

# Carbon Acidity. 74. The Effects of Hetero-Substituted Pendant Groups on Carbanion Reactivity. Solvent-Separated-Contact Ion Pair Equilibria and Relative $pK_{Li/THF}$ 's for 9-Substituted Fluorenyllithiums in Tetrahydrofuran. The Importance of Internal Chelation

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**Abstract:** For a series of 9-substituted fluorenyllithiums (substituents:  $CH_3OCH_2CH_2-$ , **1**;  $(CH_3)_2NCH_2CH_2-$ , **2**;  $CH_3SCH_2CH_2-$ , **3**;  $CH_3CH_2CH_2CH_2-$ , **4**;  $CH_3OCH_2CH_2OCH_2CH_2-$ , **5**;  $H-$ , **6**) the equilibria between solvent-separated ion pairs (SSIP's) and contact ion pairs (CIP's) have been determined in tetrahydrofuran (THF) with UV-vis spectroscopy. Either oxygen or nitrogen in the pendant group favors CIP formation by the ability of the heteroatom to form an internal chelate. This chelation can lead to over 100-fold shifts in the relative stabilities of SSIP's and CIP's. Thermodynamic parameters ( $\Delta H^\circ$  and  $\Delta S^\circ$ ) for the equilibria are presented and indicate that formation of the CIP releases coordinating solvent—this effect is greater if the CIP forms an internal chelate. The  $pK_{Li/THF}$ 's,  $pK_{Li/THF}$ (SSIP)'s and  $pK_{Li/THF}$ (CIP)'s of the substituted fluorenes (relative to fluorene,  $pK_{Li/THF}$ (SSIP) = 22.9) are presented and show that oxygen or nitrogen in the pendant group stabilizes the SSIP's somewhat ( $\approx 0.5$  pK units) but stabilizes the CIP's dramatically ( $>2$  pK units). Although sulfur substitution does not lead to internal chelates, it does lead to a substantial stabilization in the SSIP. Finally, neither aggregation nor SSIP internal chelation appears to be important in these fluorenyllithium derivatives; that is, internal chelation can be important in CIP's but is much less important in SSIP's for this class of organolithium compounds.

The formation of new carbon-carbon bonds with use of carbanionic intermediates is one of the most useful techniques in modern synthetic organic chemistry.<sup>1</sup> The importance of these types of reactions has led to considerable interest in structure-reactivity relationships involving carbanions.<sup>2,3</sup> Recently, the effects of nonconjugated, yet nearby heteroatoms (usually oxygen or nitrogen) on the relative stabilities and kinetic reactivities of carbanion salts (particularly lithium salts) have been noted by several workers.<sup>4-13</sup> In these systems, the heteroatom near the carbanionic center may interact with the gegenion providing what can be described as internal chelation. This effect is most prominent with lithium salts because of strong lithium cation-Lewis base interactions. The importance of heteroatom participation is greatest in weakly basic solvents (e.g., hydrocarbons)

because the internal chelate provides further coordination to the cation without invoking aggregation; however, in moderately basic solvents (e.g., ethers) the pendant heteroatom may compete with solvent for coordination either through favorable entropy effects (liberation of free solvents) or through higher basicity (nitrogen versus ether oxygen).

The existence of internal chelates is well documented in the solid phase. X-ray crystal structures of 3-methoxypropyllithium and 3-(dimethylamino)propyllithium have been reported by Klumpp and co-workers.<sup>4,5</sup> The two structures are quite similar and both are found as tetramers. In each case, the heteroatom interacts with the lithium to give a five-membered chelate ring. In another recent example, the crystal structure of a vinylolithiated enamine with a pendant amino group shows interaction of the lithium with both the conjugated nitrogen (formally conjugated to the double bond, but not the carbanion) and the pendant nitrogen.<sup>7a</sup> There is also evidence of internal chelates affecting the solution stability of lithium salts. The effects of ortho-alkoxy groups on the stabilities of metalated benzene derivatives has been extensively studied;<sup>4,8</sup> however, some conjugation is involved in these cases. Recently, it was shown that in THF the lithium enolate salt of *o*-methoxyacetophenone is more than 7 pK units less basic than the analogous cesium salt presumably because the lithium cation forms a better internal chelate;<sup>9a</sup> a 3-5 pK<sub>a</sub> unit difference in lithium and cesium ion pair acidities is expected for a normal enolate.<sup>9b</sup> Additional evidence indicates that this internal chelation results in the lithium salt being less aggregated than the cesium salt. Regan and Staunton<sup>10</sup> have presented an interesting example of internal chelation involving lithium amide salt in which internal chelation to a methoxy group reduces the effective basicity of the amide. Furthermore, through precoordination, hetero-substituted pendant groups play significant roles in a variety of kinetic processes,<sup>6</sup> and these kinetic reactivities undoubtedly have important correlations with the thermodynamic stabilities of the salts.<sup>12-14</sup> Nonetheless, little quantitative work has been presented on the stabilities of internally chelated carbanions.<sup>4,8,11</sup>

To gain a further understanding of the extent and importance of internal chelation in a coordinating solvent, tetrahydrofuran (THF), we have studied the lithium salts of a series of 9-substituted fluorenes with a number of techniques. For this work, fluorenes

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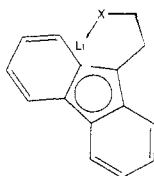


Figure 1. Idealized fluorenyllithium internal chelate.

with the following heteroatom-containing substituents were considered:  $\text{CH}_3\text{OCH}_2\text{CH}_2-$  (1),  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2-$  (2),  $\text{CH}_3\text{SCH}_2\text{CH}_2-$  (3), and  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$  (5). This series contains both hard (oxygen and nitrogen) and soft (sulfur) bases and a substituent capable of bidentate chelation (5). As references for comparison, 9-*n*-butylfluorene (4) and fluorene (6) were also considered. The choice of a two-carbon spacer group between the heteroatom and the fluorene is based on a previous study by Japanese workers (see below).<sup>11</sup> The fluorenyl system is a useful basis for this study in which the goal was to determine effects large enough to measure and not so large as to be totally off-scale. Moreover,  $\lambda_{\text{max}}$ 's in the UV-vis spectra of fluorenyl salts indicate the type of ion pairing. In their pioneering work in the 1960's, Hogen-Esch and Smid<sup>15</sup> showed that in THF, delocalized anions, such as fluorenyl, may be present as either solvent separated ion pairs (SSIP's), contact ion pairs (CIP's), or mixtures of the two types. Since the SSIP's and CIP's have distinctive absorptions, they may be identified by the positions of their  $\lambda_{\text{max}}$ 's. The ability of the CIP to form a five-membered internal chelate ring (Figure 1)<sup>16</sup> with a hetero-substituted pendant group should lead to an enhancement of its stability with respect to the SSIP. Therefore, the position of the SSIP  $\rightleftharpoons$  CIP equilibrium gives an indication of the importance of internal chelation in the fluorenyl salt. With a group of 9-substituted fluorenes, the Japanese group found that having an oxygen or a nitrogen  $\gamma$  with respect to the formal anionic center (as in this study) favors contact ion pair formation.<sup>11</sup> They also noted that heteroatoms in the  $\delta$  position (formally a six-membered chelate ring) had much weaker effects. However, these workers never quantified their results. A quantitative study of this type of ion pairing behavior can give a measure of the extent of internal chelation and of the thermodynamic parameters associated with the chelate ion pairing equilibrium ( $\Delta H^\circ$  and  $\Delta S^\circ$  for CIP(chelate)  $\rightleftharpoons$  SSIP).

In addition to ion pairing studies, fluorene derivatives have  $\text{p}K_{\text{Li}/\text{THF}}$ 's accessible with the recently published lithium ion pair indicator scale;<sup>17,18</sup> consequently, the net thermodynamic stabilization gained by having a heteroatom in the pendant group may be observed relative to an appropriate reference (9-*n*-butylfluorene). These stabilizations can be dissected to give the contributions in the SSIP's and CIP's, and in this way the complementary effects of coordinating and inductive interactions may be resolved and quantified. Furthermore, to fully understand the role these pendant groups play in the deprotonation step (kinetic acidity), one must understand their role in the product salts ( $\text{p}K_{\text{Li}/\text{THF}}$ 's). This combination of CIP-SSIP equilibria and relative  $\text{p}K$ 's provides a unique opportunity to compare the effect of internal chelation on CIP's and SSIP's. The effect of these two types of internal chelation and thermodynamic acidities on the corresponding kinetic acidities is discussed in the following paper.<sup>19</sup>

## Results and Discussion

### Determination of SSIP $\rightleftharpoons$ CIP Equilibria for the 9-Substituted Fluorenes. The first step in studying the 9-substituted fluorenes

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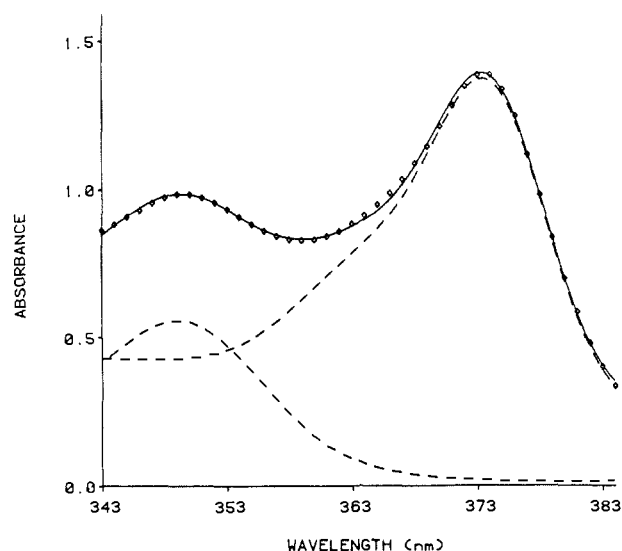


Figure 2. Spectrum of fluorenyllithium (6a) in THF at 25 °C in THF. The diamonds are the experimental points, the solid line is the simulated spectrum, and the dashed lines are the CIP (348 nm) and SSIP (373 nm) contributions.

was to examine the ion pairing equilibria of the lithium salts because this information is required for the  $\text{p}K_{\text{Li}/\text{THF}}$  studies. Since the contact (CIP) and solvent separated (SSIP) ion pairs have distinctive absorptions, Hogen-Esch and Smid were able to analyze the fluorenyllithium ion pairing equilibrium with UV-vis spectroscopy.<sup>15b</sup> Buncel and co-workers<sup>20</sup> have employed similar techniques with the lithium salts of polyarylmethanes in THF. In separate studies, O'Brien<sup>21</sup> and Jackman<sup>22</sup> have had success in employing NMR spectroscopy to determine the position of the SSIP  $\rightleftharpoons$  CIP equilibrium for a number of systems. In general, both spectroscopic techniques have yielded similar results, but the NMR studies generally require higher concentrations and a greater risk of aggregation. Our UV-vis studies are completed in dilute solution ( $10^{-3}$  to  $10^{-4}$  M) where aggregation is unlikely.

In Figure 2, the 25 °C spectrum of fluorenyllithium in THF is given. The peaks at 373 and 348 nm are characteristic of the SSIP and the CIP, respectively. There is a small contribution to the SSIP absorbance by free ions, but it is only a few percent in this concentration range ( $>10^{-3}$  M).<sup>18,19</sup> The relative positions of the  $\lambda_{\text{max}}$ 's of the SSIP's and CIP's of substituted fluorenes may be generalized:  $\lambda_{\text{max}}$  for SSIP's are between 370 and 390 nm and for CIP's are between 345 and 365 nm.<sup>17,24</sup> In order to determine the relative concentrations of these ion pair types, the equilibrium spectrum must be deconvoluted into its components, the contributions from the SSIP's and CIP's; however, this type of analysis requires spectral examples of the isolated species (pure CIP and pure SSIP). Since the rapid equilibrium does not allow for chemical separation, one must seek model spectra to approximate those of the isolated ion pair types—the NMR studies have used extrapolation techniques.<sup>21,22</sup> In the past, several methods have been used to obtain the necessary UV-vis model spectra.<sup>15b,20</sup> For this study, we have chosen the spectra of the lithium salts in diethyl ether or the cesium salts in THF as models for CIP's and the spectra of the lithium salts in THF with 15-crown-5 as models for SSIP's. The 15-crown-5 is a powerful coordinating agent for lithium and forces the equilibrium fully toward SSIP's. It was found that the lithium salt in ether as a CIP model gives better deconvolutions with the substituted fluorenes, but with fluorene itself the spectrum of the cesium salt in THF is a better CIP model. In the text, values from the better deconvolution are reported.

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Table I. Equilibrium Constants and Thermodynamic Parameters for SSIP  $\rightleftharpoons$  CIP of Lithium Salts in THF<sup>a,b</sup>

	$K_{eq}^c$	$\Delta H^\circ$ (kcal mol <sup>-1</sup> )	$\Delta S^\circ$ (eu)	temp range <sup>d</sup>
1a	1.9	5.2	18.6	-30 to 35
2a	4.8	2.9	12.5	-55 to -5
3a	<0.03			
4a	<0.03			
5a	1.1	6.0	20.3	-25 to 40
6a	0.41	3.8	11.0	-10 to 55

<sup>a</sup> For the reaction SSIP  $\rightleftharpoons$  CIP. <sup>b</sup> Average values from two or more measurements. Estimated errors: 10–20% in  $K_{eq}$ ,  $\pm 1$  kcal mol<sup>-1</sup> in  $\Delta H^\circ$ , and  $\pm 2$  eu in  $\Delta S^\circ$ . <sup>c</sup> At 25 °C for  $K_{eq} = \text{CIP}/\text{SSIP}$ . <sup>d</sup> Typical temperature range in °C used for van't Hoff plots.

Given model spectra, a deconvolution technique must be chosen. Since the system has two unknowns (SSIP and CIP concentrations), at least two equations must be considered. Hogen-Esch and Smid analyzed the equilibrium spectrum at two points, the  $\lambda_{max}$ 's of the SSIP and CIP, and solved for the concentrations using the extinction coefficients found for the model spectra at these wavelengths.<sup>15b</sup> However, since model spectra are involved, it would be useful to have some idea of how well the combination of these model spectra fits the observed equilibrium spectrum. For this reason, we undertook an over-determined least-squares approach and analyzed the equilibrium spectra with 30 to 40 data points. In this way, one could check the fit by the least-squares error and a graphical representation of the simulated equilibrium spectrum. The details of this deconvolution technique are presented in Appendix A (see below). For the deconvolution, it was necessary to assume that the extinction coefficients for the SSIP and CIP at their respective  $\lambda_{max}$  are the same and that they change uniformly with temperature. This approximation should be valid based on previous comparisons of the extinction coefficients of SSIP's and CIP's and should lead to only small errors in  $K_{eq}$  (<10%).<sup>17,25,26</sup> However, the change in shape of the model spectra with temperature was taken into account in the deconvolution. Equilibrium constants derived from the deconvolutions are given in Table I. Neglecting the contribution by free ions to the SSIP absorbance will tend to underestimate the  $K_{eq}(\text{CIP}/\text{SSIP})$  by a few percent. Including errors derived from the necessary assumptions, the  $K_{eq}$  values are expected to be accurate to within 20%, but reproducibility is on the order of  $\pm 5\%$ .

The first compound to consider is fluorenyllithium (6a). In Figure 2, the diamonds are the experimental absorbances, the solid line is the simulated spectrum, and the dashed lines are the SSIP (373 nm) and CIP (348 nm) contributions to the simulated spectrum. It can be seen that the fit is excellent; therefore the SSIP and CIP (fluorenylcesium in THF) models are accurately representative in this system. The deconvolution leads to an equilibrium constant of 0.41 (29% CIP, 71% SSIP) at 25 °C. The alternative CIP model, fluorenyllithium in ether, gives a poor deconvolution, but a similar equilibrium constant (0.45). The possibility of this type of error in the deconvolution was not considered in the previous studies of SSIP  $\rightleftharpoons$  CIP equilibria using model spectra (no simulation is possible in the NMR studies).<sup>15,20–22</sup> The over-determined least-squares approach along with the simulated equilibrium spectrum are necessary to judge the quality of the deconvolutions. Our result may be compared to Hogen-Esch and Smid's analysis that gave about 80% SSIP.<sup>15b</sup>

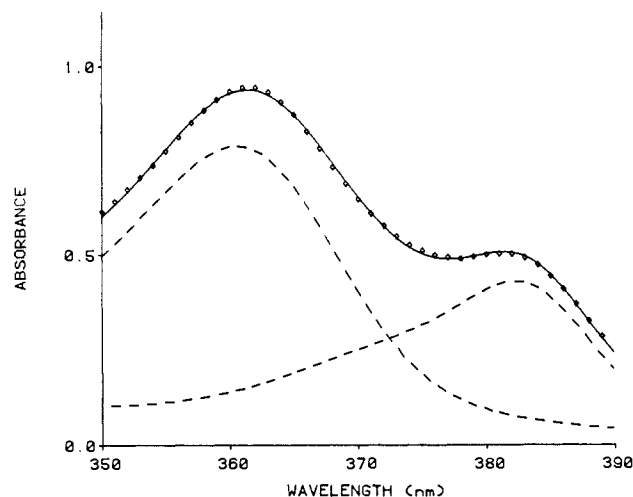


Figure 3. Spectrum of 9-(2-methoxyethyl)fluorenyllithium (1a) in THF at 25 °C in THF. The diamonds are the experimental points, the solid line is the simulated spectrum, and the dashed lines are the CIP (360 nm) and SSIP (382 nm) contributions.

NMR studies of fluorenyllithium in THF give SSIP percentages of 77<sup>21</sup> and 90%.<sup>22</sup> Although the percentages differ from study to study, they all indicate that the SSIP is significantly favored over the CIP at room temperature.

The next compound to consider is the reference for the series of substituted fluorenes, 9-*n*-butylfluorene (4). In this case, the pendant group has no heteroatom with which to form an internal chelate. The spectrum of the lithium salt, 4a, at 25 °C has a single peak at 387 nm indicating that only SSIP's are present to a significant extent. There may be a small CIP concentration at 25 °C, but it is less than 10% of the total; model studies showed that this much CIP would have been clearly evident in the spectra. Apparently, the bulk of the *n*-butyl group sterically disfavors the formation of the CIP. Recall the fluorenyllithium gives a mixture of CIP's and SSIP's (Figure 2). Although the lithium cation is small, its solvation shell gives it a large steric requirement. It is unfortunate that an equilibrium constant for the SSIP  $\rightleftharpoons$  CIP equilibrium could not be measured because 4 is a reference compound for others in this series. We can, however, set an upper limit to this equilibrium constant. Even at 50 °C no absorbance could be seen in the neighborhood of 365 nm where we would expect the CIP.<sup>23</sup> The temperature coefficient based on other compounds (vide infra) means that the amount of CIP at 25 °C is <3% or that the equilibrium constant is <0.03.

The spectrum of the lithium salt of 9-(2-methoxyethyl)fluorene (1a) at 25 °C is given in Figure 3. In this compound the pendant group has nearly the same steric bulk as the *n*-butyl group, but it has an oxygen capable of coordination. The spectrum is made up of two distinct peaks; the CIP appears at 362 nm and the SSIP at 382 nm. The fit of the simulated spectrum with the data points is excellent; consequently, the models are also representative in this system. Deconvolution leads to an equilibrium constant (CIP/SSIP) at 25 °C of 1.9 (65% CIP). Therefore, the ability of the pendant group to form an internal chelate favors the CIP relative to the SSIP by nearly 2:1. Evidence that internal chelation is involved and not simply inductive effects is given by the thermodynamic parameters (see below). The effect of internal chelation is more dramatic when one recalls that in 4a the SSIP is favored by over 30:1. The net result of having a coordinating pendant group is over a 60-fold shift in the relative stabilities of the SSIP's and CIP's.

The dimethylamino functionalized pendant group in 2 is bulkier than the methoxyethyl group of 1, but the enhanced basicity of the nitrogen can overcome this effect. The spectrum in Figure 4a shows that the CIP absorbance (362 nm) is more dominant for 2a than for 1a (Figure 3). This figure shows a reasonable fit of the derived spectrum with the data points, but the fit is better at temperatures where the SSIP and CIP concentrations are more similar (Figure 4b). Deconvolution gives an equilibrium constant of 4.8 at 25 °C which is equivalent to 83% CIP. This value

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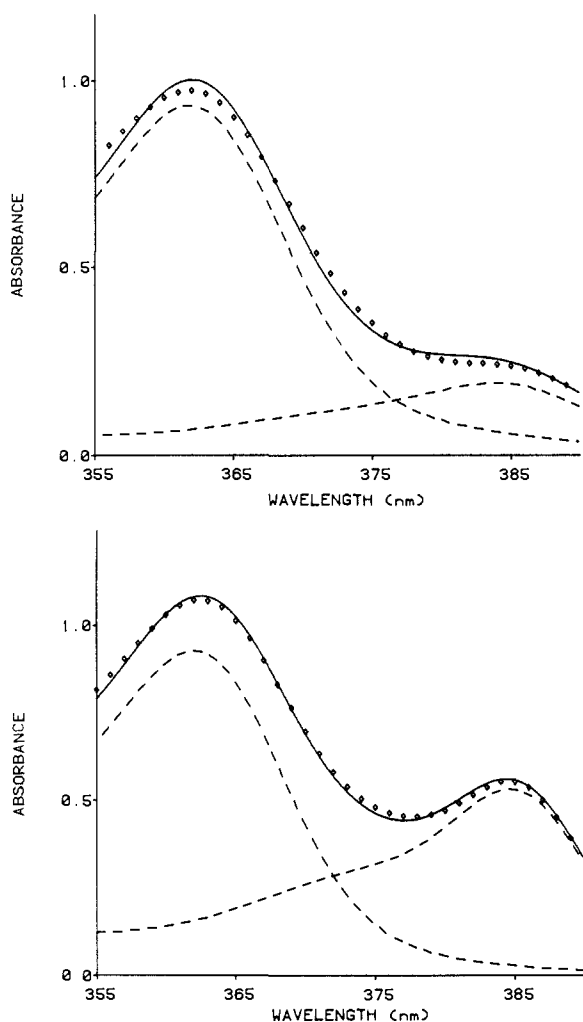
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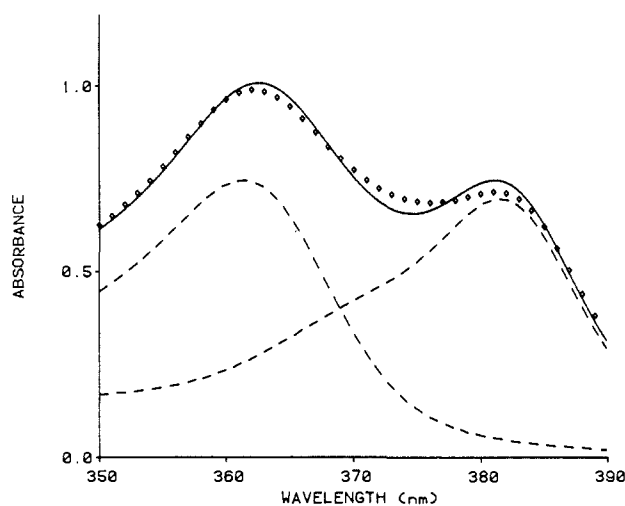


**Figure 4.** Spectrum of 9-(2-(dimethylamino)ethyl)fluorenyllithium (**2a**) in THF at 25 °C (a, top) and -20 °C (b, bottom) in THF. The diamonds are the experimental points, the solid line is the simulated spectrum, and the dashed lines are the CIP (362 nm) and SSIP (382 nm) contributions.

confirms that a pendant nitrogen group is indeed more effective than oxygen in forming internal chelates.

To test the coordinating ability of a second-row substituent in the pendant group, the SSIP  $\rightleftharpoons$  CIP equilibrium was determined for the lithium salt of a sulfur-containing fluorene, **3a**. At 25 °C, one peak at 382 nm is observed in the spectrum indicating that only SSIP's are present. Apparently, the sulfur is too soft a Lewis base to effectively coordinate the lithium cation. As with **4**, the bulk of the pendant group in **3a** disfavors the CIP. The absence of lithium coordination to sulfur has been observed in previous studies where coordination to oxygen and nitrogen was observed.<sup>12c,d</sup>

The possibility of bidentate chelation was considered by using a fluorene containing two heteroatoms in the pendant group. Compound **5** is basically fluorene with a glyme group directly attached. The spectrum of **5a** along with the deconvolution is given in Figure 5. The derived equilibrium constant is 1.1 (52% CIP) indicating that the addition of a second oxygen does not further stabilize the CIP, but in fact destabilizes it with respect to the SSIP. Recall that the methoxyethyl-substituted fluorene gave an equilibrium constant of 1.9 (65% CIP). This result implies that the second oxygen does not play a role in internal chelation and that the larger size of this pendant group is interfering with the formation of CIP's. Inspection of the deconvolution (Figure 5) shows that the fit of the derived spectrum to the data points is not nearly so good as in the previous examples; the model spectra are apparently not as representative in this system. The errors for **5a** persist with either CIP model and at all temperatures and SSIP/CIP ratios. Evidently, the availability of two oxygens to chelate lithium results in a solvation structure that cannot be adequately modeled by the SSIP or CIP models. However, the



**Figure 5.** Spectrum of 9-(2-(2-methoxyethoxy)ethyl)fluorenyllithium (**5a**) in THF at 25 °C in THF. The diamonds are the experimental points, the solid line is the simulated spectrum, and the dashed lines are the CIP (362 nm) and SSIP (382 nm) contributions.

deconvolution is adequate to show that the addition of a second oxygen to the pendant group disfavors CIP's.

The studies at 25 °C show that the oxygen and nitrogen containing pendant groups strongly stabilize their respective CIP's. It is of interest to consider also the thermodynamic aspects of the equilibrium ( $\Delta H^\circ$  and  $\Delta S^\circ$ ). In forming the SSIP, the lithium cation gains greater freedom of motion with respect to the anion; however, this effect is outweighed by the need to localize more solvent molecules in the SSIP. The net result is that the SSIP is disfavored entropically with respect to the CIP, but the greater number of solvent-lithium cation interactions in the SSIP leads to an enthalpic stabilization with respect to the CIP. Therefore, as the temperature of the solution is lowered, the equilibrium is shifted toward the SSIP.<sup>15</sup> To determine the  $\Delta H^\circ$  and  $\Delta S^\circ$  values, the equilibrium constants were determined at a number of temperatures and analyzed with van't Hoff plots. The temperature ranges were chosen to keep the equilibrium constant between 4 and  $1/4$ , if possible, because when the equilibrium is biased too far toward one ion pair type, slight errors in the models can lead to large errors in  $K_{eq}$ . Table I lists the thermodynamic parameters and temperature ranges employed for each of the fluorenes. Given the errors in  $K_{eq}$ , the thermodynamic parameters are expected to have errors of about  $\pm 1$  kcal mol<sup>-1</sup> in  $\Delta H^\circ$  and  $\pm 2$  eu in  $\Delta S^\circ$ . Generally, the largest errors are systematic; therefore, the absolute values may be affected, but relative values should be consistent.

First, consider the parameters derived for fluorenyllithium with measurements from 50 to -10 °C. We obtain  $\Delta H^\circ$  and  $\Delta S^\circ$  values of 3.8 kcal mol<sup>-1</sup> and 11.0 eu, respectively, for the reaction SSIP  $\rightleftharpoons$  CIP. Both values are positive, as expected. Hogen-Esch and Smid examined this equilibrium at temperatures of 25 °C and lower and were only able to estimate  $\Delta H^\circ$  (about 7 kcal mol<sup>-1</sup>)<sup>15b</sup> because in their temperature range the equilibrium is too strongly biased toward the SSIP for accurate analysis. NMR studies of the equilibrium with a temperature range similar to ours led to  $\Delta H^\circ = 4.9$  kcal mol<sup>-1</sup> and  $\Delta S^\circ = 14$  eu.<sup>21</sup> Considering the inherent errors in these experiments, the NMR result is in good accord with our UV-vis study.

Since the CIP requires less solvation from THF, if the pendant group coordinates the lithium, it will be further favored entropically with respect to the SSIP when such internal chelation is important. This effect is borne out in the  $\Delta S^\circ$  value for **1a** (18.6 eu). The entropy change is about 7 eu greater than that for **6a** indicating that internal chelation is indeed important in **1a**. The difference in  $\Delta S^\circ$  between **1a** and **6a** (7 eu) underestimates the change in entropy due to freeing solvent because the  $\Delta S^\circ$  value for **1a** includes a contribution from restricting the motion of the pendant group in the internal chelate CIP—an effect that counteracts the freeing of solvent. The  $\Delta H^\circ$  values for **1a** and **6a** are also significantly different. In **1a** the enthalpy change is 5.1 kcal mol<sup>-1</sup> whereas in **6** it is only 3.8 kcal mol<sup>-1</sup>. The implication is that the

pendant group oxygen is less favorable enthalpically in coordinating to lithium than are the THF oxygens. This effect may be the result of geometric restrictions in the internal chelate.

The nitrogen in the pendant group of **3** is more basic than an oxygen; consequently, the lithium salt of **3** should suffer less enthalpically in forming a CIP. The  $\Delta H^\circ$  value for the ion pair equilibrium in **2a** (SSIP  $\rightleftharpoons$  CIP) is only 2.9 kcal mol<sup>-1</sup> as compared to 5.1 kcal mol<sup>-1</sup> for **1a**. In other words, a nitrogen enthalpically stabilizes the internal chelate by about 2 kcal mol<sup>-1</sup> relative to an oxygen. The  $\Delta S^\circ$  value for **2a** (12.5 eu) indicates that substitution of a dimethylamino group for a methoxy group leads to an entropic destabilization of the internal chelate. This  $\Delta S^\circ$  value is about the same as that for **6a**; therefore the solvent liberating effect of the internal chelation is almost completely offset by some opposing effect. Apparently, the combination of the stronger Li-N interaction and the additional methyl group in the pendant group intensifies the effect of pendant group restriction in this internal chelate. Compared to **1a**, however, the advantage in the enthalpy change outweighs the disadvantage in the entropy and the CIP is more favored for **2a**.

With the bidentate pendant group, **5**, the ion pair equilibrium gives thermodynamic parameters similar to those for **1a**. Compared to **1a**, both the  $\Delta H^\circ$  and  $\Delta S^\circ$  for **5a** are slightly less favorable for the formation of the CIP. These results are consistent with the second oxygen group providing little coordination to the lithium and destabilizing the internal chelate CIP by unfavorable steric effects.

**Definition of  $pK_{Li/THF}$ ,  $pK_{Li/THF}(SSIP)$ , and  $pK_{Li/THF}(CIP)$ .** The ion pairing study of the 9-substituted fluorenes gives an indication of the stabilization that an internally chelated CIP gains relative to an SSIP; however, through inductive effects the dipolar nature of the hetero-substituted pendant groups will tend to stabilize both the CIP's and SSIP's. These effects can be further evaluated by comparison of the relative ion pair  $pK_a$ 's.

In the preceding paper in this series<sup>18</sup> the lithium and cesium ion pair scales were interrelated through the dissociation to free ions using as reference the  $pK_a$  (22.9 per H) of fluorene in dimethyl sulfoxide as measured by the Bordwell group.<sup>27</sup> The scale of transmetalation potentials or relative ion pair acidities for the cesium salts is straightforward because only contact ion pairs are involved. The lithium scale, however, is more complicated because both CIP's and SSIP's may be involved. Consequently, we define two scales for lithium salts in THF,  $pK_{Li/THF}(SSIP)$  and  $pK_{Li/THF}(CIP)$ . We choose the reference value of 22.90 for the SSIP scale. By this choice, for the many reference compounds whose lithium salts are exclusively SSIP the corresponding  $pK_{Li/THF}(SSIP)$  is equal to the observed  $pK_{Li/THF}$  defined in terms of total equivalents of organolithium measured. If measurable amounts of both CIP and SSIP are present the corresponding  $pK$ 's can be derived from the observed  $pK_{Li/THF}$  and the SSIP  $\rightleftharpoons$  CIP equilibrium constants

$$pK_{Li/THF}(SSIP) = +K_{Li/THF} - \log f_{SSIP} \quad (1)$$

$$pK_{Li/THF}(CIP) = +K_{Li/THF} - \log f_{CIP} \quad (2)$$

where  $f_{SSIP}$  and  $f_{CIP}$  are the fractions of the salt present as SSIP and CIP, respectively. This is equivalent to substituting the specific ion pair concentration (SSIP or CIP) for the total anion concentration in the relative  $K_{Li/THF}$  term. The original lithium scale was made up of indicators whose lithium salts are almost all SSIP; revised values for these compounds with the new reference are listed in the preceding paper.<sup>18</sup> For fluorene itself  $f_{SSIP} = 0.71$ ; hence, the observed  $pK_{Li/THF}$  is 22.75. Since the other indicators have amounts of CIP too small to determine, a comparable  $pK_{Li/THF}(CIP)$  scale cannot be given at this time although the value of  $pK_{Li/THF}(CIP)$  for fluorene can be derived from eq 2 as 23.29. Note in the above discussion the general use of  $pK_{Li/THF}$  instead of  $pK_a$  to emphasize the difference between these relative transmetalation potentials and true acidities. Nevertheless, since the  $pK_{Li/THF}$  nomenclature is somewhat awkward, we will frequently use the terms ion pair  $pK$  or simply  $pK$  when the context is clear. The full nomenclature, however, is used in the tables.

**Determination of Ion Pair  $pK$ 's for the 9-Substituted Fluorenes.** The necessary spectral data for the ion pair  $pK$  determinations

Table II. Spectral Data for Lithium Salts of the 9-Substituted Fluorenes in THF

	$\lambda_{max}$ (nm)	$\epsilon^a$		$\lambda_{max}$ (nm)	$\epsilon^a$
<b>1a</b>	360	11 000	<b>4a</b>	387	16 000
<b>2a</b>	362	11 400	<b>5a</b>	362	10 400
<b>3a</b>	382	15 000	<b>6a</b>	373	9 300

<sup>a</sup> Molar extinction coefficient. Estimated error  $\pm 5\%$ .

Table III. Transmetalation Potentials of Substituted Fluorenes in THF at 25 °C<sup>a</sup>

	$pK_{Li/THF}^b$	$pK_{Li/THF}(CIP)^c$	$pK_{Li/THF}(SSIP)^c$
<b>1</b>	21.06 $\pm$ 0.02 <sup>d</sup>	21.2	21.5
<b>2</b>	21.23 $\pm$ 0.03	21.3	22.0
<b>3</b>	21.35 $\pm$ 0.03	>22.9	21.4
<b>4</b>	22.36 $\pm$ 0.02	>23.4	22.4
<b>5</b>	21.21 $\pm$ 0.01	21.5	21.5
<b>6</b>	(22.75)	(23.29)	(22.90)

<sup>a</sup> Relative to fluorene,  $pK_{Li/THF} = 22.75$ ,  $pK_{Li/THF}(SSIP) = 22.90$ , and  $pK_{Li/THF}(CIP) = 23.29$ . <sup>b</sup> Estimated error  $\pm 0.1$ . <sup>c</sup> Estimated error  $\pm 0.2$ . <sup>d</sup> Standard deviation.

are listed in Table II, and the  $pK$ 's for the fluorenes are given in Table III. The ion pair  $pK$  of the reference for the series of fluorenes, 9-*n*-butylfluorene, is 22.36. Since **4a** forms only SSIP's, the measured ion pair  $pK$  is equivalent to the  $pK(SSIP)$ . The  $pK(CIP)$  can only be estimated because the relative stabilities of the SSIP and CIP are not known; however, since the ion pair equilibrium constant ( $[SSIP]/[CIP]$ ) is greater than 30, the  $pK(CIP)$  for 9-*n*-butylfluorene can be estimated at >24. The true value may be considerably higher than this limit. Since the  $pK(SSIP)$  of 9-*n*-butylfluorene is about 0.4 unit lower than that of fluorene, it is evident that simple *n*-alkyl-substitution at the 9-position increases the acidity of fluorenes.

The ion pair  $pK$  for 9-(2-methoxyethyl)fluorene (**1**) is 21.06 indicating that the oxygen-containing pendant group provides about 1.3  $pK$  units of stabilization relative to an *n*-butyl group. Knowing the equilibrium constant for the ion pair equilibrium, the individual ion pair  $pK$ 's may be derived,  $pK(SSIP) = 21.5$  and  $pK(CIP) = 21.2$ . If one assumes that coordination to the pendant group is not important in the SSIP (see below), then by inductive effects the methoxyethyl group is providing about 0.9  $pK$  unit of stabilization to the SSIP relative to an *n*-butyl group. In the CIP, the formation of an internal chelate greatly enhances the effect of the oxygen. In terms of  $pK(CIP)$ 's, the CIP of **1** is at least 2.5  $pK$  units more stable than that of the reference, **4a**. In other words, the ability of the oxygen to coordinate lithium more than doubles its effectiveness in stabilizing the carbanion.

The ion pair  $pK$  of the fluorene with the bidentate oxygen pendant group, **5**, is nearly the same as that for the fluorene with a single oxygen. The measured ion pair  $pK$  for **5** is 0.15 unit higher than that for **1** and leads to derived  $pK$ 's of 21.5 for both the SSIP and CIP. Comparing these ion pair  $pK$ 's to those from **1**, it is evident that the addition of a second oxygen group leads to a destabilization in the CIP and little effect in the SSIP. This result is consistent with the second oxygen group being sterically unfavorable without providing any additional coordination; steric destabilization is more important in the CIP.

The observed ion pair  $pK$  (21.23) for the (dimethylamino)-ethyl-substituted fluorene, **2**, is 0.2 unit higher than the ion pair  $pK$  for **1**; therefore, although the ion pair equilibrium indicates that internal chelation is more important with nitrogen, the net stabilizing effect of the pendant group is greater with an oxygen. Applying the ion pair equilibrium to the  $pK$  leads to derived ion pair  $pK$ 's of 22.0 and 21.3 for the SSIP's and CIP's of **2**, respectively. Relative to *n*-butyl, the nitrogen-substituted pendant group provides a modest stabilization to the SSIP (0.4  $pK$  unit), but a substantial stabilization to the CIP (over 2.5  $pK$  units). The  $pK(SSIP)$  for **2** is higher than that for the oxygen-substituted fluorene presumably because the less polar C-N bonds provide weaker inductive stabilization to the SSIP; however, the preference for internal chelation to nitrogen gives **1** and **2** similar  $pK(CIP)$ 's.

The ion pair  $pK$  of the sulfur-substituted fluorene, **3**, is surprisingly low given that the sulfur is not involved in internal

**Table IV.** Aggregation Study of 9-(2-Methoxyethyl)fluorenyllithium (**1a**) in THF at 25 °C

indicator <sup>a</sup>	10 <sup>4</sup> [ <b>1a</b> ]		indicator <sup>a</sup>	10 <sup>4</sup> [ <b>1a</b> ]	
	(M)	p <i>K</i> <sub>Li/THF</sub>		(M)	p <i>K</i> <sub>Li/THF</sub>
BA	1.77	21.03	BnMP	13.2	21.07
BA	9.93	21.08	BnMP	17.0	21.07
BA	10.4	21.03	BnMP	19.7	21.07
BA	16.1	21.05	1,2-BF	7.24	21.04
BnMP	13.1	21.06			

<sup>a</sup> Abbreviations as follows: 1,2-BF, benzo[*a*]fluorene; BA, benzanthrene; BnMP, 9-benzyl-9-*H*-benzo[*def*]fluorene.

**Table V.** Thermodynamic Parameters for the Reaction RLi + InH ⇌ RH + InLi in THF<sup>a</sup>

RH	InH <sup>b</sup>	SSIP		CIP	
		Δ <i>H</i> <sup>o</sup>	Δ <i>S</i> <sup>o</sup>	Δ <i>H</i> <sup>o</sup>	Δ <i>S</i> <sup>o</sup>
<b>1</b>	BnMP	-0.2	-0.1	-5.6	-19.2
<b>3</b> <sup>c</sup>	BA	-2.6	-3.2		
	BnMP	0.3	1.2		

<sup>a</sup> Enthalpies in kcal mol<sup>-1</sup> and entropies in eu. Entropies corrected for symmetry. <sup>b</sup> Abbreviations in Table IV. <sup>c</sup> These measurements imply Δ*H*<sup>o</sup> = 2.9 kcal mol<sup>-1</sup> and Δ*S*<sup>o</sup> = 4.4 eu for the reaction of BAl with BnMP. The values derived from the indicator scale for this reaction are Δ*H*<sup>o</sup> = 2.9 kcal mol<sup>-1</sup> and Δ*S*<sup>o</sup> = 4.5 eu; see Table VI.

chelation. Since only SSIP's are present at 25 °C, the observed ion pair p*K* (21.35) is equivalent to the p*K*(SSIP), and the p*K*(CIP) is at least one unit higher (>22.4). Apparently, the polarizability of the sulfur combined with the dipolar nature of the C-S bond is responsible for the high acidity of **3**. In fact, these effects give **3** the lowest p*K*(SSIP) in the study. It is remarkable that although the sulfur is neither chelated to the gegenion nor particularly close to the formal anionic center, it is still able to provide about one p*K* unit of stabilization relative to a methylene group (9-*n*-butylfluorene).

To give our results greater utility, a few extended studies were undertaken. Given the affinity for lithium salts to aggregate in THF,<sup>28-30</sup> it is important to show that only monomers are participating in the p*K* and ion pair studies. Although unlikely, it may be argued that the pendant groups can be involved in both intra- and intermolecular coordination. For example, the pendant group could be involved with both lithium cations in a dimer structure. As a test system, the ion pair p*K* of **1** was measured varying the concentration of the 9-(2-methoxyethyl)fluorenyllithium salt almost tenfold. If the lithium salt of **1** is forming aggregates, the observed ion pair p*K* should be lower at higher concentrations.<sup>17</sup> The results in Table IV indicate that the ion pair p*K* is concentration independent; therefore, as has been shown for other lithium salts of delocalized carbanions in THF,<sup>17,9b</sup> **1a** is present predominantly, if not exclusively, as a monomer in the concentration range of interest. This conclusion probably applies as well to the other fluorenes in this study.

Another consideration is whether the pendant group can coordinate the gegenion not only in the CIP but also in the SSIP. Again, **1** was used as a test system. If any unusual ion pairing were occurring in the SSIP, it should be observable in the thermodynamic parameters associated with the SSIP (relative Δ*H*<sup>o</sup> and Δ*S*<sup>o</sup>). The ion pair p*K* of **1** was determined as a function of temperature and dissected into p*K*(SSIP) and p*K*(CIP) at each temperature. Δ*H*<sup>o</sup> and Δ*S*<sup>o</sup> for the proton transfer were then determined via van't Hoff plots. The results of three runs versus the indicator BnMP are given in Table V. It is more instructive to compare these values to those of a number of compounds by including **1** in the relative Δ*H*<sup>o</sup> and Δ*S*<sup>o</sup> scales that were developed along with the indicator ion pair p*K* scale.<sup>17</sup> Since all of the indicators form SSIP's, their relative Δ*H*<sup>o</sup> and Δ*S*<sup>o</sup> values are typical of non-internally coordinated SSIP's. From the values in Table VI, it is evident that both the Δ*H*<sup>o</sup> and Δ*S*<sup>o</sup> for the SSIP of **1a** are consistent with those from the indicator scale. One would expect pendant group coordination in the SSIP to liberate solvent and therefore lead to a greater relative entropy in the anion (higher Δ*S*<sup>o</sup> on the scale). The entropy term for **1** is a little high, but

**Table VI.** Relative Enthalpy and Entropy Scales: 9-PhFili + RH ⇌ 9-PhFl + RLi in THF<sup>a</sup>

RH <sup>b</sup>	Δ <i>H</i> <sup>o</sup>		Δ <i>S</i> <sup>o</sup>		
	(kcal mol <sup>-1</sup> )	(eu)	(kcal mol <sup>-1</sup> )	(eu)	
9-PhFl	0.0	0.0	DiBF	7.4	2.0
3,4-BF	2.8	2.0	2,3-BF	7.7	2.0
1,2-BF	3.9	3.8	<b>1</b> (SSIP)	6.4	4.3
BA	3.3	-0.3	<b>1</b> (CIP)	11.8	23.4
9-BnFl	5.9	2.9	<b>3</b>	5.9	3.0
BnMP	6.2	4.2			

<sup>a</sup> Entropy values corrected for the symmetry component. Errors estimated at ±0.5 kcal mol<sup>-1</sup> in Δ*H*<sup>o</sup> and ±1.0 eu in Δ*S*<sup>o</sup> except for **1** (CIP) and **1** (SSIP) (±1 kcal mol<sup>-1</sup> and Δ*H*<sup>o</sup> and ±2 eu in Δ*S*<sup>o</sup>). See ref 17. <sup>b</sup> Abbreviations in Table IV.

the deviation from the other compounds is less than the estimated errors; hence, internal chelation in the SSIP is of little importance in the stability of **1a**. In contrast, the relative enthalpy and entropy for the CIP of **1a** are much different from those found with the SSIP indicator salts because of the previously explained differences in SSIP and CIP solvation.

As a further check, the thermodynamic parameters for the sulfur-substituted fluorene, **3**, also were obtained. This was done to show directly that the low p*K*(SSIP) was not a consequence of unusual coordination in the SSIP. The measurements versus two indicators are given in Table V, and **3** is included in the scales found in Table VI. It is readily apparent that the relative entropy and enthalpy changes are consistent with those found for the indicator salts. Therefore, internal chelation is not important in the SSIP of **3a**. An interesting coincidence is that the Δ*H*<sup>o</sup> and Δ*S*<sup>o</sup> values for **3** are nearly the same as those for 9-benzylfluorene, another indicator presumably stabilized by polarization of the substituent.

## Conclusions

Substitution in the 9-position of fluorenyllithium destabilizes the CIP relative to the SSIP, but this effect may be overcome by chelation to oxygen or nitrogen containing pendant groups. That is, coordination of lithium cation by a γ-oxygen or nitrogen in a 9-substituted fluorenyl anion is important in the contact ion pair but is not important in the solvent separated ion pair. A second oxygen as in **5a** is not involved in coordination and, in fact, has a destabilizing effect because of steric hindrance. Coordination to the pendant group in the CIP can lead to over 100-fold shifts in the relative stabilities of the CIP's and SSIP's. The SSIP ⇌ CIP equilibria are associated with large entropy changes because of further solvent localization in the SSIP. Entropy values for the fluorenes with coordinating pendant groups indicate that internal chelation in the CIP displaces solvent.

The ion pair p*K*'s show that hetero-substitution in the pendant group leads to stabilization of both the SSIP and CIP; however, the effect is greatest when the heteroatom is able to coordinate to the lithium and can lead to over 2.5 p*K* units of stabilization for internally chelated CIP's relative to normal CIP's. Surprisingly, although sulfur does not coordinate lithium, its polarizability provides 1 p*K* unit of stabilization for the carbanion and the lowest p*K*(SSIP) in the present study. Finally, neither aggregation of the lithium salts nor internal chelation of the SSIP's appear to be important in these systems.

## Experimental Section

**General.** Starting materials were obtained commercially and purified, as needed, by either recrystallization or distillation. Melting points were determined on a Büchi device and are uncorrected. Proton NMR spectra were determined on the UCB-200, a 200 MHz FT instrument. Chemical shifts are reported in parts per million downfield relative to (CH<sub>3</sub>)<sub>4</sub>Si. Anion spectra were recorded on an IBM 9430 UV-vis spectrometer attached to a Vacuum Atmospheres double glovebox system. The details of this apparatus have been described previously.<sup>17</sup> All computer programs were written within the research group; however, some commercially supplied subroutines were employed.

Determinations of the relative p*K*<sub>Li/THF</sub>'s were done using the same techniques detailed in a previous publication.<sup>17</sup> One exception is that some of this work was completed with triphenylmethylithium (TPMLi)

rather than diphenylmethylolithium (DPMLi) as the base to generate anion concentrations. The TPMLi was synthesized and used in the same manner as DPMLi. All of the necessary indicators were available from previous studies. Solvents were purified as detailed in previous publications.<sup>17</sup> In general, the ion pair equilibrium measurements employed the same techniques as the acidity measurements. The experiments involved allowing a THF solution of the appropriate fluorene to react with enough TPMLi to give a reasonable absorbance spectrum. The solution was then equilibrated at the desired temperature and the spectrum was recorded with a correction for base line absorbances. Model spectra for the ion pairs were generated in the same manner, but for the CIP, a diethyl ether solution of the fluorene was employed (the base solution contained THF, but the 2–5  $\mu\text{L}$  of THF in 2 mL of diethyl ether is of little consequence). The CIP models using cesium salts were generated by using a THF solution of diphenylmethylcesium as the base. The model spectra of the SSIP were derived from THF solutions of the fluorenyllithium salts to which about 1–2  $\mu\text{L}$  of 15-crown-5 had been added. 15-Crown-5 (PCR) was degassed by the freeze–pump–thaw method and stored in the glovebox over activated sieves.

**Fluorenes.** The 9-substituted fluorenes were all synthesized by the nucleophilic addition of either fluorenyllithium or fluorenylmagnesium bromide to a derivative of the pendant group that contained a good leaving group in the 2-position (halide or mesylate). Each of the reactions was carried out under argon in diethyl ether solution and purified by multiple extractions followed by column chromatography and either recrystallization/sublimation or fractional distillation. Purities were assessed by NMR spectroscopy, combustion analysis, and melting point, if possible. Mesylates were generated from the appropriate alcohols by reaction with mesyl chloride in dichloromethane with triethylamine.<sup>31</sup> Example syntheses are given below.

**2-Methoxyethyl Methanesulfonate.** To a solution of 3.5 mL of 2-methoxyethanol (0.044 mol) and 9.5 mL of triethylamine in 200 mL of  $\text{CH}_2\text{Cl}_2$  cooled to 0 °C was added 3.9 mL of methanesulfonyl chloride (0.050 mol) over 10 min. The solution was stirred for an additional 20 min. Extractions with  $\text{H}_2\text{O}$ , 10% aqueous HCl, saturated aqueous  $\text{NaHCO}_3$ , and saturated aqueous NaCl followed to give a slightly yellow organic layer. The solution was dried over anhydrous magnesium sulfate and the solvent was removed by rotary-evaporation under reduced pressure to give a slightly yellow oil:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.3 (m, 2 H), 3.6 (m, 2 H), 3.3 (s, 3 H), 3.0 (s, 3 H).

**9-(2-Methoxyethyl)fluorene (1).** To a 0 °C solution of 5.2 g of fluorene (0.031 mol) in 200 mL of ether was added over 10 min 16 mL of about 2 M *n*-butyllithium (in hexane). The resulting yellow solution was added over 90 min to a solution of 5.1 g of 2-methoxyethyl methanesulfonate (0.033 mol) in 100 mL of ether. After being stirred an additional 1 h, the reaction mixture was extracted with saturated aqueous  $\text{NH}_4\text{Cl}$  and  $3 \times \text{H}_2\text{O}$  to give a light yellow ether solution. After rotary evaporation at reduced pressure of the  $\text{MgSO}_4$  dried ether layer, a yellow oil remained. Column chromatography on silica gel with cyclohexane/ethanol (100:1) as the elutant gave a slowly moving colorless fraction. Rotary evaporation of this fraction gave a white solid which yielded large white crystals on recrystallization from petroleum ether. Final purification was by sublimation at 50 °C (ca. 15 mTorr): mp 59–60 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.7 (d,  $J = 7$  Hz, 2 H), 7.5 (d,  $J = 7$  Hz, 2 H), 7.4–7.2 (m), 4.1 (t,  $J = 6.5$  Hz, 1 H), 3.3 (m, 5 H), 2.0–2.2 (q,  $J = 6$  Hz, 2 H). Anal. ( $\text{C}_{16}\text{H}_{16}\text{O}$ ) C, H.

**9-*n*-Butylfluorene (4).** From the reaction of fluorenyllithium with *n*-butyl bromide in ether: bp 80 °C (ca. 15 mTorr);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.6 (d,  $J = 6.5$  Hz, 2 H), 7.4 (d,  $J = 6.5$  Hz, 2 H), 7.3–7.2 (m), 3.9 (t,  $J = 6$  Hz, 1 H), 2.0–1.9 (m, 2 H), 1.3–1.0 (m, 4 H), 0.7 (t,  $J = 7$  Hz, 3 H). Anal. ( $\text{C}_{17}\text{H}_{18}$ ) C, H.

**9-(2-(Dimethylamino)ethyl)fluorene (2).** From the reaction of fluorenylmagnesium bromide with 2-(dimethylamino)ethyl chloride<sup>32</sup> in ether and purified as the picrate; mp 182–183 °C (lit.<sup>33</sup> mp 182–183 °C). 2: bp 100 °C (ca. 15 mTorr);  $^1\text{H NMR}$   $\delta$  7.6 (d,  $J = 7$  Hz, 2 H), 7.4 (d,  $J = 6$  Hz, 2 H), 7.2 (m), 4.0 (t,  $J = 5$  Hz, 1 H), 2.2–2.0 (m, 10 H). Anal. ( $\text{C}_{17}\text{H}_{19}\text{N}$ ) C, H, N.

**9-(2-(Methylthio)ethyl)fluorene (3).** From the reaction of fluorenyllithium with 2-(methylthio)ethyl chloride in ether, sublimed at 35 °C (ca. 15 mTorr): mp 44–45 °C;  $^1\text{H NMR}$   $\delta$  7.6 (d,  $J = 7$  Hz, 2 H), 7.4 (d,  $J = 7$  Hz, 2 H), 7.3–7.1 (m), 4.0 (t,  $J = 5$  Hz, 1 H), 2.3–2.1 (m, 4 H), 1.9 (s, 3 H). Anal. ( $\text{C}_{16}\text{H}_{16}\text{S}$ ) C, H, S.

**2-(2-Methoxyethoxy)ethyl Methanesulfonate.** From the reaction of 2-(2-methoxyethoxy)ethanol with methanesulfonyl chloride in  $\text{CH}_2\text{Cl}_2$  with triethylamine:  $^1\text{H NMR}$   $\delta$  4.3 (t,  $J = 4.5$  Hz, 2 H), 3.7 (t,  $J = 4.5$

Hz, 2 H), 3.6 (m, 2 H), 3.5 (m, 2 H), 3.3 (s, 3 H), 3.0 (s, 3 H).

**9-(2-(2-Methoxyethoxy)ethyl)fluorene (5).** From the reaction of 2-(2-methoxyethoxy)ethyl methanesulfonate with fluorenyllithium in ether: bp 115 °C (ca. 15 mTorr);  $^1\text{H NMR}$   $\delta$  7.7 (d,  $J = 7$  Hz, 2 H), 7.5 (d,  $J = 7$  Hz, 2 H), 7.4–7.2 (m), 4.1 (t,  $J = 6$  Hz, 1 H), 3.5–3.3 (m, 9 H), 2.2 (q,  $J = 7$  Hz, 2 H). Anal. ( $\text{C}_{18}\text{H}_{20}\text{O}_2$ ) C, H.

**Triphenylmethylolithium.** All of these manipulations were carried out in a glovebox. To a solution of 100 mg of biphenyl in about 3 mL of THF was added 400 mg of triphenylmethane and 50 mg of freshly cut lithium (Aldrich, 99.9+%). After 24 h, the solution was decanted from residual lithium. The THF solution gave a  $\lambda_{\text{max}}$  of 502 nm (lit.<sup>20a</sup> 500 nm). This base was stored at –30 °C to limit possible decomposition.

**Diphenylmethylcesium** was derived by allowing a THF solution of diphenylmethane to react with cesium metal. The sample was supplied by Dr. Michael J. Kaufman.

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#### Appendix A. Deconvolution Technique

The deconvolution of the equilibrium spectrum is based on solving the following general set of  $n$  equations

$$A(\lambda_i) = \epsilon_{\text{CIP}}(\lambda_i)C_{\text{CIP}} + \epsilon_{\text{SSIP}}(\lambda_i)C_{\text{SSIP}} \quad i = 1 \rightarrow n$$

where  $A(\lambda_i)$  is the measured absorbance at wavelength  $\lambda_i$  and  $\epsilon_{\text{CIP}}(\lambda_i)$  and  $\epsilon_{\text{SSIP}}(\lambda_i)$  are the extinction coefficients for the CIP and SSIP models at  $\lambda_i$ . Hogen-Esch and Smid solved the equations directly for the specific case  $n = 2$ . However, we used an over-determined least-squares approach with  $n = 30$  to 40. The over-determination allows a check of the fit of the simulated spectrum with the actual observed absorbances. This technique requires the extinction coefficients for the model spectra over a wide range of wavelengths. For practical purposes (see below), it is useful to represent the extinction coefficients as a function rather than an array. For this reason, the form of the model spectra was approximated with a series of gaussian functions

$$\epsilon^f(\lambda_i) = \sum_{j=1}^3 a_j \exp[-b_j(\lambda_i - c_j)^2] \quad (1)$$

The arbitrary parameters  $a$ ,  $b$ , and  $c$  are fit by using a nonlinear least-squares approach. In all cases, the functionalized form of the extinction coefficients reproduced the model spectra with no appreciable error. Functions for the extinction coefficients were generated at several temperatures, and intermediate temperatures were derived by interpolations.

In particular, the ion pairing spectra were deconvoluted by solving the following set of equations

$$A(\lambda_i) = \epsilon^f_{\text{SSIP}}(\lambda_i - \theta_{\text{SSIP}})C_{\text{SSIP}} + \epsilon^f_{\text{CIP}}(\lambda_i - \theta_{\text{CIP}})C_{\text{CIP}} \quad (2)$$

The  $\theta$ 's are correction terms for the differences in  $\lambda_{\text{max}}$  between the model spectra and those found in the equilibrium spectrum. The  $\theta$ 's are screened such that the CIP model peak could not represent the SSIP in the equilibrium spectrum and vice versa ( $\theta < [\lambda_{\text{max}}(\text{SSIP}) - \lambda_{\text{max}}(\text{CIP})]$ ). The need for these corrections leads to the use of functionalized extinction coefficients because with functions, no interpolations are necessary to allow for non-integral values of  $\theta$ . Since only relative concentrations are required and it is assumed that the model spectra have equivalent extinction coefficients at their respective  $\lambda_{\text{max}}$ 's, the  $\epsilon^f$  terms can be normalized such that  $\epsilon^f(\lambda_{\text{max}}) = 1$ , and the deconvolution is solved by using these normalized functions. To allow for optimization of the  $\theta$  terms, equation system 2 was solved with a nonlinear least-squares approach to yield the best  $C_{\text{SSIP}}$ ,  $C_{\text{CIP}}$ ,  $\theta_{\text{SSIP}}$ , and  $\theta_{\text{CIP}}$  values to fit the equilibrium spectrum. The  $C_{\text{CIP}}/C_{\text{SSIP}}$  ratio is equivalent to  $K_{\text{eq}}$  for the ion pair equilibrium  $\text{SSIP} \rightleftharpoons \text{CIP}$ . The correctness of fit can then be analyzed by the least-squares error and the match of the simulated spectrum to the experimental points.

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