The situation is more complex if one considers odd-even interactions, *e.g.*, 1–4 interactions.

Let us first consider the 1–4 interaction in an eight-membered ring. In this case the non-nearest-neighbor interaction splits the total system into a four- and a six-membered ring. If all overlap integrals are positive, it follows from eq 5 and 7 that the contributions to the resonance energy obtained from the two subsystems have opposite signs so the total contribution is small. If there is one negative overlap integral, terms occur in which both the four- and the six- membered rings are aromatic but these are compensated by terms in which both subsystems are nonaromatic. We thus may conclude that non-nearest-neighbor interactions have no influence on the aromatic or nonaromatic character of $4n$-membered rings ($n = 1, 2, 3, \ldots$).

Unfortunately, a similar conclusion cannot be made in the case of $(4n + 2)$-membered rings. *E.g.*, a 1–4 interaction splits a six-membered ring into two four-membered rings. Now, if all overlap integrals are positive as in benzene, both subsystems are nonaromatic so the 1–4 interaction diminishes the resonance energy. On the other hand, it must be noted that, just as in the case of 1–2 interactions, the 1–4 interactions enter the resonance energy through a product of all overlap integrals of the subsystem, so the difficulty is probably not too serious.

Acidity of Hydrocarbons. XLIV. Equilibrium Ion-Pair Acidities of 9-Alkylfluorenes in Cyclohexylamine[1]

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Abstract: The pK values of several 9-alkylfluorenes were measured by the competition method with both cesium and lithium cyclohexylamides. The equilibrium constants of the Cs and Li salts are converted to pK values by taking the standard 9-phenylfluorene = 18.49 with both gegenions. The resulting pK values for Cs and Li, respectively, are: fluorene, 22.74, 22.50; methyl, 22.33, 22.60; ethyl, 22.60, 22.96; isopropyl, 23.20, 23.75; *tert*-butyl, 24.25, 24.82; benzyl, 21.27. The cesium acidities, except for *tert*-butyl but including benzyl, give a good $\rho\sigma^*$ correlation with $\rho = 4.55$. The relative acidities of 9-methylfluorene and fluorene are discussed. Temperature coefficients for most of the substituents were determined and the derived enthalpy and entropy values are discussed in terms of ion-pair interactions.

The relative acidities of conjugated hydrocarbons are important in structure–reactivity relationships. Different methods have been employed by different investigators[2] in various solvent systems in measurements of acidities of carbon acids. In our studies,[3] we have used a competition method of two hydrocarbons with insufficient strong base in cyclohexylamine to measure the equilibrium

$$R_1^-M^+ + R_2H \rightleftharpoons R_1H + R_2^-M^+ \qquad (1)$$

The determination of the acidities of 9-alkylfluorenes is of considerable interest to help establish the nature of the electronic effect of alkyl groups at a sp^2-hybridized carbanion center. Bowden, Cockerill, and Gilbert,[4] using the H_- technique in dimethyl sulfoxide–water, reported the acidity of a series of 9-substituted fluorenes. One significant finding in their results is that 9-methylfluorene is more acidic than fluorene, contrary to the common expectation that alkyl groups are electron releasing and destabilize carbanions in solution. Ritchie and Uschold[5] also found 9-methylfluorene more acidic than fluorene in dimethyl sulfoxide. In both of these cases, the carbanions involved are free ions in a polar solvent. However, in cyclohexylamine, a relatively nonpolar solvent, the carbanions are present essentially entirely as ion pairs.[6]

Experimental Section

Materials Used. Fluorene (Fl), 2,3-benzfluorene (2,3-BF), and 9-methylfluorene were described previously.[7] 9-Benzylfluorene (9-BF) was prepared by treating fluorenyllithium with benzyl chloride, mp 134–135° (lit.[8] 135°). The rest of the 9-alkylfluorenes[9]

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[1] This research was supported in part by Grant No. 12855 of the National Institutes of Health, U. S. Public Health Service.

[2] For general reviews in this area, see: (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965; (b) A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 3, 41 (1965); (c) H. Fischer and D. Rewicki, *Progr. Org. Chem.*, 7, 116 (1967); (d) H. F. Ebel, "Die Acidität der CH-Säuren," G. Thieme Verlag, Stuttgart, 1969.

[3] (a) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Amer. Chem. Soc.*, 89, 59 (1967); (b) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, 89, 63 (1967); (c) A. Streitwieser, Jr., C. J. Chang, W. Hollyhead, and J. R. Murdoch, *ibid.*, **94**, 5288 (1972).

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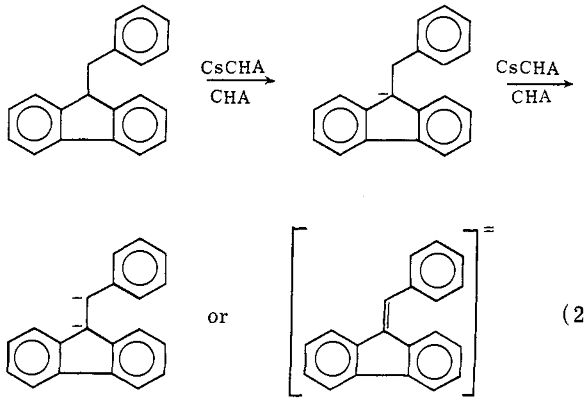
were prepared by the method suggested by Anet and Bavin.[10,11] Fluorene-9-carboxylic acid, prepared by carboxylation of fluorenyllithium, was esterified and the methyl ester was alkylated with the appropriate alkyl halide. The substituted ester was decarboxylated to give the 9-alkylfluorene, which was recrystallized from methanol to give: 9-methylfluorene (9-MF), mp 45.5–46.5°; 9-ethylfluorene (9-EF), mp 18–19° (lit.[12] mp −3°); 9-isopropylfluorene (9-*i*-PF), mp 54–55° (lit.[13] mp 53.9–54°); 9-*tert*-butylfluorene (9-*t*-BF), mp 103–104° (lit.[10] mp 101.5°).

Spectral and Equilibrium Measurements. The apparatus and the procedure for spectral and equilibrium measurements at room temperature have been described previously.[3,14]

The apparatus and the procedure for temperature dependence studies were essentially the same as described previously.[2c,15] The temperature range studied was from −10 to 35°. The freezing point of CHA is −17.7°, which limits the range at the lower end. At higher temperatures, side reactions became relatively rapid, and the base was destroyed at a relatively fast rate. At 35°, however, such decomposition was only a minor problem.

Results and Discussion

Spectral Results. Spectral data for cesium and lithium salts of fluorene and 2,3-benzfluorene have been reported.[16] Spectral results for the 9-alkylfluorenes are shown in Table I. In obtaining the spectrum of 9-benzylfluorenylcesium with CsCHA in CHA, the expected 9-benzylfluorenylcesium was formed at low base concentration as indicated by the similarity of its spectrum (λ_{max}^{nm} at 476, 500, 536) with all of the other 9-alkylfluorenylcesiums. However, at higher base concentration, the solution changed color from orange to dark red and an entirely different spectrum (λ_{max}^{nm} at 435 with much higher ϵ) was obtained. It was further demonstrated that upon gradual addition of base the spectrum was also gradually changed from the 9-alkylfluorenyl type to the new spectrum, and that the 9-alkylfluorenyl-type spectrum reappeared upon quenching part of the base with a small amount (one drop) of water. This spectral change indicates two species in reversible equilibrium. The species at higher base concentration is undoubtedly the corresponding dianion of a fulvene, 6-phenyldibenzofulvene.



(2)

Table I. Spectra of 9-Alkylfluorenyl Anions

Hydrocarbons	λ_{max}^{nm} (ϵ_{max}) Cs salt, CHA	Li salt, CHA	$(CH_3)_4NOH$-DMSO-H_2O[a]
Fluorene	447	452	460
	472	477	490
	504[b]	510[b]	525
9-MF	477 (953)	481 (1113)	490
	505 (1170)	513 (1353)	520
	541 (819)	552 (944)	562
9-EF	476 (890)	481 (1031)	490
	505 (1107)	513 (1353)	520
	541 (775)	552 (944)	560
9-*i*-PF	476 (910)	481 (1020)	486
	504 (1124)	513 (1328)	521
	540 (769)	552 (916)	560
9-*t*-BF	471 (925)	476 (1017)	484
	496 (1164)	508 (1293)	515
	532 (795)	546 (903)	558
9-BF	476 (1064)		
	500 (1425)		
	536 (1079)		

[a] K. Bowden and A. F. Cockerill, *J. Chem. Soc. B*, 173 (1970). [b] Reference 16.

Because of the presence of the dianion at higher base concentration, it is difficult to obtain a good value of the extinction coefficient for 9-benzylfluorenylcesium. The ϵ_{max} in Table I was estimated from the spectrum at which the maximum amount of base was added before the appearance of the peak from the dianion and the disappearance of monoanion peaks.

The spectral comparisons in Table I show that λ_{max} of alkylfluorenyl anions shift to longer wavelength when the solvent system is changed successively from CsCHA–CHA to LiCHA–CHA to $(CH_3)_4$NOH–DMSO–H_2O. Hogen-Esch and Smid[17] studied the spectral data of alkali metal salts of fluorene in a number of solvents and reported that the spectrum of a contact ion pair shifts to longer wavelength as the size of the cation increases. However, a further increase in wavelength was observed in going from the contact ion pair to solvent-separated ion pairs since the interionic distance increases. Finally, the longest wavelength was observed for the free anions where the interionic distance is effectively infinite. The current spectral results undoubtedly indicate that we are dealing with the contact ion pair, solvent-separated ion pair, and free ion in CsCHA–CHA, LiCHA–CHA, and $(CH_3)_4$NOH–DMSO–H_2O, respectively.

In our other temperature dependence studies on the spectra of fluorenylcesium and fluorenyllithium in cyclohexylamine, we found[15] that the cesium salt is the contact ion pair over the temperature range of −20 to 90°, whereas the lithium salt is 95% solvent-separated and 5% contact ion pairs at room temperature. The current temperature dependence studies on cesium and lithium salts of 9-alkylfluorenes as well as 2,3-benzfluorene from −10 to 30° show that the decrease of absorbance on increasing temperature is relatively small and in all cases no shift in the absorption maximum was observed. There was no change in the shapes of the spectra except for a broadening of the peaks. Solvent expansion and broadening of the peaks at high temperature can account for the observed small decrease in absorbance. Clearly, at temperatures from −10 to 30°, 9-alkylfluorenylcesium and

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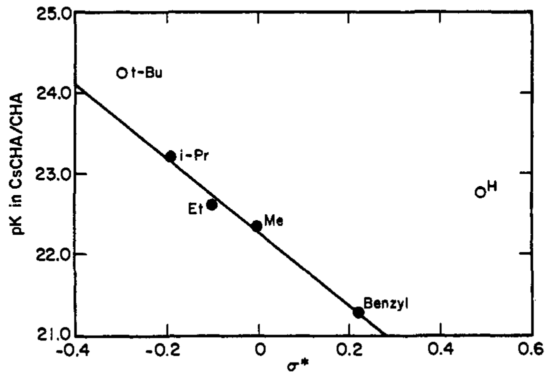

Figure 1. Correlation of pK values of 9-alkylfluorenes with σ^*. The least-squares line shown is based on the four filled circles; slope = −4.547; intercept = 22.270; corr coeff = 0.994 with a standard deviation of 0.11.

2,3-benzfluorenylcesium exist solely as contact ion pairs, whereas the corresponding lithium salts are entirely solvent-separated ion pairs. The spectrum of 9-*tert*-butylfluorenyllithium could be taken up to 95° but no changes in the spectrum were observed except for those mentioned above. Chan and Smid[18] have reported that the 9-substituted fluorenes generally yield higher fractions of solvent-separated ion pairs than does fluorene itself with lithium as the cation. The steric hindrance effects that seem clearly to be involved may operate not between the bulky alkyl substituents of the carbanion and the small cation but may involve instead the solvent molecules providing the remaining solvation of the cation. It is this steric hindrance to cation solvation that may facilitate separation of the two ions.

The visible spectra of Li-9-*t*-BF and Cs-9-*t*-BF suggest that the 9-*t*-BF anion is distorted from a planar fluorenyl system. In Table I, the absorption maxima of 9-MF$^-$, 9-EF$^-$, and 9-*i*-PF$^-$ are essentially the same, whereas those of 9-*t*-BF$^-$ are shifted to shorter wavelength by 2–8 nm. Such shifts may be attributed to a smaller degree of conjugation in the anion, which would result if the 9-carbon is slightly pyramidal. A pyramidal carbon is suggested to relieve steric interactions between the methyl groups of the *tert*-butyl substituent and the 1- and 8-fluorenyl hydrogens.

Equilibrium Constants. Table II shows the results of equilibrium constant measurements of 9-alkylfluorenes in CsCHA–CHA at room temperature relative to Fl or 2,3-BF. 9-Benzylfluorene was measured

$$R_1H + R_2^-Cs^+ \overset{K}{\rightleftharpoons} R_1^-Cs^+ + R_2H \qquad (3)$$

by the regular method, and 9-*tert*-butylfluorene was measured by the sealed cell technique. For 9-MF, 9-EF, and 9-*i*-PF, where the equilibrium constants were obtained by both methods, the agreement is good except for 9-MF. However, in the regular method, 9-MF was measured against fluorene, Fl, whereas in the sealed cell method it was measured against 2,3-BF. K between Fl and 2,3-BF was not measured directly, but was bridged with 4,5-methylenephenanthrene (4,5-MP).[3b] Nevertheless, the direct comparison (9-MF *vs.* 2,3-BF) differs from the indirect comparison (9-MF *vs.* Fl, Fl *vs.* 4,5-MP, 4,5-MP *vs.* 2,3-BF), by only 0.15 pK unit. In these measurements summarized in Table II the alkylcesium concentrations were generally about 10^{-3} M but ranged from 10^{-4} to 10^{-2} in different cases. These concentrations were generally varied by severalfold from one run to the next with the same system. The insensitivity of the equilibrium constants to this variation in carbanion concentration suggests that aggregation is not important in the CHA system for this concentration level.

Table II. Equilibrium Constants of 9-Alkylfluorenes in CsCHA–CHA

$$K = [R_1Cs][R_2H]/[R_1H][R_2Cs]$$

Run	R_1H	R_2H	K	p$K^{c,d}$ of R_1H
CC[a]-18	9-MF	Fl	3.09 ± 0.05	
CC-20			2.60 ± 0.13	
DR[b]-91a		2,3-BF(Fl)	5.26 (1.95)	
Av		Fl	2.55 ± 0.40	22.33 ± 0.05
CC-24	9-EF	2,3-BF	3.24 ± 0.04	
CC-26			4.26 ± 0.02	
CC-30			3.63 ± 0.04	
DR-95b			3.77	
Av			3.73 ± 0.28	22.60 ± 0.03
CC-24	9-*i*-PF	2,3-BF	0.94 ± 0.04	
CC-27			1.04 ± 0.01	
DR-90			0.82	
Av			0.93 ± 0.08	23.20 ± 0.03
CC-65	9-BF	Fl	24.4 ± 0.4	
CC-66			33.2 ± 0.7	
CC-67			30.5 ± 0.9	
Av			29.4 ± 3.3	21.27 ± 0.04
DR-82	9-*t*-BF	2,3-BF	0.082	24.25

[a] Runs by C. J. C. and measured by the regular method. [b] Runs by D. M. E. R. and measured by the sealed cell method. [c] Based on pK of 9-phenylfluorene equal to 18.49; see ref 3b. [d] pK of Fl, 22.74; 2,3-BF, 23.17 (ref 3b). Note that the RCs concentrations were in the range 10^{-4}–10^{-2}.

Table III compares the pK values of the 9-alkylfluorenes at room temperature in CsCHA–CHA and LiCHA–CHA with the DMSO–H_2O results of Bowden, Cockerill, and Gilbert.[4] The results in LiCHA–CHA were obtained by the sealed cell method. The pK values in CsCHA–CHA and in DMSO–H_2O are similar except for 9-BF, despite the great solvent difference between the two systems. However, the pK values for the LiCHA scale increase more rapidly along the alkyl series. The pK values of the 9-alkylfluorenes in CsCHA–CHA are plotted against Taft's σ^* values[19] in Figure 1. Fluorene itself and 9-*t*-BuF do not fit the correlation. The parent compound often deviates from the correlation shown by substituted compounds; in the present case the secondary hydrogens of fluorene might well be expected to correspond to a different acidity order than the tertiary hydrogens of the 9-alkylfluorenes. 9-*t*-BuF is less acidic than expected from the $\rho\sigma^*$ correlation, undoubtedly because of a relative increase in steric strain in going from hydrocarbon to carbanion.

The other four substituents give an excellent linear correlation with $\rho = 4.55$. Correlations with σ^* have usually been considered in terms of the relative "inductive effects" of substituents, although such correlations are less meaningful when based on alkyl groups alone. The inductive effect of alkyl substituents is still

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Table III. Acidity of 9-Alkylfluorenes in Various Solvent Systems

Compd	CsCHA-CHA[a,b] pK	CsCHA-CHA[a,b] ΔpK	LiCHA-CHA[b,c] pK	LiCHA-CHA[b,c] ΔpK	$(CH_3)_4NOH$-DMSO-H_2O[d] pK	$(CH_3)_4NOH$-DMSO-H_2O[d] ΔpK
Fl	22.74	0.00	22.55	0.00	22.10	0.00
9-MF	22.33	−0.41	22.60	0.05	21.80	−0.30
9-EF	22.60	−0.14	22.96	0.41	22.22	0.12
9-*i*-PF	23.20	0.46	23.75	1.20	22.70	0.60
9-*t*-BF	24.25	1.49	24.82	2.27	23.41	1.31
9-BF	21.27	−1.47			21.20	−0.90

[a] From Table II. [b] Relative to 9-phenylfluorene equal to 18.49. [c] Measured by the sealed cell method. [d] Reference 4.

a matter of controversy[20] although there appears to be abundant evidence that alkyl groups are generally electron donating relative to a trigonal carbon; an sp^2 carbon orbital is more electronegative than an sp^3. Consequently, the fit of the benzyl substituent in the present correlation is especially significant. All criteria indicate this substituent to be electron attracting relative to alkyl, and its σ^* value properly places it on a scale of usual inductive substituents. Thus, the correlation in Figure 1 does suggest that alkyl groups are effectively electron donating in the present system.

Nevertheless, 9-methylfluorene is more acidic than fluorene itself, not only in the ionic systems studied previously[4,5] but also in the present ion-pair systems; even for LiCHA 9-MF is more acidic than Fl on a per hydrogen basis. Bowden, Cockerill, and Gilbert[4] interpreted this higher acidity as a superposition on a normal inductive effect of other effects, of which anionic hyperconjugation was suggested as most likely. They noted that the number of hydrogens available for such hyperconjugation, Me > Et > *i*-Pr, follows the same order as the effect on acidity. Ritchie and Uschold[5] suggested an alkyl group stabilization of carbanions by dispersion interactions. Such an effect, an internal van der Waals or London electron correlation effect, is certainly responsible for the acidity order of alcohols in the gas phase[21] where any region of polarizability close to the negative charge provides stabilization. In solution, however, this effect is greatly diluted by the many regions of polarizability provided by solvent molecules. Finally, Evans, *et al.*,[22] have also recently claimed greater charge delocalization into methyl groups.

We suggest that the stabilization of fluorenyl anions by alkyl groups results from the σ-bond strength change, C_{sp^3}–C_{sp^3} in the hydrocarbon to C_{sp^3}–C_{sp^2} in the carbanion. In fluorene itself the comparable bond change is C_{sp^3}–H to C_{sp^2}–H and there are abundant analogies that putting more s character into a C–C bond provides greater stabilization than in a C–H bond. Examples are found in the stabilization of olefins by alkyl substitution and in the effect of alkyl substituents on the acidity of nitroalkanes.[2b] The two factors, inductive effect and σ bond change, should vary with structure in a predictable way. In the case of fluorenyl anion the negative charge is so delocalized that the σ bond stabilization effect dominates slightly for methyl substitution. The inductive effect term is increasingly important, however, for the higher alkyl substituents. For carbanions in which there is more negative charge at the site of substitution, the inductive effect component may be expected to dominate at the methyl substituent level; that is, the σ bond stabilization term is essentially independent of charge, whereas the inductive effect term depends on the charge density at the site of substitution. With these principles we predict that toluene has equilibrium acidity greater than ethylbenzene in solution.

Temperature effects on the equilibria between 9-alkylfluorenes and 2,3-benzfluorene in LiCHA–CHA and CsCHA–CHA were studied at temperatures from −10 to 30°. In these determinations several experimental difficulties were encountered. The equilibria in the LiCHA–CHA system were established relatively slowly and the sealed cell system had to be retained in the cell holder in the Cary spectrometer for up to 3 hr. However, the spectra in this system are relatively stable and these long times incur little error. The equilibrium constants depend somewhat on the wavelength used for the determination but the differences are sufficiently small so that they have a negligible effect on the derived thermodynamic quantities. The reactions in the CsCHA–CHA system, on the other hand, are relatively fast, but so are side reactions that generate colored species that interfere with the absorption spectra of the 9-alkylfluorenyl anions. These side effects were minimized by keeping the cells frozen when not in use; however, in the case of 2,3-BF *vs.* Fl, these side reactions were so extensive that no usable data could be obtained.

$$\text{9-X-F} + \text{M}^+\text{2,3-BF}^- \overset{K}{\rightleftharpoons} \text{M}^+\text{9-X-F}^- + \text{2,3-BF} \qquad (4)$$

The equilibrium constants for eq 4 were treated with the ACTENG program[23] and the results were converted to the least-squares ΔH and ΔS values summarized in Tables IV and V. In the Cs system the entropies are essentially constant and virtually all of the effects of alkyl structure on equilibrium constant show up in the

Table IV

$$\text{9-X-F} + \text{Cs}^+\ \text{2,3-BF}^- \rightleftharpoons \text{Cs}^+\ \text{9-X-F}^- + \text{2,3-BF}$$

X	$K_{20°}$	$\Delta H°$, cal/mol	$\Delta S°$, eu
H	2.8		
CH_3	5.3	−740 ± 40	0.7 ± 0.2
Et	3.8	−650 ± 50	0.4 ± 0.2
i-Pr	0.82	400 ± 40	1.0 ± 0.2
t-Bu	0.082	1320 ± 40	0.6 ± 0.2

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(21) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).

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Table V

$$9\text{-X-F} + \text{Li}^+\ 2,3\text{-BF}^- \rightleftharpoons \text{Li}^+\ 9\text{-X-F}^- + 2,3\text{-BF}$$

X	$K_{20°}$	$\Delta H°$, cal/mol	$\Delta S°$, eu
H	4.1	−290 ± 60	1.8 ± 0.2
CH_3	3.74	−780 ± 50	0.0 ± 0.2
Et	1.57	−770 ± 40	−1.8 ± 0.2
i-Pr	0.26	180 ± 40	−2.1 ± 0.2
t-Bu	0.021	1140 ± 40	−3.8 ± 0.2

enthalpy term. As discussed above these equilibria involve contact ion pairs. We interpret the results with a model in which the cesium cation is located above and approximately at the center of the five-membered ring in the planar 9-alkylfluorenyl ions. In this location the cation is at the "center of gravity" of negative charge for best electrostatic attraction and does not interfere significantly with rotation of the alkyl group about its bond to the 9-carbon.

On the other hand, the equilibria in the Li case involve changes in both entropy and enthalpy. The ion pairs in this system are largely solvent separated; solvation of the small Li cation is an important component. In these ion pairs increased branching in the 9-alkyl group clearly produces increased steric interactions with solvent molecules solvating the Li cation. Such interactions can result in a progressive decrease in entropy by increased hindrance to rotation about the R–C-9 bond and/or by changes in the entropy of solvation of the Li cation by increased restrictions in the motion of solvating solvent close to the 9 substituent.

We conclude that all of the results on relative ion-pair acidities of 9-alkylfluorenes are completely consistent with the application of conventional physical organic inductive, field, and bond strength effects to contact and solvent-separated ion pairs and do not require such additional effects as anionic hyperconjugation and unusual dispersion interactions.

Conformational Analysis. LXXXIV. A Study of the Structures and Energies of Some Alkenes and Cycloalkenes by the Force Field Method[1,2]

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Abstract: Our earlier described force field has been extended to include compounds containing (nonconjugated) olefinic linkages. The structures and energies of small alkenes are adequately calculated. A number of conformational problems were studied: cyclopentene; the cis and trans isomers of cyclohexene, cycloheptene, cyclooctene, and cyclodecene; 1,4-cyclohexadiene; 1,5-cyclooctadiene; and some bicyclic olefins. The results are in general in good to fair agreement with the literature in cases where comparisons can be made. In cases where literature data do not exist for the structures or energies, predictions are made regarding these items.

In recent papers we have described the development of a force field method for the calculation of structures and energies of hydrocarbons[5a] and for ketones.[5b] In this paper will be described the extension of the same method in a compatible way to include alkenes and related compounds. An ordinary alkene can be treated by the methods of molecular mechanics just as a saturated hydrocarbon can; it is only necessary to know the values for the natural angles, force constants, etc., which are different in and about the double bond. For conjugated systems, or for systems that cannot be adequately described by a single Kekulé structure, more sophisticated methods are in general necessary. These will be the subject of a later paper. This paper will be concerned only with molecules containing isolated double bonds.

The force field and attendant parameters developed in earlier work for hydrocarbons and ketones carry over here.[6] It is only necessary to assign values to

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(1) Paper LXXXIII, M. T. Tribble and N. L. Allinger, *Tetrahedron*, **28**, 2147 (1972).

(2) Supported in part by Grant No. GP-15263 from the National Science Foundation.

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(5) (a) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971); (b) N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972).

(6) In our earlier paper, the stretch-bend interaction term was calculated by multiplying the amount of stretching in a bond by the absolute value of the angle bending for the angles at the ends of the bond. Such a term does not correspond to the kind of term one expects in a Taylor's expansion truncated at the quadratic approximation. While we recognize that there is no theoretical basis for such a term, it was used for the sake of expediency, because it was observed that when bond angles close down (as in cyclobutane) the bonds stretched, but when the bond angles were opened up (as in hexamethylethane) the bonds were also stretched. At the urging of Professor L. S. Bartell, to whom we are indebted for his persistent concern, we have looked into this matter and find now that results very similar to those obtained before can be obtained by the use of a stretch–bend interaction term in which the absolute value of the angle bendings is replaced by a signed quantity, and the signs are chosen such that the bonds are stretched when the angle closes (as in cyclobutane). In order to prevent the bond lengths from contracting in a molecule such as hexamethylethane, it is necessary to add a cubic term to the bond stretching. Evidence indicating that this is an appropriate addition has been given by H. B. Burgi and L. S. Bartell, private communication, and we have used a value for the cubic constant as they have recommended ($a = 2\ \text{Å}^{-1}$). A rough reoptimization of the various parameters entering into the calculations was then carried out, and it