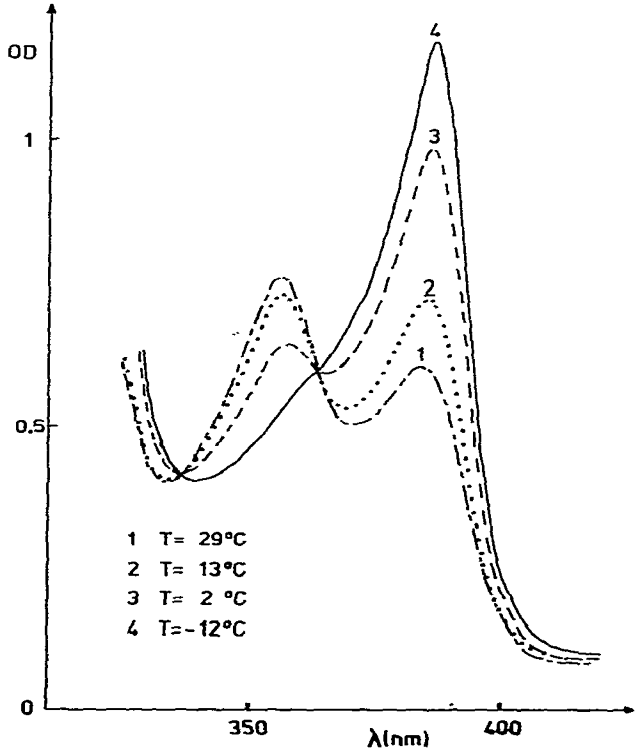


Fig. 3. Spectrum of strontium bis(9-fluorenyl)hexane in THF between 29 and —12°C; [carbanion] = 3×10^{-3} *M*.

the 361 nm tight ion pair band persists also at low temperature. Loose ion pairs are formed in a two step solvation process,

$$\mathrm{Fl^-, M^{2+}, Fl^-} \overset{K_1}{\rightleftharpoons} \mathrm{Fl^-, M^{2+}\|Fl^-} \overset{K_2}{\rightleftharpoons} \mathrm{Fl^-\|M^{2+}\|Fl^-} \qquad (1)$$

and in the second step, as in the ionization of a divalent salt, a greater electrostatic energy must be overcome resulting in a smaller negative value of the solvation enthalpy.

Similar spectral changes can be observed for the strontium salts of 9-butylfluorenyl and the salts of II and III. However, while in THF strontium butylfluorenyl still contains a fraction of tight ion pairs at −100°C, the difluorenylbutane and hexane salts give exclusively loose ion pairs below −30°C as shown for compound II in Fig. 3. Interaction of THF with Sr^{2+} is stronger than with the larger Ba^{2+}, and formation of loose ion pairs is easier with Sr^{2+} as cation [10]. The tight ion pair for all strontium salts is at 357 nm, which is again 14 nm higher than found for the unsubstituted strontium difluorenyl (343 nm).

A different behavior is found for the barium and strontium salts of bis(9-fluorenyl)ethane. No change in optical spectrum is observed on cooling their THF solutions down to −90°C. Further cooling does not change the barium salt, but time-dependent changes occur at around −100°C for the strontium salt, the 361 nm tight ion pair peak being gradually replaced by the 391 nm peak of the loose ion pair, followed by precipitation of the salt. We will discuss this peculiar observation later.

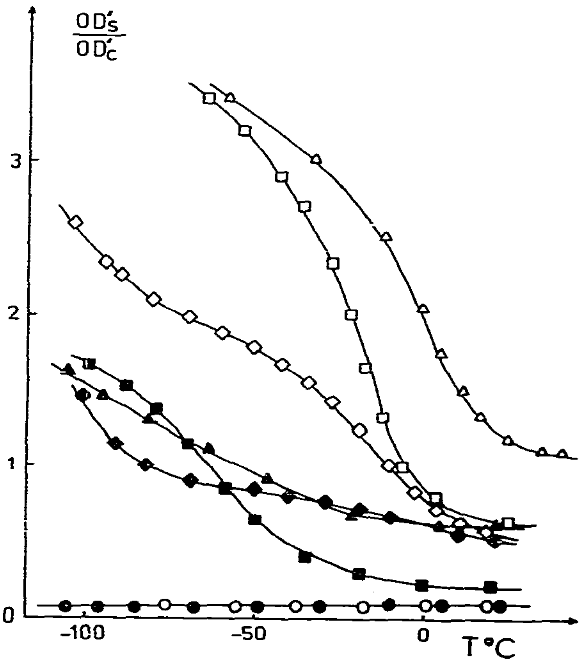


Fig. 4. Temperature dependence of the ratio OD'_s/OD'_c in THF for barium (◆) and strontium (◇) salts of 9-butylfluorenyl, and for the barium (●, ■, ▲) and strontium (○, □, △) salts of bis(9-fluorenyl)ethane, -butane and -hexane, respectively.

The difference in ion pair solvation of the various barium and strontium difluorenyl salts is graphically depicted in Fig. 4. The ratios of the optical densities, measured at the respective absorption maxima of the loose and tight ion pair (corrected for changes in volume on cooling) are plotted as a function of temperature. This quantity qualitatively measures the ratio of the fraction of the two kinds of ion pairs belonging to the three species of equilibrium 1. Note that the ratio is very low and nearly temperature independent for barium and strontium bis(9-fluorenyl)ethane, but reaches a value larger than 3.0 for the strontium salts of bis(9-fluorenyl)butane and -hexane. A value 2.5 at 25°C and 3.5 at —80°C is found for the cryptand[2.2.2.] complex of barium 9-butylfluorenyl, a complex whose spectrum does not show any contribution of a tight ion pair band. The ratios for the barium salts remain substantially below these values, implying that at —100°C tight ion pairs still exist, most likely in the form $Fl^-, M^{2+}||Fl^-$. The bolaform salts of III have higher fractions of loose ion pairs than those of II. Apparently, a longer chain separating the two fluorenyl carbanions facilitates the formation of loose ion pairs, an observation that is confirmed from data obtained on glyme interactions with the alkali salts of these dicarbanions [6]. Note also that the ratio OD'_s/OD'_c (Fig. 4) between 25°C and about —25°C is nearly constant but different for the barium salts of I, II and III, the values being 0.1, 0.2 and 0.6, respectively. The spectrum of II and especially of III show a distinct shoulder at the λ_m of the loose ion pair. This was also observed in barium difluorenyl [9], and in this compound the ratio OD'_s/OD'_c remains essentially the same down to —90°C. This transition at 386 nm in the tight ion pair spectrum is not due to the presence of a small fraction of loose ion pairs, but has been attributed to exciton coupling between the two fluorenyl carbanions [22]. The intensity and position of this transition depends on the distance and angle between the two chromophores, factors which are expected to depend on the chainlength. The same transition probably exists for the strontium salts of II and III but it is masked by the loose ion pair band which is already strong at 25°C.

Cryptand[2.2.2.] forms a 1 : 1 loose ion pair complex with barium bis(9-fluorenyl)hexane and -ethane, both giving a sharp absorption maximum at 387 nm. The complexes are not very soluble. With benzo-18-crown-6, the main peak is at 387 nm, with a distinct shoulder at 367 nm. The spectrum is the same at crown to Ba^{2+} ratios of 1 and 2. The species most likely is a 1 : 1 crown-barium complex as found for barium difluorenyl and dibenzo-18-crown-6 [9]. The latter species is a mixed tight-loose ion pair Fl^-, Ba^{2+}, Cr, Fl^-, with distinct maxima at 347 nm and 372 nm. For the bolaform salt the species Fl^-, Ba^{++}, Cr, Fl^- may not be able to maintain its cyclic structure due to steric interference of the large crown ligand (see below).

By calculating the ratio R of loose to tight carbanion pairs, $[Fl^-||M^{2+}]/[Fl^-, M^{2+}]$, it is possible to obtain the enthalpy change for the first solvation step of the barium salts. Assuming a two-step solvation (eq. 1) it can be easily shown that $R = (1 + 2K_2)/(1 + 2/K_1)$ [10]. For the barium salts, $K_2 \ll K_1$, hence $R = 1/(1 + 2/K_1)$, or $K_1 = 2R/(1 - R)$. The enthalpy of the first solvation step, ΔH_1, can now be obtained by plotting $\log 2R/(1 - R)$ versus $1/T$. The ratio R can be calculated at each temperature by determining the optical density contributions of the tight and loose ion pairs, and the ratio of the two extinction

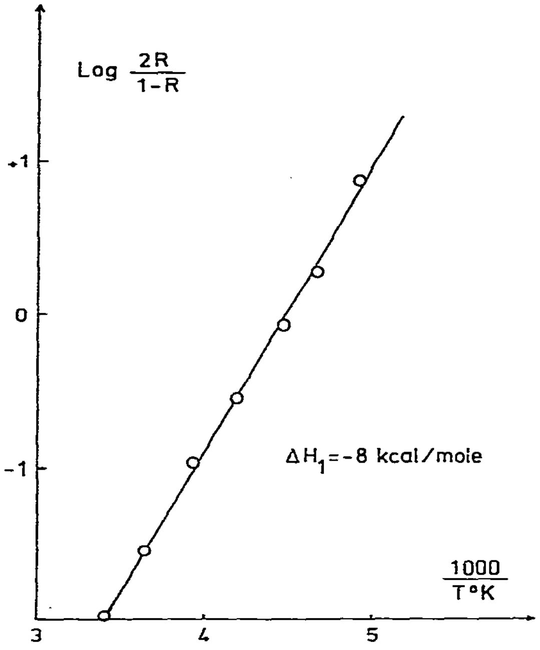


Fig. 5. Plot of log $2R/(1-R)$ versus $1/T$ for barium bis(9-fluorenyl)butane in THF.

coefficients, i.e., $R = \mathrm{OD_s}\epsilon_c/\mathrm{OD_c}\epsilon_s$. To calculate these contributions, solution spectra of carbanions are used which over the entire temperature range exist as either tight or loose ion pairs [8]. For this purpose, the cryptand complex of barium 9-butylfluorenyl can serve as the loose ion pair, while barium (9-fluorenyl)ethane is an example of a tight ion pair. Corrections were made for contributions at the 387 nm peak resulting from exciton coupling.

Figure 5 depicts a plot of log $2R/(1-R)$ vs. $1/T$ for barium bis(9-fluorenyl)-butane. The thermodynamic parameters for the first solvation step calculated from the straight line are $\Delta H_1 = -8$ kcal/mol, $\Delta S = -36$ e.u. The data are more difficult to interpret for the strontium salts, since both solvation steps overlap. Assuming both separation steps to act independently (i.e., $K_1 = 4K_2$) one obtains a reasonably straight line by plotting log R vs. $1/T$ yielding $\Delta H = -13$ kcal/mol, close to the —12.3 kcal/mol found for strontium difluorenyl in THF [10]. The accuracy in the ΔH values is probably not better than 2 or 3 kcal/mol since the assumption was made that the tight ion pair spectrum of $\underline{\mathrm{Fl}^-, \mathrm{M}^{2+}, \mathrm{Fl}^-}$ is identical to that of the tight ion pair end of the mixed ion pair $\underline{\mathrm{Fl}^-, \mathrm{M}^{2+}\|\mathrm{Fl}^-}$. However, hypochroism and exciton coupling (see above), both of which depend on the distance and angle between the fluorenyl rings, may give different extinction coefficients for the two ion pairs, although we have evidence that the differences are not great. Unfortunately, conductance measurements from which frequently conclusions can be drawn regarding the thermodynamics of the solvation process [8,13] cannot be used with the alkaline earth salts of the difluorenylpolymethylenes since species such as $\underline{\mathrm{Fl}^-, \mathrm{M}^{2+}, \mathrm{Fl}^-}$ are non-conducting. Nevertheless, we believe that the reported thermodynamic parameters are reasonable.

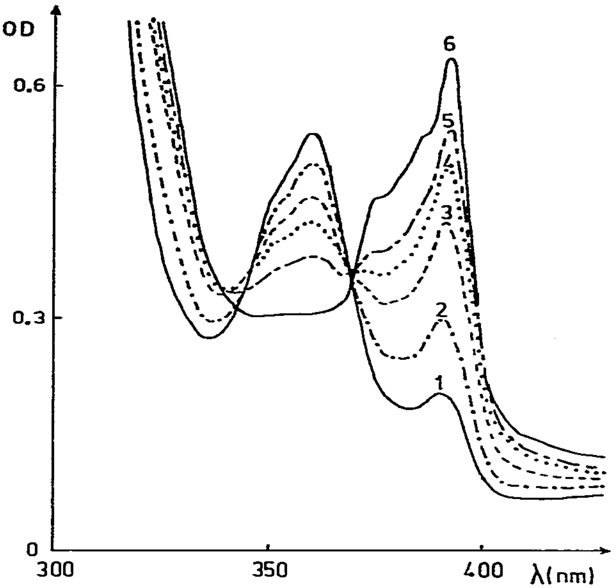
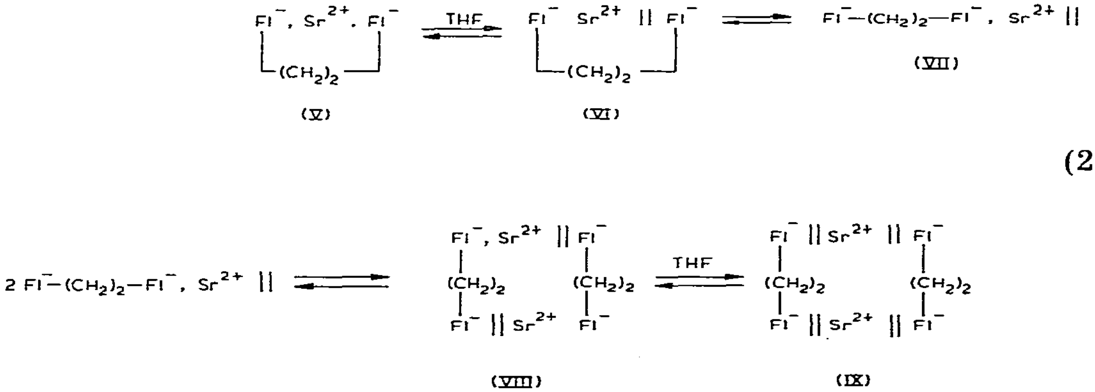


Fig. 6. Spectral changes as a function of time for strontium bis(9-fluorenyl)ethane in THF at —100°C. Time: (1) 6 min; (2) 13 min; (3) 19 min; (4) 23 min; (5) 28 min; (6) 60 min.

Let us now return to the peculiar phenomenon observed for strontium bis(9-fluorenyl)ethane. Down to —90°C only the 361 nm tight ion pair band can be seen. At about —92°C a very small but distinct peak emerges at 391 nm, but it does not increase over a two hour period. However, further cooling to —100°C causes this peak to increase at the expense of the 361 nm band, and in less than one hour only the 391 nm loose ion pair band is present (the small bathochromic shift in the tight and loose ion pair maximum of the ethane salt as compared to the butane and hexane salt was also noted for sodium bis(9-fluorenyl)-ethane [6]). The spectral changes are reproduced in Fig. 6. Note the isosbestic point, although close to the end of the reaction slow precipitation occurs, and the two spectra recorded at high conversion do not pass through the isosbestic point. The entire process is reversible. Raising the temperature back to —90°C solubilizes the precipitate, the absorption maximum being again at 361 nm.

Experiments carried out previously with the sodium salt of bis(9-fluorenyl)-ethane revealed that, once the first cation is solvated, the second sodium ion is held more tightly between the two fluorenyl rings. For example, in 1,2-dimethoxyethane the sodium salts of the compounds II and III are loose ion pairs, but the ethane salt is present in the form $\mathrm{Na}^+\|\underbrace{\mathrm{Fl}^-, \mathrm{Na}^+, \mathrm{Fl}^-}$ [6]. Also, in tetrahydropyran as solvent, addition of tetraethylene glycol dimethyl ether leads to glyme-separated ion pairs. For compounds II and III the two carbanionic ends act independently, the ratio of the glyme-separation constants being 4. But for compound I the ratio is 15, implying that the second Na^+ is more reluctant to separate from the dicarbanion [6]. Therefore, it is not surprising that with a divalent cation the species $\underbrace{\mathrm{Fl}^-, \mathrm{M}^{2+}, \mathrm{Fl}^-}$ is found to be exceptionally stable when only two CH_2 groups separate the two fluorenyl carbanions. It makes it difficult for these barium and strontium salts to form loose ion pairs at temperatures where the butane- and hexane-strontium salts are already fully separated. In fact, the latter salts form loose ion pairs easier than the 9-butylfluorenyl salts.

At very low temperature the solvent interaction with Sr^{2+} is apparently strong enough to separate this cation (but not Ba^{2+}) from at least one of the two carbanionic ends. This would form the solvated complex $Fl^-\|Sr^{2+}, Fl^-$, but to accommodate the THF molecules the cyclic structure, due to the short $(CH_2)_2$ chain will probably open up to form $Fl^-(CH_2)_2\,Fl^-Sr^{2+}\|$. However, a high concentration of free Fl^- ends is unlikely, since conductance measurements on the bis(9-n-butyl fluorenyl) salts show that in THF the dissociation constant for the strontium salt at −95°C is only 2.3×10^{-7} *M* and that for the barium salt 1.9×10^{-7} *M*. Therefore, the species $Fl^-(CH_2)_2Fl^-Sr^{2+}\|$ most likely will dimerise to form the aggregate VIII. Aided by the presence of a neighboring Fl^- group in VIII, the second Fl^-Sr^{2+} tight ion pair bond can now be transformed into a loose ion pair by binding of additional THF molecules to Sr^{2+}. This then forms the fully solvated dimeric complex IX which should give one absorption maximum at 391 nm. The sequence of transformations is shown in equations 2.



(2)

Most likely, higher aggregates can also form. A possible and alternative mechanism to explain the slow transformation of V into a solvent-separated complex is that species VI associates with the dimer complex IX. Loose ion pair complexes, due to their larger dipole moment, often show a greater preference for aggregation than solvated tight ion pairs. This can lead to shifts in ion pair equilibria at higher concentration [20]. Also, the often low solubility of solvated loose ion pair complexes suggests a more effective aggregation of these species. Once VI is complexed to IX, the Sr^{2+}, Fl^- ion pair in VI can be changed to $Sr^{2+}\|Fl^-$, again aided by the close proximity of the Fl^- in IX. It is unlikely that many linear aggregates such as $Sr^{2+}(Fl^-(CH_2)_2\,Fl^-\|Sr^{2+})_n\,Fl^-(CH_2)_2\,Fl^-$ will be present since, as pointed out, the concentration of free ionic ends must be low.

Aggregate structures such as VIII and IX may also exist for the fully solvated strontium salts of compounds II and III, but this was not verified. The solvation processes for the latter compounds are rapid. Additional experiments are needed to determine with more certainty the mechanism of these interesting solvation reactions, especially what constitutes the rate determining step of the ion pair transformation reaction for the strontium salt of I. The available evidence so far suggests that reversible aggregation processes play an important role in the behavior of this salt at low temperature.

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