basis of the dielectric continuum model, a plot of λ_{max} of the intervalence transfer band in different solvents vs. $(1/D_{op} - 1/D_s)$ can be used to obtain values for the solvent reorganizational energy and the internal reorganizational energy for electron transfer.[18,19] The data above provide three points for such a plot for **3**. Unfortunately, attempts to make additional measurements of **3** with other suitable solvents were not successful, primarily due to dissociation of the complex **3** in these other solvents. In our opinion three points are not adequate for making such a plot, and so we have not made an analysis of this type.

Compounds **2** and **4** show only end absorption, beginning strongly at 380 nm and tailing off into the visible but with very weak absorption above 440 nm. Thus, the chromophores present in **2** and **4** have essentially no effect with respect to the absorption band presented in Figure 5. The absorption spectra of solutions of **3**, both in acetone and in dichloromethane, were measured through the range of 800 to 1900 nm on a Perkin Elmer Coleman EPS-3T instrument. No absorption was detected other than a small amount of tailing at 800 nm from the absorption band shown in Figure 5.

Registry No. 2, 82871-70-3; **3**, 104350-57-4; **4**, 104335-71-9; **8**, 32732-05-1; bis(η^6-hexamethylbenzene)dichloro-di-μ-chlorodiruthenium-(II), 67421-02-7; [2₄](1,2,4,5)cyclophane, 54100-59-3.

Carbon Acidity. 71. The Indicator Scale of Lithium Ion Pairs in Tetrahydrofuran

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Abstract: An equilibrium lithium ion pair indicator scale has been established for eight hydrocarbons that form solvent-separated ion pairs in THF. The scale covers the pK_a range from 18.49 to 23.84 relative to 9-phenylfluorene at $pK_a = 18.49$. This range allows the study of enolates and other highly stabilized anions under realistic synthetic reaction conditions. Equilibria were monitored with UV–vis spectroscopy, and the indicator anion spectra are reported. Thermodynamic measurements of the indicator equilibria yield small $\Delta S°$ values indicating that all of the solvent-separated ion pairs must have similar structures and solvation. Comparison of these thermodynamic parameters with those measured for the analogous cesium ion pairs points out the more complex nature of organocesium ion pairing. Aggregation studies indicate that the organolithium salts exist predominantly, if not exclusively, as monomers in the concentration range employed (10^{-3}–10^{-4} M).

One of the most important reaction sequences in modern synthetic organic chemistry is metalation with lithium amide or an alkyllithium, usually the commerically available butyllithium, in an ether solvent followed by treatment with an electrophilic reagent.[1] The metalation process is usually kinetically controlled although thermodynamic acidities play an important role. Careful control of reaction conditions and sequences are important for directing regio- and stereoselectivity in these syntheses. Consequently, there has been recent intense interest in the structures, stabilities, and reactivities of ion pair salts of carbanions, especially with lithium as the gegenion.[2,3]

A lithium ion pair carbon acidity scale in THF, a solvent frequently used in metalation sequences, would clearly be of enormous use in synthetic design. The establishment of such a scale, however, is complicated by the complex nature of lithium ion pairs. Lithium salts of carbanions in ethers are known to form contact and solvent-separated ion pair structures to varying degrees as well as aggregates.[4–16] Accordingly, our first research in this direction established a carbanion indicator scale in THF with cesium as the gegenion.[17] Cesium salts of carbanions generally form contact ion pairs that we considered would provide a simpler reference system. Related carbon acidity scales have been es-

(1) (a) Stowell, J. C. *Carbanions in Organic Synthesis*; Wiley: New York, 1979. (b) Augustine, R. L. *Carbon–Carbon Bond Formation*; Dekker: New York, 1979. (c) Eliel, E. L.; Otsuka, S. *Asymmetric Reactions and Processes in Chemistry*; American Chemical Society: Washington, 1982. (d) House, H. O. *Modern Synthetic Reactions*; Benjamin/Cummings: Menlo Park, 1972.

(2) (a) Buncel, E.; Durst, T. *Comprehensive Carbanion Chemistry: Part A*; Elsevier: New York, 1980. (b) Buncel, E.; Durst, T. *Comprehensive Carbanion Chemistry: Part B*; Elsevier: New York, 1984.

(3) Coetzee, J. F.; Ritchie, C. D. *Solute-Solvent Interactions*; Dekker: New York, 1969.

(4) Smid, J. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York.

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

(6) (a) Grutzner, J. B.; Lawlor, J. M.; Jackman, L. M. *J. Am. Chem. Soc.* **1972**, *94*, 2306. (b) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633. (c) Menon, B.; Buncel, E. *J. Organomet. Chem.* **1978**, *159*, 357. (d) Buncel, E.; Menon, B. C.; Colpa, J. P. *Can. J. Chem.* **1979**, *57*, 999. (e) Fraenkel, G.; Geckle, M. J.; Kaylo, A.; Estes, D. W. *J. Organomet. Chem.* **1980**, *197*, 249. (f) Parkes, H. M.; Young, R. N. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1137. (g) Chan, L. L.; Smid, J. *J. Am. Chem. Soc.* **1968**, *90*, 4654. (h) Bushby, R. J.; Patterson, A. S. *J. Chem. Res. Synop.* **1980**, 306. (i) Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661.

(7) Velthorst, N. H. *Pure Appl. Chem.* **1979**, *51*, 85.

(8) (a) Wiedrich, C. R.; Catlett, D. L., Jr.; Sedgwick, J. B.; Stevenson, G. R. *J. Phys. Chem.* **1983**, *87*, 578. (b) Müllen, K.; Huber, W.; Meul, T.; Nakagawa, M.; Iyoda, M. *Tetrahedron* **1983**, *39*, 1575. (c) Young, R. N. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*.

(9) (a) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 318. (b) Smid, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 112.

(10) (a) McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 1805. (b) Holm, T. *Acta Chem. Scand., Ser. B* **1978**, *32*, 162.

(11) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972.

(12) (a) West, P.; Waack, R.; Purmont, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 840. Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 2456. (c) West, P.; Waack, R. *J. Am. Chem. Soc.* **1967**, *89*, 4395.

(13) Exner, M. M.; Waack, R.; Steiner, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 7009.

(14) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1967**, *89*, 2764.

(15) Hassig, R.; Seebach, D. *Helv. Chim. Acta* **1983**, *66*, 2269.

(16) Takai, U.; Hogen-Esch, T. E.; Smid, J. *J. Phys. Chem.* **1972**, *76*, 2152.

(17) Bors, D. A.; Kaufman, M. J.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6975.

Li Ion Pairs in Tetrahydrofuran

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tablished in other solvents: cyclohexylamine,[18] dimethoxyethane,[19] Me$_2$SO,[20] and aqueous and alcoholic mixtures of Me$_2$SO.[21] However, these solvents are less commonly used than THF for syntheses.

In the present study we introduce a carbanion indicator scale in THF that consists of solvent-separated lithium ion pairs. As with the organocesium scale,[17] the organolithium equilibria were characterized by the UV–vis absorption spectra of the equilibrium mixtures. As a part of this analysis, the λ_{max} and extinction coefficients of the indicator anions are reported. Equilibrium constants were measured as a function of temperature and the related enthalpy and entropy values demonstrate the comparable nature of all of the ion pairs. Independence of the equilibrium constants to concentration shows that all of the indicator ion pairs are present as monomers in the concentration region used (10^{-3}–10^{-4} M).

Results

The first step to developing an acidity scale in THF was to find a suitable base for generating carbanions. The base must be strong enough to completely deprotonate all the compounds of interest, and once protonated, its quenching product must not interfere with the carbanion equilibria or the UV–vis spectra of the equilibrium mixtures. Moreover, it should be easily prepared in high purity and be reasonably stable in a glovebox atmosphere.

Initially, ethyllithium was investigated as a possible base. It has an advantage over commercially available organolithium salts in that it can be recrystallized to remove impurities, especially lithium halides and hydroxides.[22] However, use of ethyllithium as a deprotonating agent proved troublesome. Since ethyllithium is known to decompose rapidly in THF solution to give ethane, ethene, and the enolate of ethanal,[23,24] it was stored as a solid in the glovebox. Unfortunately, the white solid yellowed in the glovebox atmosphere over a period of days. To prevent decomposition, the ethyllithium was used immediately to generate a THF solution of diphenylmethyllithium. Based on the difficulties in purifying ethyllithium, a simpler route to diphenylmethyllithium was sought.

Unlike diphenylmethylcesium, the lithium salt cannot be prepared by the direct reaction of the hydrocarbon with the metal. However, it can be prepared by the reaction of diphenylmethane with the radical anion of biphenyl which can, in turn, be generated by the direct reaction of biphenyl with lithium metal.[6a] This proved to be an excellent method for producing the base. The reaction can be carried out in the glovebox and avoids contamination by lithium halides. Diphenylmethyllithium is strong enough to deprotonate all of the indicators studied and also has the advantage of indefinite stability. The products of the reaction have not appeared to affect the equilibria or interfere with any necessary portion of the UV–vis spectrum.[25]

Anion Spectra. It is well-known that in THF, alkali salts of delocalized anions, such as fluorenyl, may exist as either contact

Table I. Extinction Coefficients of Organolithium and Cesium Salts[a]

compound[b]	Li λ_{max} (ϵ)	Cs[c] λ_{max} (ϵ)
9-PhFl	411 (25 300)	397 (24 000)
3,4-BF	387 (7 740)	374 (7 580)
	410 (6 650)	394 (5 240)
1,2-BF	454 (8 530)	433 (9 710)
BA	447 (35 000)	
	661 (8 000)	
9-BnFl	381 (15 400)	371 (13 300)
BnMP	535 (6 700)	
DiBF	497 (56 200)	480 (53 260)
2,3-BF	430 (25 500)	415 (22 000)

[a] λ_{max},s are in nm and ϵ represents the molar extinction coefficient. [b] Abbreviations as follows: 9-PhFl, 9-phenylfluorene; 3,4-BF, 3,4-benzofluorene; 1,2-BF, 1,2-benzofluorene; BA, benzanthrene; 9-BnFl, 9-Benzylfluorene; BnMP, 9-benzyl-9-*H*-benzo[*def*]fluorene; DiBF, 2,3-6,7-dibenzofluorene; 2,3-BF; 2,3-benzofluorene. [c] See ref 17.

(CIP) or solvent-separated (SSIP) ion pairs[4] (free ion concentrations are small).[9a] In some cases the equilibrium mixture contains measurable amounts of both types of ion pairs, and, in others, only one type is observed. With these salts the interaction of the anion with the alkali cation is relatively weak so that THF may compete for coordination sites on the cation. Solvent-separated ion pairs are most likely with the smaller alkali cations (Na$^+$, Li$^+$) because they have the strongest interaction with THF. The thermodynamic parameters for ion pairing equilibria are large (ΔH° = 7.6 kcal/mol and ΔS° = 33 eu for fluorenylsodium[5]); hence, these equilibria are highly temperature dependent with the solvent-separated ion pair being favored at lower temperatures.

It is possible to identify the type of ion pairing by the UV–vis absorption spectrum of the anion. The solvent-separated ion pair is generally characterized by a red-shift in λ_{max} with respect to the contact ion pair. This shift is readily rationalized in the following way. Excitation generally shifts electron density to the periphery of a delocalized carbanion, farther from the positively charged gegenion and producing a reduction in electrostatic stabilization. The closer the gegenion is to the carbanion in the ground state, the greater the loss of electrostatic stabilization and the greater the energy required for excitation. Since the contact ion pair has the most intimate cation–anion interaction, it suffers the most from this effect, and its absorptions are shifted to shorter wavelengths than those of the corresponding solvent-separated ion pair.[7]

The presence of more than one type of ion pair would unnecessarily complicate the initial development of an organolithium acidity scale. By coupling two more equilibria to the acidity measurements, assignment of the pK_a's would become dependent on an accurate knowledge of these ion pair equilibrium contants. Since these values are not easily obtained, this is a significant problem. Furthermore, the large thermodynamic parameters of ion pairing equilibria could overwhelm subtle effects in the transmetalation equilibria. Our first step was to limit the acidity scale to only one type of ion pair. A solvent-separated ion pair acidity scale was developed first because solvent-separated ion pairs are generally involved with the delocalized lithium salts useful as indicators in the pK_a range of interest. Although fluorenyllithium itself yields a mixture of contact and solvent-separated ion pairs,[5] derivatives that are either further delocalized or more sterically encumbered do give exclusively solvent-separated ion pairs.[6g]

For the purposes of this study, the following criteria were used to evaluate the nature of the ion pairing. The major type of ion pair was determined by the relative positions of the λ_{max}'s of lithium salts with respect to the corresponding cesium salts. The λ_{max} of the contact ion pair of a given anion increases with the size of the cation, but it is always lower than that of the corresponding solvent-separated ion pair.[5] The cesium salts of interest exist exclusively as contact ion pairs so their λ_{max} are at higher wavelengths than the corresponding lithium contact ion pairs; however, the λ_{max} of the cesium salt is lower than that of the lithium solvent-separated ion pair. Therefore, the type of ion pairs

(18) Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In ref 2a.

(19) Petrov, E. S.; Terekhova, M. I.; Shatenstein, A. I. *Zh. Obshch. Khim.* **1974**, *44*, 1118; *Engl. Transl.* **1974**, *44*, 1075.

(20) (a) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (b) Bordwell, F. G.; Matthews, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 1214, 1216. (c) Bordwell, F. G.; Bartmess, J. E.; Drucker, G. E.; Margolin, Z.; Matthews, W. S. *J. Am. Chem. Soc.* **1975**, *97*, 3226. (d) Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325.

(21) (a) Steiner, E. C.; Gilbert, J. M. *J. Am. Chem. Soc.* **1965**, *87*, 382. (b) Bowden, K.; Stewart, R. *Tetrahedron* **1965**, *21*, 261. (c) Steiner, E. C.; Starkey, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 2751. (d) Bowden, K.; Cockerill, A. F. *J. Chem. Soc. B* **1970**, 173. (e) Cox, R. A.; Stewart, R. *J. Am. Chem. Soc.* **1976**, *98*, 488. (f) Cockerill, A. F.; Lamper, J. E. *J. Chem. Soc. B* **1971**, 503.

(22) (a) Brown, T. L.; Rogers, M. T. *J. Am. Chem. Soc.* **1957**, *79*, 1859. (b) Talalaeva, T. V.; Kocheshkov, K. A. *J. Gen. Chem. U.S.S.R.* **1953**, *53*, 399.

(23) (a) Asami, R.; Levy, M.; Szwarc, M. *J. J. Chem. Soc.* **1962**. 361. (b) Russell, G. A. *J. Am. Chem. Soc.* **1959**, *81*, 2017.

(24) Rembaum, A.; Siao, S.; Indretor, N. *J. Polym. Sci.* **1962**, *56*, 517.

(25) Residual biphenyl appeared in the spectrum of the quenched base but at too short a wavelength to interfere with the indicator anions.

Table II. Equilibrium Measurements[a]

R_1H[b]	R_2H	ΔpK_a	ΔH°[c]	ΔS°[d]
9-PhFl	BA	2.53 ± 0.03	-3.3 ± 0.1	0.3 ± 0.1
3,4-BF	BA	0.82 ± 0.01	-0.4 ± 0.1	2.3 ± 0.1
1,2-BF	BA	0.43 ± 0.02	0.7 ± 0.1	-4.3 ± 0.1
3,4-BF	1,2-BF	0.44 ± 0.01	-1.1 ± 0.1	-1.8 ± 0.1
1,2-BF	9-BnFl	1.67 ± 0.01	-2.1 ± 0.1	0.7 ± 0.3
BA	9-BnFl	1.21 ± 0.02	-2.4 ± 0.2	-2.9 ± 0.2
BnMP	9-BnFl	0.03 ± 0.01[e]	0.3 ± 0.1[e]	1.2 ± 0.3[e]
9-BnFl	2,3-BF	1.61 ± 0.01	-2.0 ± 0.1	0.7 ± 0.1
BnMP	2,3-BF	1.59 ± 0.01[e]	-1.5 ± 0.1[e]	2.4 ± 0.1[e]
DiBF	2,3-BF	0.26 ± 0.01	-0.3 ± 0.1	0.0 ± 0.1
BnMP	DiBF	1.32 ± 0.04		

[a] For the deprotonation of more acidic compound, R_1H. Equilibrium constants on per hydrogen basis at 25 °C. [b] See Table I for key to abbreviations. [c] In kcal mol^{-1}. [d] In entropy units corrected for the symmetry component. [e] There were only two measurements in these cases so the absolute difference is given as the error.

Table III. Overlapping pK_a Measurements

R_1H[a]	R_2H	ΔpK_a[b]
3,4-BF	BA	0.82
BA	1,2-BF	-0.43
3,4-BF	1,2-BF	0.39 (0.44)[c]
1,2-BF	BA	0.43
BA	9-BnFl	1.21
1,2-BF	9-BnFl	1.64 (1.67)
9-BnFl	BnMP	-0.03
BnMP	2,3-BF	1.59
9-BnFl	2,3-BF	1.56 (1.61)
BnMP	DiBF	1.32
DiBF	2,3-BF	0.26
BnMP	2,3-BF	1.58 (1.59)

[a] See Table I for key to abbreviations. [b] Corresponding to $pK_a(R_2H)$ - $pK_a(R_1H)$ (per hydrogen at 25 °C). [c] Direct measurements in parentheses.

Table IV. Comparison of pK_a Values from Various Acidity Scales[a]

compound[b]	THF/Li	THF/Cs[c]	Me$_2$SO/K[d]
9-PhFl	(18.49)[e]	(18.49)[e]	17.9 (18.5)[f]
3,4-BF	20.18	19.90	
1,2-BF	20.59	20.54	
BA	21.02		
9-BnFl	22.25	20.92	21.4 (22.0)
BnMP	22.24		
DiBF	23.57	23.35	
2,3-BF	23.84	23.15	23.4 (24.0)

[a] All pK values on per hydrogen basis. [b] See Table I for key to abbreviations. [c] See ref 17. [d] See ref 20. [e] pK_a values referenced to 9-PhFl = 18.49. [f] Values in parentheses have 0.6 added to them to give the same reference point as the THF scales (9-PhFl, pK_a = 18.5).

could be unambiguously assigned depending on whether the λ_{max} of the lithium salt is higher (SSIP) or lower (CIP) than that of the corresponding cesium salt. To insure that the lithium salts do not have significant concentrations of contact ion pairs in the equilibrium mixtures, the effects of temperature on the spectra were studied. Since ion pairing equilibria are highly temperature dependent, the relative heights or shapes of the peaks should change with temperature if such an equilibrium mixture were present. If the spectrum did not change with temperature, then all of the peaks could be assigned to a single species. In short, if λ_{max} of the lithium salt is red-shifted with respect to the cesium salt, and the spectrum is insensitive to temperature, then the salt was considered to exist solely as a solvent-separated ion pair. Although this analysis does not eliminate the possibility of a small contact ion pair concentration at the higher temperatures, it limits this concentration to values too small to interfere with our experiments. We estimate the maximum amount of contact ion pairs at 35 °C is less than 10%.

From Table I it can be seen that all of the lithium salts have λ_{max}'s at higher wavelengths than their cesium analogues. The difference in λ_{max} range from 10 nm for 9-benzylfluorenyl to 21 nm for 1,2-benzofluorenyl but are generally about 15 nm. The unusually large change with 1,2-benzofluorenyl is a result of the flat shape of its peak. Its extinction coefficient changes little over a wide range so that the exact value of λ_{max} loses significance. The extinction coefficients of the anions vary with the change in gegenion and ion pairing. This can partly be ascribed to changes in the way peaks overlap because some of the transitions appear to be shifted more or less than others on changing ion pair type, and therefore, peak shapes change somewhat. The general trend is that the extinction coefficients are higher for the lithium salts, but the differences are rather small (10–15%).

The extinction coefficients were measured in more than one way, and the procedures are discussed in the Experimental Section. The techniques afford an experimental precision of about ±4% depending on the technique. This uncertainty leads to the largest errors in the pK_a measurements.

Transmetalation Equilibria. The general procedure for these measurements has been described in detail in previous publications.[26] Briefly, the concentration of the anions can be determined by deconvolution of the UV–vis spectrum of the equilibrium mixture and comparison with the individual organolithium spectra. The effects of temperature on the THF volume and indicator extinction coefficients were taken into account in the deconvolution process.[9a,17]

Transmetalation equilibrium constants were obtained for a number of hydrocarbon indicator combinations. For each comparison, a minimum of three measurements was used, unless otherwise noted, and the results are tabulated as log K along with the standard deviations (Table II). The greatest error in these

measurements results from the deconvolution and Beer's law analysis of the equilibrium spectra to yield anion concentrations. As stated earlier, there is some error in the extinction coefficient measurements. In cases where the absorbances of the two anions are significantly overlapped, the equilibrium constant becomes sensitive to slight changes in the analysis and gives rise to significant scatter in the results. Errors are also large when one of the hydrocarbons is almost completely deprotonated in the equilibrium mixture because its concentration is determined indirectly by subtracting the anion concentration from the starting hydrocarbon concentration. When the anion concentration approaches the starting hydrocarbon concentration, the result is a small difference of two large numbers with resultant error. For this reason experiments were designed to maintain reasonable hydrocarbon concentrations at all times. This was done by forcing the equilibria from side to side with excesses rather than deficiencies of reagents. For practical reasons this approach limits the range of K's that can be measured (about 10^{-2}–10^2).[27] The resultant pK's are estimated to be correct to ±0.1 units although the precision of the experiments is generally better than this value. The accuracy of these values was also assessed by using overlapping measurements.

In some cases it was possible to measure the equilibrium between indicators directly and also by combining measurements to a third indicator. This gives an independent method of checking the direct measurements and should point out any peculiarities in the indicator equilibria. In Table III, the direct measurements of the equilibria are listed along with two equilibria to a third, bridging indicator. In each case, the indirect values match up quite well with those from direct measurements. Moreover, all of the differences are less than the estimated errors.

Given the series of indicator equilibrium measurements, it is possible to develop a scale quantitatively ranking their transmetalation potentials. In order to do so, however, a common reference point is convenient. In accord with previous acidity scales

(26) (a) Streitwieser, A., Jr.; Chang, C. J.; Hollyhead, W. B.; Murdoch, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 5288. (b) Streitwieser, A., Jr.; Hammons, J. H.; Ciuffarin, E.; Brauman, J. I. *J. Am. Chem. Soc.* **1967**, *89*, 59.

(27) These limits are based on the solubilities and availabilities of the hydrocarbons.

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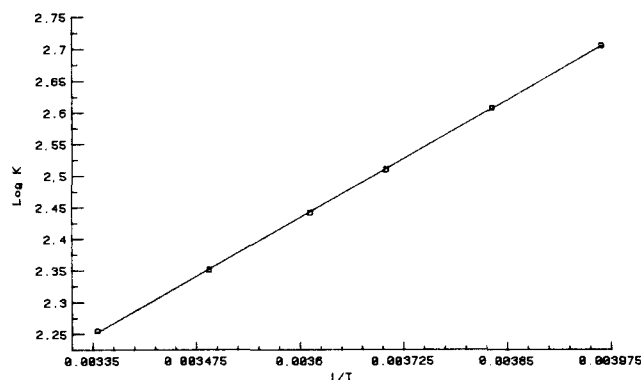*J. Am. Chem. Soc., Vol. 108, No. 22, 1986* 7019

Figure 1. Van't Hoff plot of typical thermodynamic run: benzanthrene vs. 9-phenylfluorene from 25 to -20.7 °C.

Table V. Overlapping Thermodynamic Measurements[a]

R_1H[b]	R_2H	$\Delta H°$[c]	$\Delta S°$[d]
3,4-BF	BA	-0.4	2.3
BA	1,2-BF	-0.7	-4.3
3,4-BF	1,2-BF	-1.1 (-1.1)[e]	-2.0 (-1.8)
1,2-BF	BA	0.7	4.3
BA	9-BnFl	-2.4	-2.9
1,2-BF	9-BnFl	-1.7 (-2.1)	1.4 (0.7)
9-BnFl	BnMP	-0.3	-1.2
BnMP	2,3-BF	-1.5	2.4
9-BnFl	2,3-BF	-1.8 (-2.0)	1.2 (0.7)

[a] For deprotonation of R_1H. [b] See Table I for key to abbreviations. [c] In kcal mol⁻¹. [d] In eu corrected for the symmetry component. [e] Direct measurement in parentheses.

from this research group,[17,28] the H_ value of 18.49 for 9-phenylfluorene was used as the starting point.[29] That is, 9-phenylfluorene is arbitrarily set at 18.49, and all of the other indicators are referenced to this value. Since there were overlapping measurements, a least-squares approach was taken to give the best $pK_{a(THF)}$ values to fit the measured equilibria.[30] Table IV gives the entire scale which includes eight indicators and covers the pK_a range from about 18.5 to 23.8. This area of pK_a's is quite significant because it contains synthetically important enolates and other strongly stabilized carbanions.[31] Extension of this organolithium acidity scale to higher pK_a values is experimentally challenging. The lithium salts reach equilibrium rather slowly, and the higher the pK_a's, the slower the exchange reactions.

Thermodynamics. In addition to the pK_a's at 25 °C, it was also possible to determine the thermodynamic parameters of the transmetalation equilibria ($\Delta H°$ and $\Delta S°$) by measurements at several temperatures.[32] In most cases, measurements were taken from 25 °C to -20 °C; however, in some instances, the measurements only went down to -10 °C. The limiting factor is the time required to reach equilibrium. With some of the more sterically encumbered indicators, it required 3 h to reach equilibrium at 25 °C, and at low temperatures, the rate of equilibration became so slow that more than 24 h were required to reach equilibrium—too long for reliable measurements. Nonetheless, it was possible to generate reasonable Van't Hoff plots which showed acceptable scatter with little or no curvature (Figure 1). The values given are expected to be correct to about 0.5 kcal mol⁻¹

(28) Streitwieser, A., Jr.; Ciuffarin, E.; Hammons, J. H. *J. Am. Chem. Soc.* **1967**, *89*, 63.

(29) This value was found by H_ measurements in aqueous mixtures of sulfolane: Langford, C. H.; Burwell, W. R., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 1503.

(30) Values were adjusted by using a program based on the "SIMPLEX" method of solving linear/nonlinear least-squares problems.
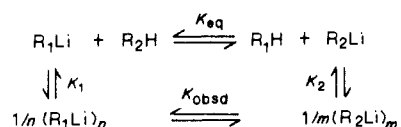
(31) (a) Kaufman, M. J.; Gronert, S.; Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.*, submitted for publication. (b) Kaufman, M. J.; Streitwieser, A., Jr., unpublished results.

(32) DeTar, D. F. *Computer Programs in Chemistry*; W. A. Benjamin: New York, 1969; Vol. 3.

Table VI. Comparison of Thermodynamic Scales[a]

Rh[b]	THF/Li		THF/Cs[c]	
	$\Delta H°$[d]	$\Delta S°$[e]	$\Delta H°$	$\Delta S°$
9-PhF	0.0	0.0		
3,4-BF	2.8	2.0	(2.8)[f]	(2.0)[f]
1,2-BF	3.9	3.8	3.1	0.2
BA	3.3	-0.3		
9-BnFl	5.9	2.9	3.0	-4.0
BnMP	6.2	4.2		
DiBF	7.4	2.0	4.9	-6.5
2,3-BF	7.7	2.0	4.5	-6.9

[a] For the reaction RH + 9-PhFlLi → RLi + 9-PhFl. [b] See Table I for key to abbreviations. [c] See ref 17. [d] In kcal mol⁻¹. [e] In eu corrected for the symmetry component. [f] The cesium scale is referenced to the lithium scale's values for 3,4-BF (ΔH = 2.8, ΔS = 2.0).

and 1.0 eu for $\Delta H°$ and $\Delta S°$, respectively.[33]

As with the pK_a's the validity of these measurements may also be gauged by overlapping measurements. The results in Table V show satisfactory agreement and indicate that there are no large systematic errors.

The best way to evaluate the thermodynamic parameters is on the basis of a scale referenced to a single indicator. For convenience, the most acidic indicator, 9-phenylfluorene, was chosen as the reference for a scale that gives the relative changes in $\Delta H°$ and $\Delta S°$ for deprotonating the indicators (Table VI). As with the pK_a's, the redundancy of the measurements was resolved by least-squares fitting.

The $\Delta S°$ values for all of the indicators vary by only about 4 eu. This is an important result in itself and implies that all of the solvent-separated ion pairs have rather similar structures and solvation. Otherwise, a wide $\Delta S°$ range would be expected because solvation and ion pairing changes usually involve large entropy effects (about 22 eu for going from the contact to the solvent-separated ion pair of fluorenyllithium).[4] These thermodynamic results are consistent with the assumption that equilibria between solvent-separated ion pairs are dominated by carbanion stability rather than solvation or ion pairing effects. It appears that solvent-separated ion pairs are nearly free of any specific cation-anion interactions, and that they are all equally solvated; consequently, they act much like loosely associated free ions. The simple nature of these solvent-separated indicator anions makes the organolithium scale exceptionally convenient for future analysis of the complicated ion pairing interactions found in more localized lithium salts.

In analyzing the thermodynamic parameters it should be noted that the neutral indicators used are, except for substituents, already locked into planar and rigid conformations; hence, entropy changes associated with deprotonation should be small and limited to substituent effects. The equilibria are, consequently, dominated by enthalpy effects. 9-Phenylfluorene has a $\Delta S°$ value about 2–4 eu below the other fluorene-based indicators because, on forming the anion, the phenyl ring of 9-phenylfluorene is less free to rotate due to conjugation.[17] The entropy variations among the benzyl- and benzo-substituted fluorene indicators are rather small and are consistent with but slight changes on deprotonation. One apparently anomalous compound is benzanthrene which has a lower $\Delta S°$ than 9-phenylfluorene, yet should be free from substituent effects; however, benzanthrene is a phenalene derivative rather than a fluorene. It is possible that the mode of solvation for phenalene systems is slightly different, in the direction of reduced freedom of motion, compared to fluorenyl systems; nevertheless, the effect is small. Since the entropy differences are so small, the enthalpy terms are most important in determining the relative acidities and result in a spread of almost 8 kcal mol⁻¹ over the acidity scale.

Aggregation Studies. When working with organolithium salts, it is necessary to consider possible aggregation effects. There is little doubt that alkyllithiums (methyl, *n*-butyl, etc.) are signif-

(33) The error bars are estimated by considering the scatter and overlap differences found for these measurements.

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icantly aggregated in THF.[10,11] The state of aggregation of more delocalized salts, however, is far from resolved. Waack and co-workers have examined alkyl-, allyl-, vinyl-, phenyl-, and benzyllithium salts for possible aggregation by using both colligative and kinetic techniques.[12] Their work indicates that the localized carbanions (alkyl, vinyl, and phenyl) are present as aggregates in THF, but that the delocalized anions (allyl and benzyl) are monomers in the concentration ranges studied (0.001–0.5 M depending on the method employed). In contrast, the Waack group reports 9-(2-hexyl)fluorenyllithium to be aggregated in THF at concentrations as low as 0.004 M.[13] Moreover, Hogen-Esch and Smid have attributed concentration dependencies to aggregation effects in the transmetalation rates of fluorenyllithium derivatives.[14] It appears rather odd that the more localized systems (benzyl and allyl) would not aggregate, and highly delocalized, solvent-separated ion pairs would aggregate.

To give our results greater utility, it must be shown that only monomers are present in the indicator equilibria. Since the literature has not clearly answered this question, we set out to determine the state of aggregation of our ion pairs. Our technique was to examine the concentration dependence of the measured equilibrium constants. If one or more species were present as a dimer or higher aggregate, then the equilibrium constant should be sensitive to changes in concentration. Consider the equilibrium equation including aggregation.

$$R_1Li + R_2H \xrightleftharpoons{K_{eq}} R_1H + R_2Li$$

$$\downarrow\uparrow K_1 \qquad \xrightleftharpoons{K_{obsd}} \qquad K_2\uparrow\downarrow$$

$$1/n\,(R_1Li)_n \qquad\qquad 1/m(R_2Li)_m$$

Aggregates and monomers are assumed to have the same electronic spectra;[34] hence, experimentally only the total (monomer + aggregates) anion concentrations can be determined by deconvolution. The two aggregate equilibria (K_1 and K_2) are obviously concentration dependent. If one considers the case where only one of the anions forms an aggregate (R_1Li), then as the concentration of R_1Li rises, a greater percentage of R_1Li will be present as an aggregate. This reduces its relative monomer concentration and forces K_{eq} toward the left increasing the total concentration of R_1Li. Therefore, at higher anion concentrations, the aggregated species (R_1H) would appear relatively more acidic.

The second case is where both of the anions are aggregated. Since 'm' may equal 'n', simply increasing the concentrations of the anions does not ensure that K_{obsd} will be affected. However, by increasing the concentration of one anion (R_1Li) while maintaining a constant concentration of the other anion, one should be able to see a change in the K_{obsd}. The increased concentration of R_1Li makes it relatively more aggregated than R_2Li and, consequently, forces K_{eq} toward the left because of a relative reduction in R_1Li monomer concentration. The result is that at higher concentrations of R_1Li, R_1H would appear to be more acidic.

In reality, the state of aggregation may be much more complicated than either of the above examples. Aggregates of various sizes may coexist in significant concentrations, and there is also the possibility of mixed aggregates [$(R_1Li)_n(R_2Li)_m$].[15] However, in a qualitative sense, the principles found in these simple examples should hold for the more complicated cases. Most importantly, increasing the concentration of a species that is to some extent aggregated increases its apparent acidity.

Table VII gives the results of three studies on the concentration dependence of K_{obsd}. In each case the concentrations of anions were varied about three- to fivefold, and in one example, the concentration of only one of the indicator anions was changed. It is quite evident from the results that K_{obsd} is hardly affected by the changes in concentration. The effects on K_{obsd} are all less than the expected error in the measurements. Since these equilibria are rather typical, there is no reason to believe that the

(34) Since no other peaks are observed, it must be concluded that either only one species is present or all species (monomers and aggregates) have the same spectra.

Table VII. Aggregation Studies[a]

System 1. BA[b] vs. 9-BnFl

[BA⁻][c]	[9-BnFl⁻]	ΔpK_a
3.78	2.52	1.24
4.06	2.57	1.19
5.42	3.95	1.21
18.1	3.66	1.23
26.8	7.81	1.22

System 2. 1,2-BF vs. BA

[1,2-BF⁻]	[BA⁻]	ΔpK_a
3.14	0.279	0.45
5.29	0.483	0.44
11.1	1.05	0.45

System 3. 3,4-BF vs. 1,2-BF

[3,4-BF⁻]	[1,2-BF⁻]	ΔpK_a
6.42	5.41	0.45
11.9	11.9	0.42
17.0	18.8	0.44

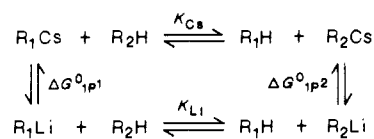[a] The more acidic compound is listed first. [b] See Table 1 for key to abbreviations. [c] Anion concentrations in molarity × 10⁴.

other equilibria would show concentration dependence. In fact, aggregation studies of other equilibria were also undertaken, but they were not as rigorous because the concentration ranges were more limited; however, concentration dependence could not be detected in any of these studies.

Another test for aggregation comes from the thermodynamic data. If the two indicator anions existed in different states of aggregation, the transmetalation reaction would result in either a net gain or loss of free molecules. As a result, the equilibrium measurements would be associated with large $\Delta S°$ values; such large values were not found and we conclude that only monomeric ion pairs are involved in these equilibria.

Discussion

It is most interesting to compare the values of this new scale with those from previous scales, in particular, the THF scale developed by our group for organocesium salts (Table IV).[17] The only real difference between the scales is the ion pairing behavior. Organocesium salts are exclusively contact ion pairs, whereas the organolithium scale was developed by using only solvent-separated ion pairs. It is useful to consider the effects of ion pairing on the equilibrium measurements. A simple thermodynamic cycle can be generated to relate the equilibria by using different cations.

$$R_1Cs + R_2H \xrightleftharpoons{K_{Cs}} R_1H + R_2Cs$$

$$\downarrow\uparrow \Delta G°_{IP1} \qquad\qquad \Delta G°_{IP2}\uparrow\downarrow$$

$$R_1Li + R_2H \xrightleftharpoons{K_{Li}} R_1H + R_2Li$$

The difference between $\Delta G°_{IP1}$ and $\Delta G°_{IP2}$ defines the change in equilibrium constant upon switching from cesium to lithium salts. Along with various transfer terms that cancel out, the $\Delta G°_{IP}$'s have two major components: the interaction of the cation with the anion and with the solvent. For solvent-separated ion pairs, the cation–anion interactions are relatively weak and probably similar for most indicators. This effect is seen in the UV–vis spectra of the anions where, for solvent-separated ion pairs, the λ_{max}'s are independent of the counterion. In contrast, contact ion pairs have strong cation–anion interactions, and their λ_{max}'s vary considerably on changing the counterion (16 nm for the fluorenyl system).[5] This implies that for the $\Delta G°_{IP}$'s the cation–anion interaction component will be dominated by the effects in the contact ion pair. As for solvation of the cation, this effect should be relatively weak for cesium salts and strong for the lithium salts. However, it is a reasonable assumption that this solvation energy is similar for all of the solvent-separated lithium salts. The thermodynamic parameters of the equilibria support this generalization (see above). Although these assumptions may not be completely correct, they should be sufficiently valid for
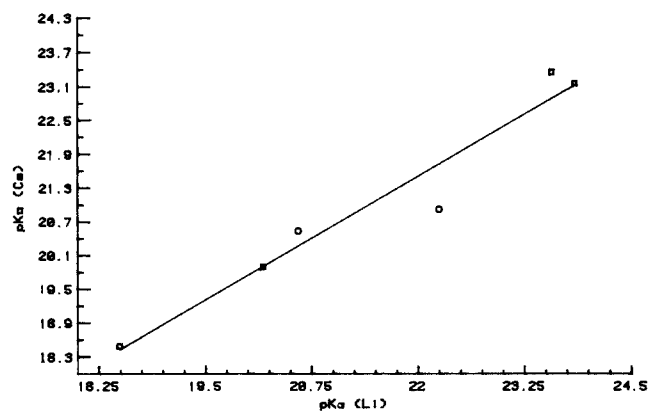
Figure 2. Comparison of pK_a's determined on the organolithium and organocesium scales. Both scales are referenced to 9-phenylfluorene, pK_a = 18.49. See text for discussion of slope and intercept.

the following qualitative arguments. Given the above considerations, the most dominant factor in the $\Delta G°_{IP}$'s would be the cesium–anion interactions in the contact ion pairs. In other words, any differences in the acidities of the two scales could be attributed to the relative strengths of these contact ion pair interactions. Since localization of the anionic charge enhances the contact ion pair interactions, one would expect the more localized anions to be relatively more acidic on the cesium scale. The pK_a's on both scales are referenced to a highly delocalized anion, 9-phenylfluorene, so that any localization of an anion's charge should result directly in a higher pK_a assignment on the solvent-separated ion pair lithium scale.

Comparing the two scales, the most dramatic difference is for 9-benzylfluorene which is 1.3 units less acidic on the lithium scale. The reason for this difference can be related to the unsubstituted parent of this indicator, fluorene, because, unlike the benzofluorenes, fluorenyllithium has a significant contact ion pair concentration in THF. Recall that this affinity for contact ion pairing led to the addition of the bulky benzyl substituent to force the equilibrium toward solvent-separated ion pairs. Nonetheless, the preference of the fluorenyl system for contact ion pairing indicates that is possesses a strong cation–anion interaction and, therefore, suffers in the conversion to a solvent-separated ion pair. The other major difference is the order of acidity between 2,3-benzofluorene and 2,3:6,7-dibenzofluorene. On the cesium scale, 2,3-benzofluorene is the more acidic, whereas on the lithium scale, it is less acidic than 2,3:6,7-dibenzofluorene. On the basis of the π energies,[35] the 2,3-benzofluorenyl anion is expected to be relatively more stable than the 2,3:6,7-dibenzofluorenyl anion, but apparently some effect in the solvent-separated ion pair is reversing the order of stability. However, this effect is minor and results in only a 0.5 unit shift in relative acidities.

A plot comparing the results of the two scales is given in Figure 2. With only six points it is difficult to do a definitive analysis, but it is evident that there are no glaring differences in acidity. It is interesting to note that the slope of the plot is about 0.9 (the intercept is about 2, but this is an artifact of arbitrarily setting 9-phenylfluorene to 18.49 on both scales). This slope indicates that at higher pK_a's, the cesium salts are relatively more acidic than the lithium salts. The rationalization is that the anions with higher pK_a's are generally more localized and, therefore, have a greater preference for contact ion pairing. It is important to remember that the absolute acidities of the scales are based on an arbitrary reference point so the above arguments in no way imply that cesium salts, or contact ion pairs in general, are inherently more stable than solvent-separated ion pairs.

A comparison of the thermodynamic parameters from this scale with those from the organocesium scale leads to a rather unusual result. Since the organocesium thermodynamic scale does not include 9-phenylfluorene, it is referenced to the values for 3,4-

benzofluorene on the organolithium scale (Table VI). Unlike the organolithium scale, the $\Delta S°$ values on the organocesium scale vary widely. On the cesium scale, the $\Delta S°$ values for 3,4-benzofluorene and 2,3-benzofluorene differ by nearly 9 eu, yet on the lithium scale, their $\Delta S°$ values are almost identical. In other words, the nature of the organocesium contact ion pairs varies greatly from compound to compound even if the compounds have similar structures. In fact, entropic effects play a major role in determining the equilibrium constants between the cesium salts. Considering the large size of the cesium anion, it was not expected that it would engage in such specific contact ion pair interactions. Since the $\Delta S°$ values for the fluorene-based indicators on the organocesium scale drop almost monotomically with increasing pK_a,[36] it is evident that the cesium salts are either further solvated or restricted at higher pK_a's. Based on the weak solvation of cesium salts, one would expect that these entropy changes are the result of the less stable organocesium salts forming tighter ion pairs. This sort of behavior is completely absent on the organolithium scale. The $\Delta S°$ values vary slightly across the organolithium scale, but they are in no way dependent on the pK_a.

Although the relative stabilities of the lithium and cesium salts of these highly delocalized hydrocarbons are rather similar, there may be large differences between lithium and cesium pK_a's when more localized anions are considered. With anions such as enolates, acetylides, and dithianes, strong lithium–anion interactions and aggregation could preferentially stabilize the lithium salts with respect to their cesium analogues.

Since the solvent-separated ion pairs appear to have some of the characteristics of free ions, it is worthwhile to compare the organolithium results with Bordwell's results for free ions in Me_2SO;[20] however, the two acidity scales have only three indicators in common. Furthermore, one of these indicators must be used as a reference point so that only two comparisons can be made. Assuming a value of 18.5 for 9-phenylfluorene (adding 0.6 units to Bordwell's numbers, see Table IV), one may compare the pK_a's of 9-benzylfluorene and 2,3-benzofluorene. For both of these indicators the differences in pK_a's are less than 0.3 units. In fact, our organolithium results for these indicators are more consistent with the Me_2SO values than the organocesium values (these indicators show the greatest difference in changing from lithium to cesium as the gegenion). Although it is difficult to make any definite conclusions based on only two points, it is apparent from these results that the effects of structure are indeed comparable for the relative stabilities of delocalized free carbanions in Me_2SO and for solvent-separated organolithium ion pairs in THF.

Conclusion

This study has resulted in a relative ion pair pK_a scale which can be used to quantitatively rank the stabilities of organolithium salts in THF. The thermodynamic parameters indicate that equilibria between solvent-separated ion pairs are free of large entropy effects and, therefore, that the solvation of all of these solvent-separated ion pairs must be similar. These results further suggest that some unusual entropy results found previously in the organocesium scale must result from cation–anion interactions. Finally, there is no evidence that any of these organolithium salts are aggregated to a significant extent.

Experimental Section

Equilibrium Measurements. The details of the procedure have been described in detail in previous publications;[26] however, some changes should be noted. In previous work it was necessary to prepare samples in the glovebox, seal them, and bring them out into the lab for spectroscopic measurements. This procedure was time-consuming and led to limited anion stability. To remedy this limitation, we searched for a way to do the spectroscopic measurements while keeping the samples in the glovebox environment. Our first attempt was to place the optical bench of an IBM 9430 UV–vis spectrometer in the glovebox. The IBM was chosen because the optics are separate from the controller so that it requires less space. Nonetheless, the addition of the spectrometer re-

(35) The predicted higher stability of the 2,3-benzofluorenyl anion is based on the Hückel delocalization: E_π(anion) − E_π(neutral).

(36) This is true for the indicators that overlap with those on the lithium scale. However, $\Delta S°$ of 9-tert-butylfluorene is not consistent with this generalization presumably due to a large substituent effect.

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quired expanding to a double-box Vacuum Atmospheres system. The resulting system was extremely convenient; however, the electronics of the instrument were not stable in the glovebox atmosphere. Attempts were made by using argon, nitrogen, and nitrogen–helium mixtures, but in each case circuit boards on the instrument failed even when the box was maintained at 56 °F. Apparently, heat transfer or static buildup in a zero humidity atmosphere is unsuitable for such instruments.

To circumvent this problem, we designed a system which places the spectrometer outside the glovebox atmosphere yet allows for measurements of samples in the glovebox. A small chamber with quartz windows was added to the bottom of the glovebox. The chamber fits into the sample compartment of the spectrometer and is aligned so that the sample beam passes through the quartz windows of the chamber. Inside the chamber, a thermostatted cell block holds the sample in the path of the spectrometer beam. The cell block can also maintain up to three more samples at the desired temperature although only one position on the cell block may be used for spectroscopic measurements. In this way, manipulations and measurements of the samples can be done in the glovebox while the spectrometer is kept outside.

Data processing and automated experiments were facilitated by an IBM 9000 computer interfaced to the spectrometer, the cell block pyrometer, and a keypad in the glovebox. The computer allows for immediate pK_a calculations and programmed experiments. This proved to be invaluable for monitoring slow equilibria. Furthermore, spectra can be stored and manipulated on the computer. The keypad is used to enter data and control the spectrometer when one's hands are in the glovebox. Programs used were written within the research group although some IBM spectrometer subroutines were employed.

Extinction Coefficients. The extinction coefficients were determined by one or both of the following methods. One technique was to slowly add diphenylmethyllithium to a known concentration of the neutral indicator. The endpoint was taken when the visible absorption of the base (diphenylmethyllithium) persisted in the spectrum. The extinction coefficient could then be calculated by knowing the indicator concentration, the path length, and the endpoint absorbance. This method, though straightforward, has some important limitations. The rate of deprotonation becomes very slow as the concentration of the indicator is depleted; consequently, it becomes difficult to identify the endpoint. Furthermore, the base has a strong absorbance in the visible range so an excess of base at the endpoint may significantly affect the observed indicator absorbance. An alternate route was to use the lithium salt of dimethyl sulfone as the base. Since this anion has no absorbances in the visible spectrum, it may be used in excess without affecting the indicator spectrum. In this case a weighed amount of the indicator was added to approximately a twofold excess of the base in a known amount of THF. Since the anion of dimethyl sulfone could conceivably interact with the indicator anion, the results of this method were compared in many cases with the extinction coefficients found by the slow addition of diphenylmethyllithium. In each instance, the results were similar; however, the dimethyl sulfone method usually gave greater precision presumably because an endpoint determination is not required.

General Methods. Starting materials for synthesis were obtained from commercial sources and purified as needed prior to use (recrystallization or distillation). Melting points (Pyrex capillary) were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on UCB-200 (a superconducting 200-MHz instrument) operating in the FT mode.

Chemical shifts are in ppm with respect to tetramethylsilane. Anion spectra were recorded on either a Cary 118 or IBM 9430 UV–vis spectrometer.

Indicators. Most hydrocarbon indicators were available from previous studies. They were purified, when necessary, by multiple recrystallizations followed by vacuum sublimations. Purities were assessed by ^{1}H NMR, melting point, or elemental analysis.

Benzanthrene. Benzanthrene was prepared by the LiAlH$_4$/AlCl$_3$ reduction of benzanthrone.[37]

9-Benzyl-9-*H*-benz[*def*]fluorene (BnMP). BnMP was prepared by the reaction of the 9-*H*-Benz[*def*]fluorenyllithium with benzyl bromide in diethyl ether: mp 84.5–85.5 °C; ^{1}H NMR (CDCl$_3$) δ 7.2–7.8 (m, 13 H), 4.76 (t, J = 8.2 Hz, 1 H), 3.23 (d, J = 8.2 Hz, 2 H). Anal. (C$_{22}$H$_{16}$) C, H.

Ethyllithium. The method of Brown and Rogers was used with modification.[22a] A 100-mL, three-necked flask equipped with reflux condenser, dropping funnel, and magnetic stirrer was flushed with argon and charged with 15 mL of pentane and 500 mg (71.4 mmol) of freshly cut lithium pellets. The flask was kept under positive argon pressure throughout the reaction. From the dropping funnel, a solution of 10 mL of pentane and 2.50 mL (3.65 g, 33.5 mmol) of ethyl bromide was added dropwise over 1 h. The solution became cloudy and was subsequently refluxed for 3 h. Pentane was evaporated by a flow of argon through the flask, and then 15 mL of benzene was added. The solution was allowed to settle for 30 min, and a solid layer of lithium bromide developed. The clear solution of ethyllithium was canulated into an argon flushed tube equipped with rubber septum and gas inlet. In the glovebox, the solution was filtered on a sintered glass frit to remove residual lithium bromide. Benzene was vacuum transferred off the solution until it began to cloud. The solution was then cooled to 0 °C; crystals formed after 1 h. The solution was filtered under argon to obtain 318 mg (26.4%) of flaky white crystals. Ethyllithium was checked for lithium halide contamination by quenching with deionized water followed by reaction with acidic AgNO$_3$. No precipitate was observed.

Diphenylmethyllithium. This procedure was carried out in the glovebox. To a solution of 0.10 g of biphenyl in about 4 mL of THF was added 0.4 g of diphenylmethane and an excess of freshly cut lithium metal (Cerac 99.9%+). After 24 h, the liquid was decanted to yield a dark yellow solution whose visible spectrum matched literature reports[6c,d] and material prepared with ethyllithium. The base appeared to be indefinitely stable, but was stored at –30 °C to limit any possible decomposition.

Tetrahydrofuran. THF was stirred over CaH$_2$ for several days before distillation into a long-necked, round bottom flask with an O-ring joint. The flask was connected to a vacuum line and degassed by the freeze–thaw method. In the glovebox, a small portion of Na–K alloy was added. The THF was stirred over the alloy overnight or until a light blue color appeared. The solvent was then vacuum transferred to a clean flask which had been flame dried under vacuum. THF prepared in this manner proved suitable for the equilibrium measurements.

(37) Preparation by C. A. MacArthur.