

# Intramolecular Ionic Interactions in Bolaform Electrolytes of $\alpha,\omega$ -Bis(9-fluorenyl)polymethylenes

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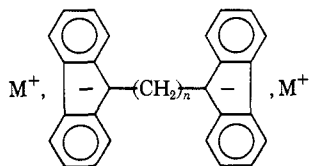
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**Abstract:** Conformational changes due to intramolecular ionic interactions in a series of bolaform electrolytes of the type  $M^+, -F(CH_2)_nF^-, M^+$  ( $M^+$  is either  $Cs^+$  or  $Na^+$ ,  $F^-$  denotes a fluorenyl carbanion and  $n = 2, 3, 4,$  or  $6$ ) were studied conductometrically in tetrahydrofuran and tetrahydropyran. The results reveal that the dissociation constants of the first dissociation step of the cesium bis(fluorenyl)polymethylene salts are 2 to 12 times higher than that of 9-( $n$ -propyl)fluorenylcesium. The enhanced dissociation is rationalized in terms of an intramolecular cyclization of the ion  $^+M, -F(CH_2)_nF^-$  formed in the first dissociation step. The ratio of the fractions of the open and closed form of this "triple ion" depends on  $n$  and increases in the order  $3 < 2 < 4 \sim 6$ . The low value found for the bolion with  $n = 3$  is attributed to steric interference between the  $Cs^+$  ion and one of the C-H bonds of the center  $CH_2$  group on formation of the cyclized triple ion. The cyclization constants for the sodium bolaform salts are considerably smaller, especially in THF, due to solvation of the sodium ion.

The fluorenyl salts have proven to be an effective probe for quantitative studies of ion and ion pair interactions with cation coordinating molecules.<sup>1</sup> The optical spectrum of the carbanion is sensitive to the interionic ion-pair distance, and different kinds of ion pairs are clearly distinguishable. The optical studies have also facilitated the interpretation of conductance data pertaining to the fluorenyl salts in ethereal solvents,<sup>2</sup> since the dissociation constants of the salts depend on the solvation state of the ion pair.

Not much is known about the solvation of ion pairs that are distributed along a polymeric chain. One anticipates that the transformation of tight to loose ion pairs and *vice versa* is influenced by the proximity of adjacent ion pairs. We are presently looking into this problem by investigating the behavior of partially and fully metalated polyvinylfluorene. Preliminary results from optical measurements show that in a solvent such as dimethoxyethane or in oxetane the loose ion pair structure of the sodium fluorenyl carbanion changes to a tight ion pair structure as the ion pair population along the polyvinylfluorene chain reaches a maximum (*i.e.*, when full metalation is achieved).

To facilitate the interpretation of the data obtained for these polyelectrolytes in low polarity media, it was decided to study in more detail the behavior of bolaform electrolytes of  $\alpha,\omega$ -bis(9-fluorenyl)polymethylenes. The salts, depicted below, contain a polymethylene chain of varying length ( $n = 2, 3, 4,$  or  $6$ ) with a fluorenyl ion or ion pair on each end of the chain.



The objective of this study was to determine the extent of intramolecular ion pair-ion pair or ion-ion pair interactions in low dielectric constant media as a function of chain length and counterion. Two approaches were followed. Firstly, the ion pair-ion pair interactions were studied by measuring spectrophotometrically the tight ion pair-loose ion pair equilibrium in different solvents or in the presence of cation coordinating agents and comparing the equilibrium constants with those obtained for 9-alkyl-substituted fluorenyl salts. The results of these studies, which will be published elsewhere, reveal that strong intramolecular ion pair interactions exist when  $Li^+$  is the cation of the bolaform salt, but other salts, noticeably those of  $Na^+$ , also exhibit some remarkable deviations from the behavior found for the normal fluorenyl salts.

The work presented in this paper follows a conductometric approach by measuring the ion pair dissociation constants of the bolaform salts and comparing them with the 9-alkylfluorenyl salts. Deviations are expected in those instances where a strong ion-ion pair interaction stabilizes the intramolecular triple ion. The usefulness of conductometric measurements in the study of molecular conformations has been established by Fuoss<sup>3</sup> and by Atkinson,<sup>4</sup> both of whom studied the conductance of bolaform electrolytes. In their work, carried out in methanol and water, the equilibrium involved is that of the triple ion dissociating into the "divalent" bolion:  $A^-, +B^+ \rightleftharpoons A^- + ^+B^+$ , the charges on the bolion B being separated by a chain of varying length. In our work, carried out in ethereal solvents, the equilibrium that is measured refers to the first dissociation step  $M^+, -F(CH_2)_nF^-, M^+ \rightleftharpoons M^+ + ^-F(CH_2)_nF^-, M^+$ , where  $F^-$  represents a fluorenyl carbanion. The results show that the stability of the cyclized intramolecular triple ion is a function of the chain length, the bolaform electrolyte with  $n = 3$  yielding the least stable triple ion, and, therefore, the lowest dissociation constant.

(1) T. E. Hogen Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966); L. L. Chan and J. Smid, *ibid.*, **90**, 4654 (1968); L. L. Chan, K. H. Wong, and J. Smid, *ibid.*, **92**, 1955 (1970); U. Takaki, T. E. Hogen Esch, and J. Smid, *ibid.*, **93**, 6760 (1971); J. Smid, *Angew. Chem., Int. Ed. Engl.*, **11**, 112 (1972).

(2) T. E. Hogen Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 318 (1966); T. Ellingsen and J. Smid, *J. Phys. Chem.*, **73**, 2712 (1969).

(3) R. M. Fuoss and V. H. Chu, *J. Amer. Chem. Soc.*, **73**, 949 (1951); H. Eisenberg and R. M. Fuoss, *ibid.*, **75**, 2914 (1953); J. C. Nichol and R. M. Fuoss, *ibid.*, **77**, 198 (1955).

(4) G. Atkinson and J. Hallada, *ibid.*, **84**, 721 (1962).

## Experimental Section

**$\alpha,\omega$ -Bis(9-fluorenyl)polymethylenes.** Two of the four bis(9-fluorenyl)polymethylenes, *i.e.*, 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 Corp. (see ref 5). The white crystals were dried in a vacuum oven at 70° for 24 hr, and the purity was checked by nmr analysis. The respective melting points are 230–231.5° ( $n = 2$ ) and 112–113° ( $n = 6$ ).

1,4-Bis(9-fluorenyl)butane was synthesized by a procedure described by Fritz, *et al.*,<sup>5</sup> in which a mixture of fluorene, 1,4-butanediol, and solid KOH (molar ratio 1:3:0.75) is heated in an autoclave at 250° for 12 hr. The required compound was recovered from methanol and purified by vacuum distillation, mp 155–159°.

The corresponding 1,3-bis(9-fluorenyl)propane cannot be prepared by this method, but may be obtained as follows. A 0.02 *M* solution of fluorenylsodium in THF (prepared *in vacuo* by stirring fluorene in THF on a sodium mirror) is slowly added under vacuum to a 0.01 *M* THF solution of 1,3-dibromopropane (Aldrich, purified by vacuum distillation from CaH<sub>2</sub>). The orange carbanion solution loses its color almost instantaneously, due to the formation of 1,3-bis(9-fluorenyl)propane and NaBr. After opening the all-glass enclosed apparatus to the atmosphere, the THF is distilled off, the remaining solids are treated with 25 ml of water, and the resulting oily layer is refluxed for 2 hr with 125 ml of methanol. The white crystals separating from this solution are filtered off, washed with cold methanol, and dried overnight. The pure product is obtained in 30% yield, mp 114–116°; nmr (CDCl<sub>3</sub>)  $\tau$  8.70 (t broad, 2, -CH<sub>2</sub>-), 8.25 (m, 4, -CH<sub>2</sub>-), 6.20 (t broad, 2, -CH-), 2.50 (m, 16, aromatic -CH-). *Anal.* Calcd for C<sub>20</sub>H<sub>24</sub>: C, 93.55; H, 6.45. Found: C, 92.89; H, 6.60.

**Preparation of Bolaform Carbanion Salts.** The cesium salts of the four bis(9-fluorenyl)polymethylenes are prepared by a procedure similar to that used for the fluorenyl salts, *i.e.*, by proton transfer to the dianion of 1,1,4,4-tetraphenylbutane.<sup>2</sup> The latter salt is formed quantitatively by stirring under vacuum a 0.05 *M* solution of 1,1-diphenylethylene in THF with a slight excess of cesium metal. The reaction is followed spectrophotometrically, and as soon as the maximum optical density is attained (*ca.* 0.5 hr), the red carbanion solution is decanted off the cesium metal. To prepare the bolaform salts, special care must be taken to mix the exact equivalent amounts of bis(9-fluorenyl)polymethylenes and Cs<sup>+</sup>,<sup>-</sup>C(Ph)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C(Ph)<sub>2</sub>,Cs<sup>+</sup> (often denoted by Cs<sup>+</sup>,<sup>-</sup>DD<sup>-</sup>, Cs<sup>+</sup>) in order to avoid a partial conversion of the bis(fluorenyl)alkane to the carbanion. This could produce species of the type F-(CH<sub>2</sub>)<sub>n</sub>F<sup>-</sup>,Cs<sup>+</sup>, the conductance of which should resemble that of the normal 9-alkyl-substituted fluorenyl salts. Therefore, the volume and concentration of Cs<sup>+</sup>,<sup>-</sup>DD<sup>-</sup>,Cs<sup>+</sup> are carefully determined (the concentration by measuring the optical density at  $\lambda_{\max}$  485 nm,  $\epsilon$  26,000 per D<sup>-</sup> group), and an equivalent amount of solid bis(9-fluorenyl)polymethylene is added. The conversion is followed by observing the disappearance of  $\lambda_{\max}$  485 nm of D<sup>-</sup>, the absorption of fluorenyl<sup>-</sup> being small at this wavelength ( $\epsilon \approx 1500$ ). The reaction is complete when the optical density reaches a steady value and the D<sup>-</sup> absorption peak is not visible anymore. The bolaform salt solutions are collected in ampoules equipped with breakseals and stored in a freezer. They are used as soon as possible to avoid destruction of the carbanion upon standing, which would yield the one ended carbanion salt.

The sodium bolaform salts are prepared in the same manner as described for the cesium derivatives, using instead <sup>+</sup>Na,<sup>-</sup>DD<sup>-</sup>, Na<sup>+</sup> ( $\lambda_{\max}$  472 nm,  $\epsilon$  26,000).

The cesium and sodium salt of 9-propylfluorene was used for comparative purposes. The hydrocarbon was also obtained from the Union Carbide Corp.<sup>5</sup> and converted to the carbanion by <sup>-</sup>DD<sup>-</sup>. In this case an excess of the hydrocarbon is no problem.

**Conductance Measurements.** The conductances of the salt solutions were measured between 10<sup>-4</sup> and 5 × 10<sup>-6</sup> *M* at 25 ± 0.05° *in vacuo* using an all-glass enclosed apparatus. Details of the entire procedure have been published previously.<sup>2,6</sup> Part of the carbanion solution is used to purge the glass wall of impurities and then poured into a side ampoule. By cooling, pure solvent is distilled back from this solution into the conductance cell (cell constant 0.0348 cm<sup>-1</sup>) and mixed with an appropriate quantity

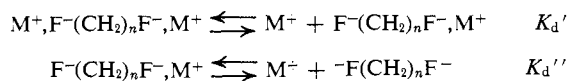
of the remaining carbanion solution to obtain an initial salt concentration of about 10<sup>-4</sup> *M*. The concentration is determined spectrophotometrically with a Cary 14 spectrophotometer, using optical cells of different path lengths directly attached to the conductance apparatus. The respective absorption maxima are 376–378 nm ( $\epsilon$  12,000) for the cesium salts in THF and 371–372 (12,000) for the sodium salts in THF and THP. The conductance is measured at 1 kHz by means of a General Radio Co. 1673 automatic capacitance bridge coupled to a 1672 digital control unit. After the measurement, the concentration is decreased by transferring part of the solution to a side arm and distilling back the solvent.<sup>2,6</sup> After each dilution the concentration and conductance are determined (five or six concentrations are used, the lowest being about 7 × 10<sup>-6</sup> *M*). No change in the concentration of the original carbanion solution is detected during the time needed to complete a series of measurements. We estimate the accuracy of the concentration determination to be better than 5%.

## Results

The optical spectra of the bis(9-fluorenyl)polymethylenecesium salts are nearly identical with that of the tight ion pair of 9-(*n*-propyl)fluorenylcesium, the  $\lambda_{\max}$  being between 376 and 378 nm. The loose ion pairs of the bolaform salts (*e.g.*, the lithium salts in THF) absorb at 388 nm, independent of the counterion. The sodium salts in THF and THP are also tight ion pairs ( $\lambda_{\max}$  371–374 nm), although a small fraction ( $\sim 0.1$ ) of loose ion pairs can be detected in THF, with the exception of sodium 1,2-bis(9-fluorenyl)ethane, where the loose ion pairs disappear when the conversion of the hydrocarbon to the bolaform salt reaches completion. Other spectral data indicate that this bolaform salt forms an intramolecular aggregate.

The reaction of <sup>-</sup>DD<sup>-</sup> with the substituted fluorenes is much slower than with fluorene itself. The latter reaction in THF is completed in a few seconds, while the reaction with the substituted fluorenes at 10<sup>-3</sup> *M* takes  $\sim 150$  sec for 70% conversion. The reaction is even slower in THP or in the presence of salts such as NaBPh<sub>4</sub>, suggesting that the reactions proceed predominantly through the free ions. The comparatively slow proton transfer, in spite of the ten p*K* units difference, is probably due to steric hindrance caused by the bulky substituent at the 9 position of fluorene.

The conductance data were analyzed by means of the Fuoss equation,  $F/\Lambda = 1/\Lambda_0 + f^2 C\Lambda/FK_d\Delta_0^2$ . The  $K_d$  for the 9-(*n*-propyl)fluorenyl salt is simply the dissociation constant of the equilibrium 9-PrF<sup>-</sup>,M<sup>+</sup>  $\rightleftharpoons$  9-PrF<sup>-</sup> + M<sup>+</sup>. For the bolaform salts the following equilibria must be considered.



Assuming that the two dissociation steps are independent of chain length and of the nature of the opposite chain end, and that the dissociation is comparable with that of a one-ended 9-substituted fluorenyl salt, then  $K_d' = 2K_d^0$  and  $K_d'' = 0.5K_d^0$ , where  $K_d^0$  in our work is taken as the dissociation constant of the 9-*n*-propylfluorenyl salt.

In principal there are two current-carrying negative ions, M<sup>+</sup>,<sup>-</sup>F<sup>-</sup> and <sup>-</sup>F<sup>-</sup>. However, since  $K_d$  for 9-*n*-PrF<sup>-</sup>,Cs<sup>+</sup> was found to be 1.6 × 10<sup>-8</sup> *M* (Table I), one calculates that in the concentration range of the measurements (10<sup>-4</sup> to 10<sup>-5</sup> *M*) the ratio [<sup>-</sup>F<sup>-</sup>]/[M<sup>+</sup>,<sup>-</sup>F<sup>-</sup>] =  $K_d''/[M]^+$  is of the order of 0.02. This means that it is justifiable to apply the Fuoss equation for 1:1 electrolytes, and the shape of the Fuoss plots

(5) H. E. Fritz, D. W. Peck, M. A. Eccles, and K. E. Atkins, *J. Org. Chem.*, **30**, 2540 (1965).

(6) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

**Table I.** Apparent Dissociation Constants ( $K_d$ ) and Cyclization Constants ( $K_c$ ) of  $\alpha,\omega$ -Bis(9-fluorenyl)polymethylene Alkali Salts<sup>a</sup> at 25°

Salt <sup>b</sup>	Cation	Solvent	$10^8 K_d, M$	$10^8 2K_d^0, M$	$K_c$
9-PrF <sup>-</sup>	Cs <sup>+</sup>	THF	1.6		
$n = 2$	Cs <sup>+</sup>	THF	14.6	3.2	3.3
$n = 3$	Cs <sup>+</sup>	THF	6.9	3.2	1.1
$n = 4$	Cs <sup>+</sup>	THF	37.6	3.2	10.8
$n = 6$	Cs <sup>+</sup>	THF	28.6	3.2	8.0
9-PrF <sup>-</sup>	Na <sup>+</sup>	THP	0.059		
$n = 2$	Na <sup>+</sup>	THP	(0.23)	0.12	(0.9)
$n = 3$	Na <sup>+</sup>	THP	0.12	0.12	0
$n = 6$	Na <sup>+</sup>	THP	0.31	0.12	1.7
9-PrF <sup>-</sup>	Na <sup>+</sup>	THF	96	192	
$n = 2$	Na <sup>+</sup>	THF	330	192	0.74

<sup>a</sup> M<sup>+</sup>, -F(CH<sub>2</sub>)<sub>n</sub>F<sup>-</sup>, M<sup>+</sup>. <sup>b</sup> The  $K_d$  for 9-(*n*-propyl)fluorenyl<sup>-</sup>, M<sup>+</sup> is taken as  $K_d^0$  for the calculation of  $K_c$ .

confirms the correctness of this procedure. The same holds for the sodium salts in THP ( $K_d^0 = 5.9 \times 10^{-10} M$ ), but some of the Fuoss plots for the sodium bolaform salts in THF ( $K_d^0 = 9.6 \times 10^{-7} M$ ) show a distinct inflection. It is also important to point out that molar concentrations should be used in the calculations. This means that the concentrations, usually calculated in equivalents of fluorenyl groups, must be divided by 2.

The calculation of the correction factors  $f$  and  $F$  requires, in addition to the viscosity and dielectric constant,<sup>2,7</sup> a knowledge of the limiting conductance,  $\Lambda_0$ . Unfortunately, the  $1/\Lambda$  vs.  $C\Delta$  plots are too steep for an accurate extrapolation. Therefore, in order to calculate  $K_d$  from the slopes ( $1/K_d\Lambda_0^2$ ) of the Fuoss plots, it is necessary to estimate  $\Lambda_0$ . The  $\Lambda_0^+$  in THF at 25° for the cations Na<sup>+</sup> and Cs<sup>+</sup> are known,<sup>8</sup> their values being 48 and 68 cm<sup>2</sup>/ohm equiv, respectively. Conductance studies on fluorenyl salts in THF and DME<sup>2</sup> yielded a  $\Lambda_0^-$  value of 50 for F<sup>-</sup> in THF. A *n*-propyl substituent at the 9 position is not expected to reduce the  $\Lambda_0^-$  by more than 10%. Hence, we have taken a  $\Lambda_0$  value of 113 and 93, respectively, for the cesium and sodium salt of 9-propylfluorenyl<sup>-</sup> in THF. Application of Walden's rule gives a  $\Lambda_0$  of 50 for the sodium salt in THP.

More difficult to estimate is the  $\Lambda_0^-$  for the bolion. It is reasonable to assume that its value lies in between that of the fully extended form (Cs<sup>+</sup>, -F-F<sup>-</sup>) and that of the closed form (F<sup>-</sup>, Cs<sup>+</sup>F<sup>-</sup>). Evidence, presented

below, shows that in most of the systems studied the cyclized triple ion is the predominant negative species. This ion may, in first approximation, be considered as a spherical particle with a radius of about 5 Å. The  $\Lambda_0^-$  of such an ion in THF at 25° will not differ much from that of ions such as BPh<sub>4</sub><sup>-</sup>, C<sup>-</sup>Ph<sub>3</sub>, or [Ph<sub>2</sub>C-CPh<sub>2</sub>]<sup>-</sup>, all of which were found to have a  $\Lambda_0^-$  equal to 41 cm<sup>2</sup>/ohm equiv.<sup>9</sup> The open conformation is likely to have a slightly lower  $\Lambda_0^-$  value, and we estimate that it will be about  $35 \pm 5$ . A change from  $n = 2$  to  $n = 6$  should not affect this value by much, judging from the less than 10% change of  $\Lambda_0^-$  values of bolaform electrolytes of  $\alpha,\omega$ -bis(trimethylammonium)- and  $\alpha,\omega$ -bis(pyridinium)polymethylene halides.<sup>3</sup> The over-

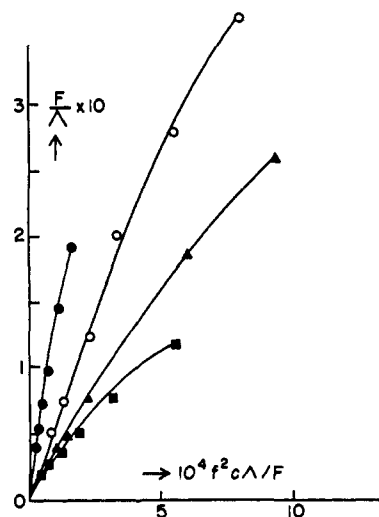


Figure 1. Fuoss plots for the cesium salts of  $\alpha,\omega$ -bis(9-fluorenyl)polymethylenes in THF at 25°: ○,  $n = 2$ ; ●,  $n = 3$ ; ■,  $n = 4$ ; ▲,  $n = 6$ .

all  $\Lambda_0^-$  in our case is given by  $\alpha\Lambda_0'^- + (1 - \alpha)\Lambda_0''^-$ , where  $\alpha$  and  $(1 - \alpha)$  are the respective fractions of the cyclized triple ion ( $\Lambda_0'^-$ ) and of the extended form ( $\Lambda_0''^-$ ). Because of the uncertainty in  $\alpha$  and in the  $\Lambda_0^-$  values, we have taken the same  $\Lambda_0^-$  value of 40 for the four bolaform electrolytes. We estimate the error in  $\Lambda_0^-$  to be less than 20%, and the resulting uncertainty in the total  $\Lambda_0 = 108$  cm<sup>2</sup>/ohm equiv is approximately 10%. The relative values of the respective dissociation constants are even less affected, since the uncertainty in  $\Lambda_0^-$  is about the same for all bolaform salts. Similar considerations led us to use a  $\Lambda_0 = 88$  for the sodium bolaform salts in THF and, by Walden's rule, a value of 48 for the  $\Lambda_0$  in THP.

The Fuoss plots for the cesium salts are depicted in Figure 1, and those for the sodium salts in Figures 2 and 3 (notice the inflection point in the  $n = 3$  sodium salt in THF; the same was observed for  $n = 6$ ). The deviation from linearity often observed in these systems above concentrations of  $\sim 10^{-4} M$  may be attributed to intermolecular triple ion formation.<sup>2</sup> The dissociation constants, calculated from the limiting slopes, are collected in Table I. The value for 1,2-bis(9-fluorenyl)ethanesodium in THP is uncertain, as the Fuoss plot showed unusual strong curvature, possibly due to intramolecular ion-pair aggregation.

## Discussion

The value  $K_d = 1.6 \times 10^{-8} M$  for 9-(*n*-Pr)F<sup>-</sup>, Cs<sup>+</sup> (Table I) is only slightly higher than that reported for F<sup>-</sup>, Cs<sup>+</sup>, i.e.,  $K_d = 1.4 \times 10^{-8} M$ .<sup>2</sup> The same holds for the two sodium salts in THF (the respective  $K_d$  values are  $9.6 \times 10^{-7}$  and  $6.2 \times 10^{-7} M$ ) and in THP ( $K_d = 5.9 \times 10^{-8}$  for *n*-PrF<sup>-</sup>, Na<sup>+</sup> and  $3.0 \times 10^{-8} M$  for F<sup>-</sup>, Na<sup>+</sup>). The inductive effect of the propyl group is apparently more than offset by the larger interionic ion pair distance which one expects as a result of steric interference in the tight ion pairs between M<sup>+</sup> and the propyl group. This is also evident from the higher fraction of solvent separated ion pairs found in THF solutions of 9-alkylfluorenylsodium salts as compared with fluorenylsodium.<sup>1</sup>

Table I reveals that the four cesium bolaform salts

(7) D. Nicholls, C. Sutphen, and M. Szwarc, *ibid.*, 72, 1021 (1968).

(8) C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, 87, 5548 (1965); G. Tersac and S. Boileau, *J. Chim. Phys. Physicochim. Biol.*, 68, 903 (1971).

(9) L. L. Chan and J. Smid, *J. Phys. Chem.*, 76, 695 (1972).

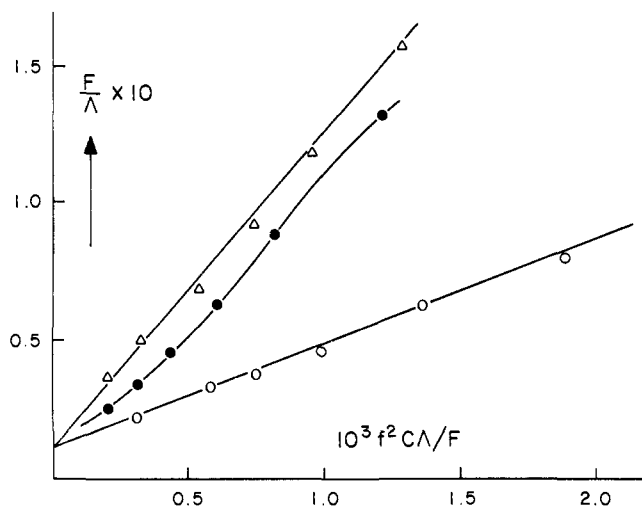
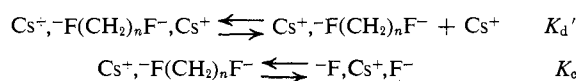


Figure 2. Fuoss plots in THF at 25° for the sodium salt of 9-(*n*-propyl)fluorenyl ( $\Delta$ ), 1,3-bis(9-fluorenyl)propane ( $\bullet$ ), and 1,2-bis(9-fluorenyl)ethane ( $\circ$ ).

have dissociation constants 2 to 12 times higher than twice the  $K_d$  value of 9-(*n*-Pr) $F^-$ ,  $Cs^+$ . This deviation is far beyond the experimental uncertainties in the estimated  $\Delta_0$  values. An increase in  $K_d$  for these types of salts was first observed by Bhattacharyya, *et al.*,<sup>6</sup> for two-ended polystyryl cesium,  $+Cs, \bar{C}H(Ph)(CH_2)_n \bar{C}H(Ph), Cs^+$ , where  $n \approx 25$ . The dissociation constant for this salt in THF was reported to be about three times higher than that for the one-ended salt. This was attributed to intramolecular triple ion formation. The same situation apparently exists in the fluorenyl bolaform salts. The first dissociation step would be modified as follows



The constant  $K_d'$  is equal to  $2K_d^0$ , where  $K_d^0$  is assumed to be identical with the dissociation constant of 9-Pr- $F^-$ ,  $Cs^+$ . The apparent dissociation constant,  $K_d$ , as determined from the Fuoss plots, is given by

$$K_d = K_d'(1 + K_c)$$

and

$$K_c = (K_d/2K_d^0) - 1$$

The intramolecular triple-ion cyclization constants,  $K_c$ , calculated from this relationship, are also given in Table I.

The most interesting observation that emerges from an inspection of Table I is the relatively low cyclization tendency of the triple ion when  $n = 3$ . It is generally found that intramolecular association of chain ends connected by a polymethylene chain is highest for  $n = 3$ . For example, Itoh and Kosower demonstrated that in  $\alpha, \omega$ -dipyridinylalkanes the strongest interaction between the pyridinyl radicals exists for a trimethylene chain.<sup>10</sup> The same was found in intramolecular excimer formation of  $\alpha, \omega$ -diphenylalkanes<sup>11</sup> and from fluorescence spectra of 1,3-dinaphthylpropane.<sup>12</sup> In pyridinyl

(10) M. Itoh and E. M. Kosower, *J. Amer. Chem. Soc.*, **89**, 3955 (1967); **90**, 1843 (1968).

(11) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).

(12) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 3586 (1970).

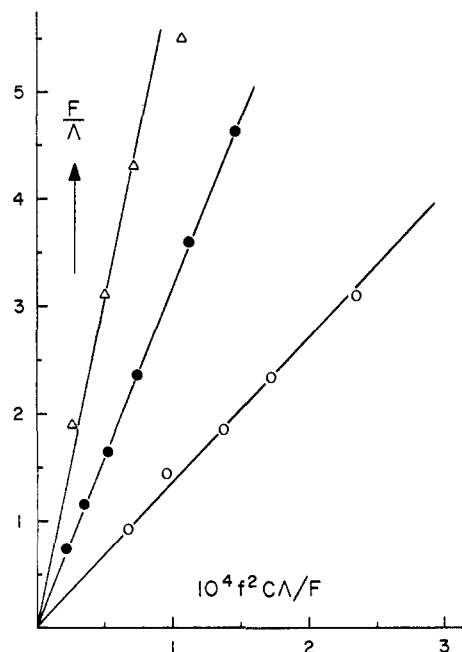


Figure 3. Fuoss plots in THP at 25° for the sodium salts of 9-(*n*-propyl)fluorenyl ( $\Delta$ ), 1,3-bis(9-fluorenyl)propane ( $\bullet$ ), and 1,6-bis(9-fluorenyl)hexane ( $\circ$ ).

type cation radicals,  $\cdot Py(CH_2)_n Py^+$ , the strongest interaction is again found for  $n = 3$ ,<sup>13</sup> and intramolecular energy transfer has been reported in dinucleotides with chromophores linked by a trimethylene chain.<sup>14</sup>

The difference between these systems and our bolaform salts is that in the closed intramolecular triple ion a relatively large positive  $Cs^+$  ion must be accommodated in the cavity formed by the two planar fluorenyl rings and the connecting polymethylene chain. If the chain were not present, the electrostatically most stable triple ion configuration would be one in which the two fluorenyl rings are nearly parallel, with the  $Cs^+$  ion sandwiched in between the rings and centered on the imaginary line connecting the two charges. The total distance between the two negative charges in such a system would be approximately 5.5–6 Å, assuming about 1 Å for the  $\pi$  cloud. For the bolaform salt with  $n = 4$ , the extended open conformation gives a distance between negative charges of close to 9.0 Å. Rotation around to various C–C bonds of the chain makes it feasible to form a cavity with 6 Å between the negative ions with the two fluorenyl rings only slightly tilted to accommodate the  $Cs^+$  ion in an electrostatically favorable position (see Figure 4a). A high  $K_c$  value can therefore be expected for  $n = 4$ . Although a more favorable orientation of the fluorenyl rings can be achieved for the hexamethylene salt ( $n = 6$ ), the loss in conformational entropy also increases, and the  $K_c$  value is nearly the same as for  $n = 4$ . For polystyrylcesium ( $n \approx 25$ )  $K_c$  is only 2.2 (the reported value  $K_c = 5.5$  was calculated incorrectly).

The maximum distance between negative charges for the open form of 1,2-bis(9-fluorenyl)ethanecesium is only about 6.3 Å. To form a cavity of 6-Å diameter, the fluorenyl rings will be strongly tilted with respect to one another (see Figure 4b). The cesium ion is thereby

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forced off the imaginary line connecting the negative charges, and the resulting triple ion is considerably less stable than that for  $n = 4$  or 6. This is reflected in the low  $K_c$  value for  $n = 2$ . This value may have even been lower were it not for the fact that the closeness of the two negative charges for  $n = 2$  also tends to make the open form less stable. The results of certain kinetic measurements on polystyryl salts indicate that this becomes an important factor when the chain is very short.<sup>15</sup>

The case of 1,3-bis(9-fluorenyl)propanecesium appears to underscore the importance of structural details in determining the stability of the closed triple ion. Models show that a stable cyclized triple ion can only be formed by having the fluorenyl rings again in a tilted position. However, in converting the open form to the closed structure, the center  $\text{CH}_2$  group rotates in such a way that one of its C-H bonds is directed into the space occupied by the cesium ion. This forces the cesium ion to the periphery of the cavity (see Figure 4c) and reduces the stability of the triple ion, as manifested by the low  $K_c$  value.

The formation of the cyclized triple ions in the case of cesium bolaform salts is facilitated by the poor solvation of  $\text{Cs}^+$  ions by THF.<sup>8</sup> The sodium ion, on the other hand, strongly interacts with the solvent. Although in principle the smaller cation can form a tighter and therefore more stable closed triple ion than  $\text{Cs}^+$ , the solvation tends to pull the  $\text{Na}^+$  out from between the fluorenyl rings and favors the open form where solvent interactions are less sterically hindered. In agreement with this is the observation that one- and two-ended polystyrylsodium salts in THF have identical dissociation constants.<sup>6</sup>

As pointed out, some of the Fuoss plots for the sodium bolaform salts in THF appear to have a slightly sigmoidal shape, presumably due to participation of the second dissociation step. However, the actual equivalent conductances for the propane and hexane bolaform sodium salts are close to those of 9-propylfluorenylsodium at comparable concentrations, indicating that little, if any, triple ion cyclization occurs. Tetrahydropyran is less basic, and cyclization in this solvent is expected to be more favorable than in THF. The data of Table I indicate that cyclization in THP does occur for  $n = 6$ . In agreement with the cesium results, the trimethylene triple ion is again the least stable, with  $K_c$  being essentially zero. The triple ion with  $n = 2$  appears to produce a closed form in both THF and THP. While the value in THP is uncertain because of possible intramolecular aggregation of the nonionized form, a good Fuoss plot is obtained in THF (Figure 3). It should be pointed out in this regard that the formation of a cyclized triple ion suppresses the second dissociation step. Also, the expected instability of  $^-\text{F}(\text{CH}_2)_2\text{F}^-$  leads to  $K_{d''} \ll K_{d'}$ , and, therefore, a more normal Fuoss plot. The difference in  $K_{d'}$  and  $K_{d''}$  for  $n = 2$  finds an analogy in the spectroscopically determined complexation constants of 1,2-bis(9-fluorenyl)ethanesodium with tetraethylene glycol dimethyl ether (glyme 5). The two constants for glyme separated ion pair formation (enlargement of the ion pair dipole!) for the two chain ends differ by a factor of 15, while for the

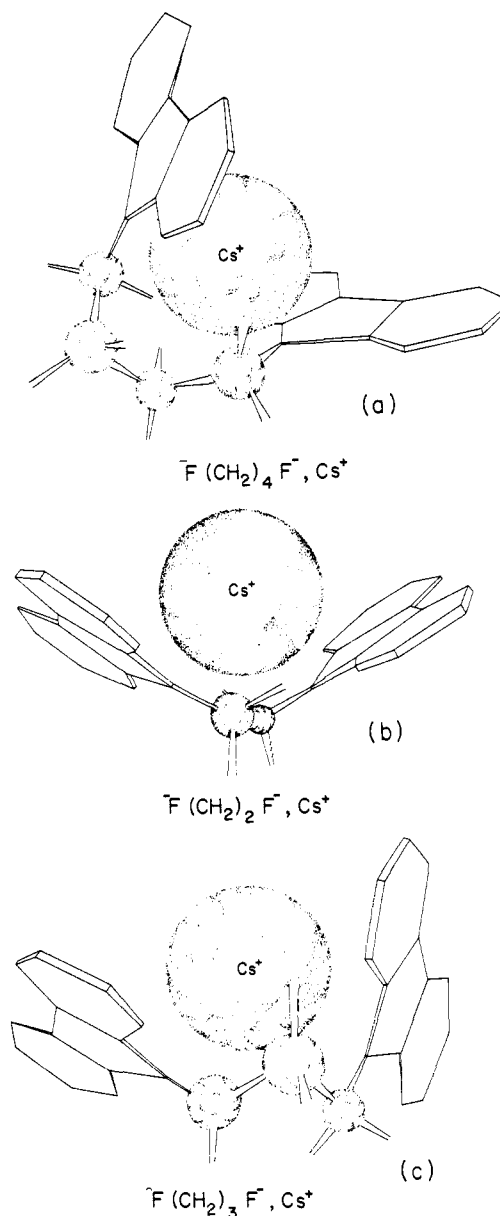


Figure 4. Proposed structures of the cyclized intramolecular triple ions of the cesium salts of  $\alpha,\omega$ -bis(9-fluorenyl)polymethylenes: (a)  $n = 4$ , (b)  $n = 2$ , (c)  $n = 3$ . Figures were drawn from projections of actual models.

salts with  $n > 2$  the ratio is close to the expected statistical factor of 4.<sup>16</sup> Also, the cyclized triple ion of the ethane salt can easily be stabilized by solvation, since the rather strongly tilted fluorenyl rings provide enough space on the periphery of the sodium ion for one or two solvent molecules (compare with Figure 4c). It is interesting in this respect that in 1,2-dimethoxyethane (DME) the bolaform sodium salts are solvent separated ion pairs (like fluorenyl- or 9-alkylfluorenylsodium), with the exception of the ethane salt where the optical spectrum gives a ratio of separated to contact ion pairs of close to unity.<sup>16</sup> Apparently, the one sodium ion sandwiched in between the two fluorenyl rings can easily be solvated by DME without formation of a separated ion pair, and without producing the less stable open form  $^+\text{Na}||-\text{F}(\text{CH}_2)_2\text{F}^-||\text{Na}^+$ .

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It would be interesting to vary the structure of the connecting chain and to study its effect on the stability of the triple ion. For example, incorporating oxygen atoms in the chain (e.g., a  $(\text{CH}_2\text{CH}_2\text{O})_n$  linkage) may lead to rather stable intramolecular cyclized triple ions.

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## On the Spectral Characteristics of the Odd-Polyenyl Carbonium Ions<sup>1</sup>

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**Abstract:** Due to the possibility that an odd-polyenyl carbonium ion might play an important role as the wavelength regulator in the chemistry of visual pigments, the spectral behavior of these cations has been investigated with the combined effects of the Pariser–Parr–Pople method and the  $\omega$  technique. Such a study has enabled us to derive what may be the most appropriate picture of charge distribution in these ions. Particular emphasis has been laid on the undecapentaenylic cation, which is the key cation in the visual pigment rhodopsin.

Among the various mechanisms<sup>2–5</sup> that have been proposed to explain the unique spectral behavior of the visual pigment molecules, the one involving the role of carbonium ions was first postulated by one of us<sup>6a</sup> (P. E. B.) and with modification has been substantiated since then by means of both the experimental as well as theoretical evidence.<sup>7–10</sup> As a result, the emerging molecular model responsible for much of the observed phenomena encompasses the following features. (1) When a  $\pi$ -molecular system with an even number of orbitals, such as a linear polyene, is transformed into one with an odd number of orbitals, corresponding either to its radical, cation, or anion for instance, the optical spectrum is greatly displaced toward longer wavelengths (bathochromic shift). This fact has been associated with the property of visual pigment molecules in which similar large bathochromic shifts are observed when the chromophore molecule (retinal, a polyene aldehyde with  $\lambda_{\text{max}}$  381 nm) is complexed *via* an azomethine type linkage to the visual protein opsin ( $\lambda_{\text{max}}$  ranging up to 575 nm). Although in a manner similar to its simple polyene Schiff base counterpart, the chromophore, while still remaining complexed with the opsin, is not a pure carbonium ion. In polyenes such a transformation can be brought about through protona-

tion. (2) The formation of a pure carbonium ion is prevented in the case of Schiff bases because of the proximity of the counteranion which localizes considerable positive charge on the nitrogen atom and thus enables only the leftover fractional charge to delocalize itself over the  $\pi$  structure. By regulating the strengths of the anionic or other electron-rich groups, the charge on the nitrogen and hence that on the chromophore can be controlled indirectly. (3) Whereas the way in which the protein controls the charge on the nitrogen can only be postulated, it must be admitted that this behavior of *N*-substituted charged polyenes differs considerably from that of pure carbonium ions. In the latter, once it is formed, the positive charge is uniformly distributed over the entire ion. Experimental evidence suggests<sup>6b</sup> that carbonium ions have little or no additional polarizability. It is true that the extent by which the  $\text{N}^+$  of the Schiff base is in conjugation with the  $\pi$  system is not known. Therefore, it is important to study the two limiting cases in which the nitrogen is completely attached to the  $\pi$  system (*i.e.*, the even orbital heteroatomic polyene) and when it is not (corresponding carbocation—an odd orbital system). These studies can then shed some light on the charge distribution patterns when  $\text{N}^+$  is only partially connected to the  $\pi$  system.

It is in connection with this anomaly of charge distribution in carbonium ions that an interesting problem is created and indeed an essential step for understanding the properties of visual pigments. For, once the charge distribution in carbonium ions is known, an exact charge distribution can be derived for the visual chromophore from knowledge of the fractional charge on nitrogen that is available for polarization in the polyene.

**Method of Calculation.** The success of Pariser–Parr–Pople<sup>11</sup> (the  $\text{P}^3$  method) in interpreting the electronic

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