and the product acetate-d_3 (401 mg, 2.30 mmol, 85%) was obtained by direct distillation, bp 57-59 °C (0.5 mmHg). The 200-MHz ^{1}H NMR spectrum[31] consisted of ring-proton absorptions at δ 1.53-1.75 and 4.92 and a barely detectable signal at δ 2.01 for trace $COCD_2H$. Comparison of the ring (δ 0.5 to -3.1) vs. methyl (δ -17.0) ^{2}H NMR signal intensities for this ester (15 mg in 400 μL of CCl_4 containing 0.5% of $CDCl_3$) in the presence of shift reagent $Pr(fod)_3$ (15 mg) gave $D_{av} = 1.395$.

^{2}H NMR Analysis of Recovered Cyclooctenes. The unconsumed cyclooctene recovered from the 30-min and 60-min partial addition reactions was analyzed for deuterium incorporation as follows. An integration-reference solution was made up of 10 μL (15.0 mg, 0.125 mmol) of $CDCl_3$ (Norell, isotopic purity >99.8%, $d = 1.500$) plus 200 μL of CCl_4 (Aldrich, Gold Label); volume additivity was assumed. The ^{2}H NMR spectrum of a sample of 30 μL (25.4 mg, 0.2303 mmol, $d = 0.846$) of the cyclooctene plus 20 μL of the integration-reference solution (containing 0.0119 mmol of $CDCl_3$) was recorded with integration of the signals for $CDCl_3$, vinylic D, allylic D, and more distal D at δ 7.27, 5.64, 2.16, and 1.52, respectively. The ring-deuterium signal intensities were referenced to the $CDCl_3$ peak intensity to calculate the percentage incorporation of deuterium at these three cyclooctene locations. The average of three such determinations ($\pm$1%) is recorded in Table II. The recovered cyclooctene from the 120-min partial addition was analyzed likewise but using 10 μL of the olefin plus 20 μL of the integration-reference solution.

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Registry No. 1, 931-87-3; **3**-OH, 79734-96-6; **3**-OTFA, 87922-05-2; **4**-OH, 55693-43-1; **4**-OTFA, 87922-06-3; **5**-OH, 79734-92-2; **6**-OH, 87922-02-9; **7**-OH, 87922-03-0; **8**-OH, 87922-04-1; **8**-OTFA, 87922-07-4; **9**-OH, 79734-94-4; **10**-OH, 58378-54-4; **11**-OH, 58378-53-3; **13**, 87922-01-8; **30**, 87922-00-7; trifluoroacetic acid, 76-05-1; trifluoroacetic acid-*d*, 599-00-8.

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^{13}C NMR Spectra of Carbanions Derived from 2-Substituted 1,3-Dithianes, 9-Substituted Fluorenes, and Biphenylylmethanes As Related to Structure and Charge Density

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Abstract: The ^{13}C NMR spectra of 1,3-dithianyllithium, (2-methyl-1,3-dithianyl)lithium, (2-phenyl-1,3-dithianyl)lithium, (2-biphenylyl-1,3-dithianyl)lithium, fluorenyllithium, (9-methylfluorenyl)lithium, (9-phenylfluorenyl)lithium, (biphenylylmethyl)lithium, and (dibiphenylylmethyl)lithium in THF solutions have been obtained. Calculations of σ and π charge densities by INDO for the anions of toluene, fluorene, and biphenylylmethane in sp^2 and sp^3 states of hybridization are used to evaluate degrees of charge delocalization into phenyl substituents adjacent to these carbanions. The dithiane series appears to have sp^3-hybridized and localized carbanions with no indication of dπ-pπ bonding. (9-Phenylfluorenyl)lithium and (biphenylylmethyl)lithium offer excellent examples of little or no delocalization of charge by resonance and maximum delocalization, respectively. The use of correlations of charge density ($\sigma + \pi$) vs. chemical shift offers new evaluations of such delocalization.

Introduction

Since the initial investigation of carbon–lithium bonding by Waack et al. using ^{13}C NMR techniques,[1,2] carbon-13 NMR has become a valuable tool in studying the properties of carbanions. It has been used to evaluate structure,[3,4] solvent effects,[5] ion pairing,[6-9] hybridization,[1,10,11] charge density,[9,12-14] and resonance effects.[15] Although care is obviously necessary in using appropriate compounds[16] for comparison and controlling the variables of the investigation, ^{13}C NMR can be used very fruitfully to study electronic structures of carbanions.

The usual method of determining the hybridization for carbon using ^{13}C–H coupling constants does not apply for carbanions.[17-19]

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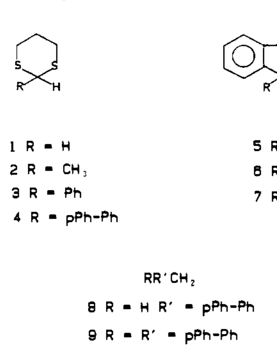

Figure 1.

It is through evaluation of the chemical shift changes which occur in forming a carbanion that charge delocalization and hybridization can be studied. The negative charge generated on a carbanion leads to shielding of the nucleus and an upfield (negative) shift. The large downfield (positive) shift frequently observed for the α-carbons in carbanions is due to rehybridization of the α-carbon from sp^3 to sp^2.

The major purpose of the present research was to establish a set of carbanion chemical shifts for both the α-carbons and the para carbons of aromatic groups attached to α-carbons that would allow one to determine the hybridization of a carbanion and to estimate the degree of charge delocalization into any attached aromatic substituents.[20-24] Although para-carbon chemical shift changes have previously been successfully utilized in inferring certain properties of carbanions,[4,6-9,14] there has been a great deal of controversy as to whether α-carbon chemical shift changes in carbanions can be used to determine structure. This is due to the possibility that the field of the cation, type of ion pairing, and degree of covalent bonding may also affect the chemical shift of the α-carbon.[10] By comparing the conclusions reached using the α chemical shift change ($\Delta\delta$) with the para $\Delta\delta$ we hope to establish the validity of carbanion structure determinations based on α-carbon chemical shift changes. This is, obviously, important because not all carbanions have aromatic groups attached to the α-carbon.

We have chosen for study a set of compounds (Figure 1) that permit one to set limits on chemical shift changes for both maximal delocalization ((biphenylylmethyl)lithium) and no delocalization (the 9-phenyl group in (9-phenylfluorenyl)lithium) and that have the possibility of varying from sp^3 to sp^2 hybridization (dithianes) as the adjacent substituent (hydrogen, methyl, phenyl, or biphenyl) is varied. Using these compounds to establish a scale for hybridization and substituent effects, we have evaluated the changes in ^{13}C chemical shift, charge density (INDO), and relaxation times, keeping variables such as temperature, concentration, metal cation, and solvent constant. Variations of such parameters in the studies already present in the literature made a quantitative approach using presently available data very risky. Data from other studies are compared to that obtained in this research in order to evaluate the effects of such variables and to establish the limits of the effects such changes will have on chemical shift. To date most investigative effort on hybridization of carbanions by ^{13}C NMR has centered on the benzyl, diphenylmethyl, and triphenylmethyl carbanions. In spite of these efforts there is still disagreement as to the hybridization state of the benzyl anion, and serious steric interactions between the phenyls of the latter two compounds limit their usefulness in studying delocalization. We felt that it was appropriate to study a set of compounds that would give more useful and definitive information.

As mentioned above, the series of compounds shown in Figure 1 have several important properties. The substituted dithianes, **1** and **2**, are well established as sp^3 hybridized (see Discussion). The series **1**–**4** thus offers the unique possibility of observing the effect of a phenyl group on an adjacent sp^3 carbanion and an experimental method of determining the amount of charge delocalized by resonance in such a situation. Biphenyl has not been studied previously by NMR as a carbanion substituent and affords the possibility of observing a changeover from sp^3 to sp^2 hybridization in carbanions having substituents (phenyl and biphenyl) with a very similar inductive effect. The 9-substituented fluorenes, **5** and **6**, have an sp^2 carbanion in the 9 position with delocalization into the fused aromatic rings. However, in 9-phenylfluorene (**7**), the attached phenyl ring cannot resonate due to steric effects and affords the first carbanion studied by ^{13}C NMR that clearly has only an inductive effect by an adjacent phenyl. Compounds **8** and **9** were chosen for study to evaluate the effect of a biphenyl group on an adjacent carbanion without the presence of sulfur. The biphenyl group in compound **8** has a greater chance of causing the carbanion to rehybridize to sp^2 than a phenyl substituent in the benzyl anion due to the greater delocalization possible. In addition, it does not have the steric problems inherent in di- and trisubstitution on methyl anions that are sp^2 hybridized. Compound **9** was chosen in order to determine the effect of such steric interactions while allowing evaluation of delocalization into the para′ position without the anisotropy and steric effects observed in studies of di- and triphenylmethyl anions.

The present investigation was also designed to use ^{13}C NMR to evaluate structures of carbanions generated α to sulfur atoms and to determine whether the stabilization of these carbanions is occurring by dπ–pπ bonding or by polarization of the sulfur.

INDO molecular orbital calculations of charge density for benzyl, fluorenyl, and biphenylmethyl anions in either sp^2 or sp^3 hybridizations and with the phenyl ring either coplanar or orthogonal were obtained for comparison with the ^{13}C chemical shifts of the anions. They allow a quantitative evaluation of the effect of such structure changes in different types of carbanions.

Experimental Section

^{13}C NMR and ^1H NMR spectra were recorded on a JEOL-90Q instrument as solutions in THF or CDCl$_3$. Chemical shifts are reported in ppm from Me$_4$Si unless otherwise noted. IR spectra were recorded on a Perkin-Elmer 137 or a Perkin-Elmer 293 spectrophotometer and are referenced to polystyrene (1601 cm^{-1}). Melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected.

Materials. THF was maintained at reflux over lithium aluminum hydride under a nitrogen atmosphere in a solvent still. *n*-Butyllithium, 2.2 M (24%) in hexane (Alfa) from a fresh bottle, was used to generate the lithium salts of the hydrocarbons.

1,3-Dithiane. 1,3-Dithiane was prepared from 1,3-propanedithiol, boron trifluoride etherate, and dimethoxymethane in glacial acetic acid–chloroform by using the procedure of Corey.[32] The product obtained in 69% yield was crystallized from methanol and further purified by sublimation under reduced pressure (mp 53.0–53.5 °C (lit. 53 °C[33])).

1,3-Dithiane-2-^{13}C. The ^{13}C-enriched compound was prepared in the same manner as 1,3-dithiane with the substitution of paraformaldehyde (^{13}C, 90%, KOR) for dimethoxymethane.

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2-Substituted 1,3-Dithianes. General Procedure.[34,35] The preparation of substituted 1,3-dithianes was accomplished by refluxing 1,3-propanedithiol, the desired aldehyde (benzaldehyde for 2-phenyl-, acetaldehyde for 2-methyl-, and *p*-biphenylcarboxaldehyde for 2-biphenylyl-1,3-dithiane), and several drops of concentrated hydrochloric acid in anhydrous benzene. Upon completion of the reaction, the benzene solution was poured into water and extracted into chloroform. The organic layer was washed twice with 10% aqueous sodium hydroxide and then water and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure by rotatory evaporation.

2-Phenyl-1,3-dithiane. Upon recrystallization from methanol, the solid was sublimed under reduced pressure (mp 71.2–72.0 °C (lit. 70 °C[35])).

2-Biphenyl-1,3-dithiane. Upon recrystallization from cyclohexane, the solid was sublimed under reduced pressure: mp 148–149.4 °C; NMR ($CDCl_3$) 2.0–2.2 (multiplet, 2 H), 2.8–3.2 (multiplet, 4 H), 5.2 (singlet, 1 H), 7.6 ppm (multiplet, 9 H). Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92; S, 23.54. Found: C, 70.61; H, 5.92; S, 23.32.

9-Phenylfluorene. The synthesis was adapted from that of 9-(*p*-biphenylyl)-10,10-dimethyl-9,10-dihydroanthracene.[36] 9-Hydroxy-9-phenylfluorene was prepared by a Grignard reaction of phenylmagnesium bromide and commercially available 9-fluorenone (Aldrich). Recrystallization of the resulting yellow solid from a mixture of benzene and hexane yielded large yellow crystals, mp 74–78 °C. Proton NMR in $DCCl_3$ showed a multiplet at 7–8 ppm (13 H) and a singlet at 2.4 ppm (1 H). The infrared spectrum in chloroform showed no remaining carbonyl absorption at 1725 cm^{-1} due to 9-fluorenone. The 9-hydroxy-9-phenylfluorene was reduced to the hydrocarbon by hydrogenolysis with perchloric acid and palladium on charcoal.[36] The product obtained was recrystallized from carbon tetrachloride to yield white crystals (mp 145.5–146 °C (lit. 145 °C[37])). The proton NMR in $DCCl_3$ showed a multiplet at 7.2–8.1 ppm (13 H) and a singlet at 5.2 ppm (1 H).

9-Methylfluorene. 9-Hydroxy-9-methylfluorene was prepared in much the same way as 9-hydroxy-9-phenylfluorene. Methylmagnesium iodide was the Grignard reagent used. The reduction of 9-hydroxy-9-methylfluorene was accomplished with zinc dust and palladium on charcoal in glacial acetic acid[38a] (mp 43.5–45 °C (lit. 45–46 °C[38b])).

4-Phenyltoluene. This compound was obtained from Aldrich at 98% purity and recrystallized from methanol and water (mp 46–47.5 °C (lit. 45–47 °C[33])).

Di-*p*-biphenylylmethane was prepared by using the procedure of Streitwieser et al.[38a] Di-*p*-biphenylylmethanol was prepared by mixing *n*-butyllithium (0.245 mol) and 4-bromobiphenyl (0.200 mol) under nitrogen at 0 °C and allowing them to react for 10 h at 5 °C. Ethyl formate was added, and the reaction was allowed to continue for an additional 24 h at 5 °C. The hydrogenolysis of the crude alcohol product (mp 135–149 °C (lit. 153–155 °C[38])) was accomplished by using glacial acetic acid, zinc dust, and palladium on charcoal.[38a] After recrystallization from methanol, the white crystals had a melting point of 159.3–162.4 °C (lit. 162 °C[38]). The proton NMR in $CDCl_3$ showed a multiplet at 7.1–7.7 ppm (18 H) and a singlet at 4.0 ppm (2 H).

Carbanion Preparations. Carbanion solutions were prepared in 10-mm, septum-capped, argon-flushed NMR tubes. One equivalent of *n*-butyllithium in hexane (24%) was added to the NMR tube while argon was vigorously being flushed through the tube. A heat gun was used to evaporate the hexane, and the hydrocarbon was injected as a solution in THF into the tube. All syringes and needles were oven-dried and flushed with argon. Reproducible spectra were obtained from these carbanions, and many of the preparations were stable for several days.

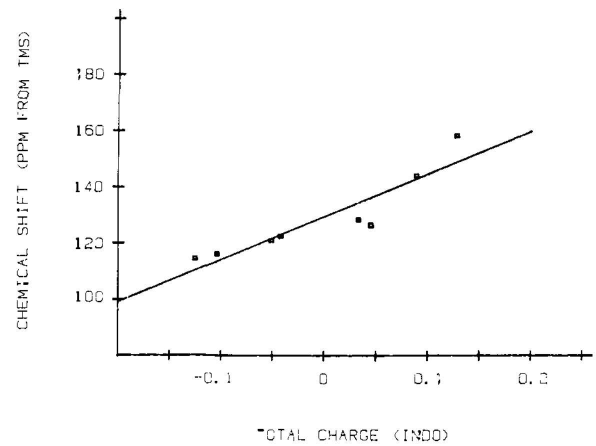

Figure 2. A plot of the chemical shifts of (biphenylylmethyl)lithium vs. the $\sigma + \pi$ charge density calculated by INDO (omitting the α-carbon).

Carbon-13 NMR Measurements. All carbon-13 spectra were obtained with a JEOL JNM/FX-90Q Fourier transform spectrometer equipped with an external D_2O lock. All spectra were recorded at 25 ± 0.5 °C. All solutions, both of the carbanions and the parent hydrocarbons, were thoroughly degassed (see preceding paragraph). Each carbanion was prepared from four to eight different times. Approximately 100–1000 transients were required to obtain satisfactory signal-to-noise ratios for proton-decoupled spectra. Chemical shifts of the anions were referenced to the upfield (26.18 ppm) resonance of THF. Chemical shifts reported are calculated with respect to Me_4Si. The T_1 relaxation times were measured by an inversion–recovery method using a 180°, τ, 90° pulse sequence. τ was varied from 5 times the longest relaxation time (τ_∞) to 0.01 s. At least seven different values of τ were used in each experiment, and each experiment was repeated with a new preparation of carbanion at least twice. The technique was tested by using phenol under conditions used by Levy,[62] and the results accurately reproduced those in the literature.

INDO MO Calculations. Standard bond angles and carbon–carbon bond lengths of 1.40 Å for aromatic carbons and 1.54 Å for carbon–carbon single bonds were employed. Carbon–hydrogen bond lengths used were 1.08 Å for C_{sp^2}–H bonds and 1.09 Å for C_{sp^3}–H bonds. The charge densities calculated for fluorene by using these parameters gave results that compared very well with CNDO calculations which used bond angles and lengths determined by X-ray crystallography of fluorenyllithium (Table VIII).

Results

The ^{13}C NMR spectra of the compounds shown in Figure 1 and of their lithium salts have been obtained in THF at 25 °C. The chemical shifts of the parent hydrocarbon and the lithium salts are reported in Tables I–III. The anion of compounds **1**, **3**, **5**, and **6** had been investigated previously by others but under different conditions. All four compounds were reexamined to allow comparison under identical preparatory procedures, temperatures, and concentration using a much simplified technique for carbanion generation. It was also necessary to determine the chemical shifts of the dithiane ring carbons, the α and ipso carbons for **3**, and the parent compound's spectrum of **6**, which were not previously reported. Compound **1** was also synthesized with the C-2 carbon enriched with ^{13}C to verify the assignments for 1,3-dithianyllithium. The carbanions were all generated in THF at several comparable concentrations with lithium as the cation at 25 °C. A comparison was made of the chemical shift changes at the deprotonated carbons with those of a larger series of carbanions generated with lithium in THF (Table IV), which were available in the literature. Corresponding changes for carbanions with different cations are presented in Table V. The results of T_1 measurements for the 2-substituted dithianes are given in Table VI. The results of INDO calculations of electron densities and correlations of these densities with chemical shifts obtained are given in Tables VII and VIII and Figure 2.

Assignments of signals in the spectra of 2-biphenylyl-1,3-dithiane (**4**), biphenyl (**8**), and dibiphenylylmethane (**9**) were made by using the results of earlier investigations of spectra of 4-substituted biphenyls that utilized correlation of chemical shift with σ_p and $\sigma_p{}^+$.[39] The assigned chemical shifts of the anions of these compounds were also consistent with the T_1 measurements of compound **4**, and with correlations with the total charge density ($\sigma + \pi$) of the anion as calculated by INDO (Table VII). The assignments and chemical shifts of the (2-phenyl-1,3-dithianyl)lithium corresponded well to the ortho, meta, and para chemical shifts reported by Eliel for 2.0 M solutions in THF-d_8.

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Table I. ^{13}C NMR Chemical Shifts of 2-Substituted 1,3-Dithianes and Their Lithium Salts in THF at 25.0 °C[a]

compound	C-2	Δδ	C-4, C-6	Δδ	C-5	Δδ	other shifts							
							ipso	Δδ	ortho	Δδ	meta	Δδ	para	Δδ
1,3-dithiane	32.2		30.4		26.2									
carbanion[c]	27.0[g]	−5.2	34.1	+3.7	31.2	+5.0								
	(26.7)[11,h]		(34.1)[11]		(31.2)[11]									
2-methyl-1,3-dithiane	42.3		31.0		26.2[b]									
carbanion[d]	31.1	−11.2	30.5	−0.5	26.5	−0.3								
2-phenyl-1,3-dithiane	51.9		32.6		26.2[b]		140.7		129.0		128.4		128.6	
carbanion[e]	42.5	−9.4	30.6	−2.0	26.8	+0.6	157.3	+16.6	122.7	−6.3	127.4	−1.0	113.5	−15.0
									(122.5)[11]		(127.3)[11]		(113.1)	
2-biphenyl-1,3-dithiane	51.6		32.4		26.2[b]		139.7		129.3		127.5		141.3	
carbanion[f]	44.9	−6.7	30.6	−1.8	27.9	+1.7	157.0	+17.3	124.4	−4.9	126.0	−1.5	124.5	−16.8
							141.7[i]		127.9[j]		127.6[k]		129.9[l]	
							143.7[i]	+1.70	124.8[j]	−3.1	128.8[k]	+1.2	122.6[l]	−7.3

[a] All chemical shifts are reported relative to Me_4Si. The 26.18 ppm peak of THF was used as the reference peak. All spectra were taken at 25 °C. [b] Peak is hidden under the 26.18 ppm peak of solvent THF. [c] Concentrations of 1.0, 0.5, 0.125, and 0.063 M gave the same spectra within experimental error. [d] 1.00 M and 0.5 M. CH_3, 21.32, 20.0 ppm for hydrocarbon and carbanion, respectively; Δδ −1.32. [e] 0.5 M and 0.125 M. [f] Saturated and 0.125 M. [g] The assignment of the C_α carbanion was verified by ^{13}C enrichment of the 2 carbon. This peak was obscured by the THF solvent peak in the natural abundance spectra. [h] 2 M. [i] Ipso'. [j] Ortho'. [k] Meta'. [l] Para'.

The assignments of (9-phenylfluorenyl)lithium were made on the basis of data available on fluorenyllithium and INDO calculations of charge density.

Our observed chemical shifts for fluorenyllithium and (2-phenyl-1,3-dithianyl)lithium as well as compounds **1** and **6** are in excellent agreement with those of earlier workers for the peaks reported[7,11] and thus substantiate our new method of forming the anions. Carbanions were generated without the use of vacuum line techniques or sealing of the NMR tubes. The metal used as counterion did not require elaborate distillation, and accurate concentrations could be determined. This technique was much faster and easier than those previously employed. The anions were also stable for several days in most cases, and spectra taken from several preparations of the same anion were very consistent. The hydrocarbon chemical shifts were reproducible to ±0.02 ppm and those of the anions from ±0.05 to ±0.1 ppm, depending on the anion. These very small deviations in chemical shift in different preparations of the anions do not affect our conclusions. The spectra of the anions were referenced to the upfield resonance of THF and are reported relative to Me_4Si. Addition of cyclohexane as an internal standard has been recommended in similar studies[7] but causes variations in the solvent composition and chemical shift positions, and Me_4Si is known to be even more sensitive to medium effects than hydrocarbons.[40] In some instances trace amounts of hexane remaining from the preparation of the anion could be used to reference the THF peak, and no variation in its position could be seen under the experimental conditions. Solutions of 1,3-dithianyllithium having concentrations of 0.625, 0.125, 0.500, and 1.00 M yielded spectra with identical chemical shifts and compared well with those of a 2.0 M solution prepared by using a more elaborate preparative procedure.[11] Similar variations of concentrations for compounds **2**, **3**, and **4** gave the same result.

In instances where the pK_a of the anion studied and that of THF were similar, the spectra of THF anion could be seen and used as a reference as well. Peaks from THF anion were visible at 158.9, 123.1, and 81.5 ppm in measurements of the spectra of the anions of **5** and **8**.

Discussion

Structures of Carbanions. There is now considerable evidence that the carbanions of unsubstituted and 2-methyl-substituted 1,3-dithiane are sp^3 hybridized and very localized. This conclusion is supported by observed substituent effects on the pK_a when cesium is the cation,[26] the X-ray crystal structure of (2-methyl-1,3-dithianyl)lithium,[45] ab initio MO calculations,[29,30] and exchange studies by Eliel et al.[27] This conclusion is further confirmed by the significant negative (upfield) shifts of −5.2 and −11.2 ppm of the ^{13}C NMR spectra for the C-2 or α-carbons reported here. It also appears reasonable that the 2-phenyl- and 2-biphenylyl-1,3-dithianyllithiums in THF are sp^3 hybridized with the charge quite localized on the C-2 carbon, since the α-carbons are still shifted upfield by −9.4 and −6.7 ppm, respectively. These examples constitute the most unambiguous cases of aromatic substituted sp^3-hybridized carbanions available. This conclusion is further substantiated when these values are compared to those of benzyllithium, whose α-carbon is most probably between sp^2 and sp^3 in hybridization,[4,18,21] but still has significant delocalization into the phenyl ring. The α-carbanion for benzyllithium is shifted downfield +15.4 ppm.[15] (Biphenylylmethyl)lithium (**8**), which has the highest probability of being sp^2 hybridized and the potential for the maximum delocalization of all the carbanions studied, shows an α-carbanion downfield shift of +21.6 ppm, providing further evidence that benzyllithium is not completely sp^2 hybridized.

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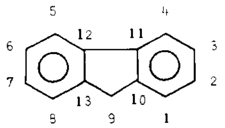
Table II. ^{13}C NMR Chemical Shifts of 9-Substituted Fluorenes and Their Lithium Salts in THF at 25 °C[a]



compound	C-9	Δδ	C-1, C-8	Δδ	C-2, C-7	Δδ	C-3, C-6	Δδ	C-4, C-5	Δδ	C-10, C-13	Δδ	C-11, C-12	Δδ
fluorene	37.2		125.5	ortho	127.2		127.2	para	120.3		143.7	ipso	142.9	ortho
carbanion[b]	80.8[b]	+43.6	116.2	−9.3	119.5	−7.7	108.3	−18.9	118.7	−1.6	137.6	−6.1	123.2	−19.7
	(81.6)[7,c]		(116.3)		(119.1)		(108.1)		(118.7)		(137.7)		(123.2)	
9-methyl fluorene	43.1		124.5		127.4		127.4		122.3		149.6		141.2	
carbanion[e]	86.9	+43.8	113.5	−11.0	118.6	−8.8	107.0	−20.4	118.6	−3.7	135.8	−13.8	122.0	−19.2
9-phenyl fluorene	55.1		125.8		127.8		127.8		120.4		141.8		142.5	
carbanion[d,f]	98.0	+42.9	114.9	−10.9	120.76	−7.0	110.53	−17.3	118.7	−1.7	135.7	−6.1	125.8	−16.7

[a] See footnote *a* in Table I. [b] 1.00 M and 0.125 M. [c] 0.3 M, ref 7. [d] 0.125 M. [e] 0.125 M. The same chemical shifts were seen for the anion at 0.3 M; ref 7. The chemical shifts for the 9-methyl carbon were 18.4 and 10.7 ppm for the hydrocarbon and carbanion, respectively, Δδ −7.7. [f] The chemical shifts for the parent hydrocarbon and carbanion for the 9-phenyl carbons are for the ipso 148.8 and 144.9 ppm, Δδ 3.9; ortho 129.1 and 126.6 ppm, Δδ 2.5; meta 128.9 and 128.1 ppm, Δδ −0.8; para 127.2 and 117.8 ppm, Δδ −9.4, respectively.

If dπ–pπ bonding explained the remarkable stabilizing effect of adjacent sulfur atoms on carbanions, one would expect rehybridization of the α carbanion in order to increase the overlap of d and p orbitals. One would also expect to see a large effect on the chemical shifts of the C-4, and C-6 carbons in the dithianyl anion. The C-4 and C-6 carbons that are adjacent to the sulfur cation have Δδ of +3.7, −0.5, −2.0, and −1.8 for compounds **1**–**4**, respectively. A much larger and positive Δδ would be expected for the C-4, and C-6 carbons for dπ–pπ bonding in which sulfur would have a significant negative charge. In *n*-butyllithium, for example, the β-carbon has a Δδ of +6.9 ppm,[18] presumably due to polarization of electron density away from the adjacent carbanion. Only 1,3-dithiane shows a positive Δδ of +3.7 ppm (note that ^{13}C enrichment verified the peak assignments for the parent hydrocarbon and anion). The 2-methyl-1,3-dithianyllithium with a Δδ of −0.5 ppm would benefit more from charge delocalization onto sulfur since alkyl groups destabilize sp^3-hybridized carbanions.[26] Hence, significant charge delocalization onto the sulfur atom would not appear to be operating.

The fluorenyllithium series (Table II), which has both fused phenyl rings planar with the 5-membered ring (as shown in the X-ray crystal structure[48]), has an sp^2-hybridized α-carbon. In this case the negative charge can resonate into both planar aromatic rings, but the 9-phenyl substituent is twisted so that it is essentially orthogonal to the other phenyl rings. The α-carbanion (C-9) in fluorenyllithium (**5**) is shifted +43.6 ppm downfield, and the 9-carbanion of 9-phenyllithium, (**7**) is also shifted downfield, by +42.9 ppm. If the 9-phenyl group could interact to delocalize the charge by resonance, there would presumably be a much greater difference between the Δδ for C-9 in **5** and **7**. For example, the α-carbon of benzyllithium has a Δδ of +15.4 while diphenylmethyllithium has a Δδ of +34.4. Likewise, (biphenylylmethyl)lithium has an α-carbon Δδ of +21.8 and (dibiphenylylmethyl)lithium has an α-carbon Δδ of +45.0. In each of these two cases the second aromatic group can resonate with the adjacent carbanion and cause additional delocation of the charge and downfield shift due to less charge density on the α-carbon. The addition of a third phenyl group in (triphenylmethyl)lithium (Table V) presumably has little effect on Δδ because all three phenyl rings are now forced to twist out of planarity due to steric interactions.

An examination of other α-carbanion chemical shifts (Table IV) shows upfield shifts for the alkyllithiums which vary from −13 ppm for methyllithium to −1.4 ppm for *n*-butyllithium. These are known to be sp^3 hybridized[21,49] and have no possibility for delocalization of charge by π bonding. The (7-phenylnorbornyl)lithium (Table IV) studied by Peoples et al.[10] was also concluded to be sp^3 hybridized, but it showed a Δδ of +10.1 ppm for the α-carbon. While this is not an upfield shift, it is certainly much smaller than Δδ for carbons known to be sp^2 hybridized. It is quite possible that this carbanion is intermediate between sp^2 and sp^3 hybridization. Such a structure would account for the experimental results showing a small (5 kcal/mol) barrier for inversion for a pyramidal carbanion.[10] This is the only other reported case of a phenyl-substituted "sp^3" hybridized carbanion. Negative chemical shift changes are also seen for anions generated α to a sulfide, sulfone, and sulfoxide[42] (Table IV) that are of the same magnitude as in the dithianes. Molecular orbital theory suggests that the addition of an oxygen to sulfur would lower the sulfur's d-orbital energy and make d–p bonding more likely. However, the Δδ supports the conclusion that these carbanions are still sp^3 hybridized. A pyramidal carbanion would explain the stereoselectivity of α-sulfonyl and α-sulfinyl carbanions generated from optically active precursors, as suggested by the results of Corey[63] and Fraser and Schuber.[64]

An examination of para-carbon chemical shifts (Table IV) leads one to the same general conclusion as those obtained from shifts of the α-carbons. It is, however, evident from MO theory and our INDO calculations that significant delocalization or polarization of the phenyl rings can occur even when the α-carbon is sp^3 hybridized. Although the para chemical shift changes afford an excellent method for judging the degree of charge delocalization into the aromatic ring, they are less sensitive to changes in hybridization of the α-carbon. Benzyllithium shows an upfield shift for the para carbon of −21.6 ppm while (biphenylylmethyl)lithium has an upfield shift of −24.5. Again, the comparison of these two compounds substantiates the conclusion that benzyllithium is not completely sp^2 hybridized. The (2-phenyl-1,3- and (2-biphenylyl-1,3-dithianyl)lithium show much smaller upfield shifts of −15.12 and −17.5, respectively. (7-Phenylnorbornyl)lithium has a chemical shift change for the para carbon of only −10.5 ppm, while the para carbon of the 9-phenyl substituent of fluorenyllithium (**7**), which has little or no resonance possibilities, has an upfield shift of −9.4. (Triphenylmethyl)lithium has a para Δδ of only −13.7 ppm in a case in which the three phenyl rings are attached to an sp^2-hybridized carbanion but are seriously twisted an average of 31.7° out of plane.[50] With an sp^2-hybridized carbon and no steric restrictions of resonance, maximum charge delocalization onto the para carbon results in a maximum Δδ of about −25 ppm. A purely inductive effect by an aromatic ring should

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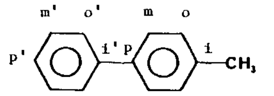
(47) Melchior, M. T.; Klemann, L. P.; Langer, A. W., Jr. *Adv. Chem. Ser.* **1974**, *No. 130*, 113.

(48) The X-ray crystal structures of fluorenyllithium with bis(quinuclidine), pentamethyldiethylenetriamine, and hexamethylphosphoramide show both phenyl rings in the same plane and the C-9 carbon pulled out of plane of one benzene ring toward the lithium cation by only 0.042 Å. The potassium analogue shows a greater deviation from planarity. See reference 47; Zerger, R.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1974**, *96*, 5441–5448.

(49) X-ray crystal structures of ethyllithium (a) and cyclohexyllithium (b) show a pyramidal metalated carbon. (a) Von Dietrich, H. *Acta Crystallogr.* **1963**, 16, 1963. (b) Zerger, R.; Rhine, W.; Stucky, G. *J. Am. Chem. Soc.* **1974**, *96*, 6048.

(50) Brooks, T. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7333.

Table III. ^{13}C NMR Chemical Shifts of Biphenylmethanes and Their Lithium Salts in THF[a]



compound[b]	C-α	Δδ	ipso	Δδ	ortho	Δδ	meta	Δδ	para	Δδ	ipso'	Δδ	ortho'	Δδ	meta'	Δδ	para'	Δδ
biphenylmethane	20.9		137.4		129.2		127.4		139.0		141.8		129.6		127.3		127.3	
carbanion	42.7	+21.8	158.3	+20.9	116.3	−12.9	126.5	−0.9	114.5	−24.5	144.1	+2.3	121.0	−8.6	128.4	+1.1	122.5	−4.8
diphenylylmethane	41.7		139.7		129.2		127.6		141.0		141.7		129.9		127.4		127.6	
carbanion	86.7	+45.0	145.0	+5.3	118.7	−10.5	125.8	−1.8	119.2	−21.8	143.2	+1.51	123.0	−6.9	128.7	+1.3	122.0	−5.6

[a] See footnote *a* in Table I. [b] 0.125 M.

Table IV. Series of Changes in Chemical Shift between Hydrocarbons and Their Lithium Salts in THF

ref	compound	Δδ α-C	Δδ para	
	1,3-dithiane (**1**)	−5.2		
	2-methyl-1,3-dithiane (**2**)	−11.2		
	2-phenyl-1,3-dithiane (**3**)	−9.4	−15.0	
	2-biphenylyl-1,3-dithiane (**4**)	−6.7	−16.8	
11	4,6-dimethyl-2-phenyl-1,3-dithiane	−9.6	−13.7	
10	7-phenylnorborane	+10.1	−10.5	
15	$PhCH_3$	+15.4	−21.6	
15	diphenylmethane	+34.4	−19.1	
15	triphenylmethane	+32.7	−13.7	
21	$PhC(CH_3)CH_2C(CH_3)_3^-$	+29.1	−36.7	
	biphenylylmethane (**8**)	+21.8	−24.5	−4.8[a]
	dibiphenylylmethane (**9**)	+45.7	−21.8	−5.6[a]
41	Ph_3Si^-	+12.3	−1.7	
41	Ph_2SiMe^-	+2.0	−5.5	
41	$PhSiMe_2^-$	+4.5	−6.1	
42	$PhSCH_3$	−11.9		
42	$PhSOCH_3$	−11.9		
42	$PhSO_2CH_3$	−9.0		
	fluorene (**5**)	+43.6	−18.9[b]	
	9-methylfluorene (**7**)	+42.9	−17.3[b]	−9.4[c]
	9-phenylfluorene (**6**)	+43.9	−20.4[b]	
15	benzene	+58.1	−5.4[b]	
15	CH_4	−13.0		
15	CH_3-*c*-$C_3H_4^-$	−6.5		
18	$CH_3CH_2CH_2CH_2^-$	−1.4		
18	$CH_3CHCH_2CH_3^-$	−8		
18	$(CH_3)_2CH^-$	−5.9		
18	$(CH_3)_3C^-$	−10.7		
15	$CH_3CH{=}CHCH_2^-$	+20.8		
15	$CH_2{=}C{=}CH^-$	+13.3		
15	$PhCHCH{=}CH_2^-$	+37.7		
7	phenol	−13.6		

[a] Para' Δδ. [b] C-3, C-6 Δδ. [c] 9-Phenyl para Δδ.

result in a negative para Δδ of <10 ppm.

With these interpretations in mind, the significance of the small para chemical shifts observed for phenyl groups α to silyl anions (Table IV) also becomes clear. Apparently the large 3p orbitals of silicon are not overlapping effectively with the 2p orbitals of the phenyl rings, and very little delocalization is occurring.[41]

It may be that some of the trend toward pyramidalization of the α-carbons is induced by the lithium cation.[10] The data reported in Table V show that the effect of varying the counterion is most significant for the α-carbon of (7-phenylnorbornyl)lithium. The C-7 for the cesium salt has been proposed to be sp^2 hybridized,[10] and this seems to be substantiated by the much larger change in the para carbon chemical shift. The Δδ for the lithium salt is −10.5 ppm vs. −20.1 and −20.7 ppm for the cesium and potassium salts, respectively. A similar large difference in Δδ for α-C in benzyllithium (+15.4 ppm) vs. that in benzylpotassium (+31.2 ppm) seems to indicate that the carbanion with lithium has significant pyramidal character. A change in ion pairing with the larger cations should lead to upfield shifts for the α-carbon and downfield shifts for the para carbon as the cation size increases,[51] but not of this magnitude. This "induced pyramidization" may explain the different conclusions reached concerning the structure of the carbanion **4** reached in our ^{13}C NMR study and that of the earlier pK_a study with cesium as the cation.[26] However, it appears that anions adjacent to sulfides and sulfoxides are still pyramidal with potassium as the cation given the Δδ for the α carbon of −9.0 and −8.5 ppm seen in Table V for $PhSCH_2^-$ and $PhSO_2^-$, as compared to Δδ of −11.9 and −9.0 ppm with lithium as the cation. Investigations of the ^{13}C NMR properties of 1,3-dithianylcesium are currently under way in order to establish the structure of that carbanion.

Ion Pairing and Aggregation. The variation of the concentrations of many of the carbanions studied over ranges as large as 0.06 to 2.0 M (see footnotes to Tables I and II) produced no

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(51) Reference 4, p 305.

Table V. Changes in Chemical Shift with Variation of Counterion

compound	$\Delta\delta$ C_α, Li^+	$\Delta\delta$ C_α, Na^+	$\Delta\delta$ C_α, K^+	$\Delta\delta$ C_α, Cs^+	$\Delta\delta$ C_{para}, Li^+	$\Delta\delta$ C_{para}, K^+	$\Delta\delta$ C_{para}, Cs^+
benzyl anion	+15.4[1a,15]		+31.2[9,6,22]		−21.6[15] (21.2)[22]	−30.1[15] (30.5)[22]	
diphenylmethyl anion	+34.4[1a,15]	+32.4[5]	+36.1[22] (36.7)[6]	+39.1[5]	−19.1[15] (19.5)[22]	−18.0[15] (−18.7)[22]	
triphenylmethyl anion	+32.7[1a,15]	+28.6[5]	+30.8[22] (30.4)[6]	31.1[5]	−13.7[15] (−14.2)[22]	−12.6[15] (−13.1)[22]	−20.1[10]
7-phenylnorbornyl anion	+10.1[10]		+33.9[10]	+37.6[10]	−10.5[10]	−20.7[10]	
$PhC(CH_3)CH_2CH_3^-$	+22.5[21]		+37.2[21]		−29.1[21]	−38.6[21]	
fluorenyl anion	+43.6[6]	+37.6[6]	+41.93[6]	+44.3[6]	−18.9 (−19.1)[7]		
	+43.4[4]	+43.2[4]	+45.7[4]	+46.1[4]	−18.9[4]	−17.7[4]	−17.2[4]
$PhSCH_2^-$	−11.9[42]		−8.4[42]				
$PhSOCH_2^-$	−11.9[42]		−9.0[42]				
	−9.0[42]		−8.5[42]				

Table VI. T_1 Values[a] for Parent Hydrocarbons and Carbanions of 2-Substituted 1,3-Dithianes[a]

compound	C-2	C-4,6	C-5	ipso	ortho	meta	para	ipso'	ortho'	meta'	para'
2-phenyl	5.1	2.0	11.8	36.7	3.6	4.0	1.6				
2-phenyl-2-*d*	29.9	1.8	2.8	37.3	5.0	5.2	3.1				
2-Lithio-2-phenyl	13.6	0.3	0.7	14.0	1.0	1.1	0.8				
2-biphenylyl	3.6	4.1		22.8	2.5	3.7	25.3	36.9	3.1	4.6	3.8
2-biphenylyl-2-*d*		1.7		40.3	2.9	3.6	25.0	34.4	2.9	2.3	3.8
2-Lithio-2-biphenylyl	10.7	0.2	0.2	8.8	0.5	0.6	10.0	14.2	1.1	0.9	0.5

[a] Relaxation times, T_1, in seconds in THF at 25 °C.

Table VII. Charge Density[a] of Selected Carbanions

compound	MO calculation	hybridization	C_α	ipso	ortho	meta	para
benzyl anion	INDO	sp^2 $\pi + \sigma$	−0.350	0.135	−0.120	0.051	−0.133
		sp^2 π	−0.538	0.114	−0.196	0.027	−0.196
		sp^3 $\pi + \sigma$	−0.402	0.149	−0.102	0.041	−0.108
		sp^3 π	−0.331	0.142	−0.160	0.019	−0.201
	SCF[43]	sp^2 π			−0.14	−0.07	−0.23
	LCAO[43]	sp^2 π			−0.14	0.00	−0.14
benzyl anion[b]	INDO	sp^2 $\pi + \sigma$	−0.593	0.190	−0.07	0.014	−0.037
		sp^2 π	−0.905	0.163	−0.48	−0.007	−0.94

compound	MO calculation	hybridization	9	1,8	2,7	3,6	4,5	10.13	11,12
fluorenyl anion	INDO	sp^2 $\pi + \sigma$	−0.214	−0.052	0.008	−0.057	0.014	0.048	−0.050
		sp^2 π	−0.345	−0.088	−0.033	−0.124	−0.004	0.022	−0.101
	CNDO II[44]	sp^2 $\pi + \sigma$	−0.26	−0.10	0.04	−0.11	0.04	0.07	−0.08

compound	MO calculation	hybridization		ipso	ortho	meta	para	ipso'	ortho'	meta'	para'
biphenylylmethyl anion	INDO	sp^2 $\pi + \sigma$	−0.303	0.128	−0.104	0.045	−0.125	0.089	−0.051	0.033	−0.042
		sp^2 π	−0.463	0.108	−0.167	0.033	−0.225	0.086	−0.080	0.012	−0.099
		sp^3 $\pi + \sigma$	−0.367	0.147	−0.097	0.038	−0.103	0.086	−0.044	0.031	−0.035
		sp^3 π	−0.293	0.143	−0.141	0.027	−0.192	0.084	−0.071	0.010	−0.088

[a] In units of the absolute value of the charge of an electron. [b] The lone pair of electrons on the α carbon is parallel to the phenyl ring; no resonance with the phenyl is possible.

detectable changes in chemical shift. Since this was true for both localized sp^3 carbanions and delocalized sp^2 carbanions, this result makes it possible to compare with confidence the many ^{13}C NMR studies of carbanions done at differing concentrations but in the same solvent with lithium as the cation (Table IV).

Another question that must be addressed in comparing different compounds even under similar conditions is the type of ion pairing and the possible effect of aggregation. The 1,3-dithianyllithium series (**1**–**4**) are at most dimers and quite likely monomers[11,45–47] and have been shown to be contact ion pairs down to −100 °C.[11] Extensive studies of ion pairing effect on fluorenyllithium in THF[6] have shown it to be approximately 50–70% contact ion pairs at 25 °C. This is probably the case for the anions of **8** and **9** as well, since they have quite similar degrees of charge delocalization by resonance. The total range of upfield chemical shift from solvent-separated to contact ion pairs for fluorenyllithium in a temperature range of −60 °C to +70 °C is only 5.5 ppm for the α-carbon, which is the most sensitive to ion pairing, and 2 ppm for the para carbon. (Diphenylmethyl)lithium in THF also showed similar changes in chemical shift of 4.2 ppm for C_α and 1.4 ppm for C-para over a 100 °C change in temperature.[5] Large delocalized systems (20 π electrons) such as (triphenylmethyl)lithium[5,6] are solvent separated at 25 °C, while (diphenylmethyl)lithium resembles fluorenyllithium. Smaller systems (8 π electrons) were contact ion pairs throughout the temperature range.[6] Similar ion pairing studies of (7-phenylnorbornyl)lithium (Table IV) for a 8 π system showed no change in C_α chemical shift in THF down to −90°C.[10]

Hence, while the state of aggregation of some of these carbanions in these solutions has not been determined explicitly, comparison of the spectra of these anions (**1**–**9**) with others reported at the same temperature should be valid. They are all either contact ion pairs or largely contact ion pairs at room temperature under approximately the same conditions. Chemical shift differences due to the degree of contact ion pairing should be negligible. Even a complete change from solvent-separated to contact ion pairing has a maximum $\Delta\delta$ of 6.0 ppm for α-carbons and only 1–2 ppm as a maximum $\Delta\delta$ for paracarbons. Our conclusions do not rely on such small variations, and we are comparing very similar types of carbanions.

In our investigations, anions adjacent to small π systems (8 π electrons) can safety be assumed to be contact ion pairs at room temperature. Those with 14 π electrons are probably in the range of 70–75% contact ion pairs. Such a difference in ion pairing

Table VIII. Correlation[b] of Chemical Shift and Electron Density ($\sigma + \pi$) Calculated by INDO[31] for Carbanions

compound	hybridization of α carbanion	ppm/charge[a,b] ($\sigma + \pi$), no α	ppm/charge[b,g] ($\sigma + \pi$), no α or ipso	ppm/charge (π),[b,e] no α
benzyl anion	sp^2	172.3	104.2	140.3
	sp^3	187.7		145.6
benzyl anion[f]	sp^2	88.5[f]	33.6	
biphenylylmethyl anion	sp^2	150.9	77.5	108.9
	sp^3	161.4		121.4
2-biphenylyl-1,3-dithianyl anion[c]	sp^2	109.1	18.7	
	sp^3	119.2		
2-phenyl-1,3-dithianyl anion[d]	sp^2	128.2	55.0	
	sp^3	141.6		
fluorenyl anion	sp^2	162.8	107.9	
7-phenylnorbornyl anion	sp^2	119.7		94.5
	sp^3	135.5		105.8

[a] Charge of an electron. [b] The shift of the α-carbon is not included in the correlation. [c] Charge density calculated for biphenylylmethyl anion is correlated with the shift for (2-biphenylyl-1,3-dithianyl)lithium. [d] Charge density calculated for benzyl anion is correlated with the shift for (2-phenyl-1,3-dithianyl)lithium. [e] α-Carbons did not fit with only the π charge density. [f] Negative p orbital parallel to the plane or the phenyl ring and correlated with the shifts for the 9-phenyl substituent in (9-phenylfluorenyl)lithium. [g] Ipso carbons are not included in the calculation.

might result in a very small upfield shift for the carbon which would be negligible for our discussion of structure. We are considering $\Delta\delta$ of 15–45 ppm for the α-carbon in the present study. Furthermore, the balance of ion pairing and aggregation at the concentrations used in this study are more applicable to the conditions and structures found under synthetic conditions than those in pK_a measurements or UV-vis studies. The structures of carbanions determined by NMR studies can, thus, be of more direct use to synthetic chemists in helping to understand the reactivity of carbanions.

T_1 Measurements. The measurement of the spin–lattice relaxation times, T_1, for the 2-phenyl- and 2-biphenylyl-1,3-dithianes and their lithium salts allowed a clear identification of the ipso carbons and α-carbons. The relaxation times for these carbons are longer than for the other carbons because they have no attached hydrogens.[61] As a result, the dipolar relaxation due to hydrogen is not as effective, and T_1 becomes longer. Deuterium was substituted at the 2-position in order to observe the effect due just to loss of a hydrogen without the significant changes in internal motion of the molecule expected for the carbanion. From the general decrease in the T_1 values for the anion in comparison to the parent hydrocarbons, one can infer a general trend in stiffening of the dithianyl moiety as well as the aromatic rings in the anions. Earlier studies by Eliel set a thermodynamic tendency for the anion to be in the equatorial position of 4–5 kcal/mol,[27] which would explain the rigidity of these anions. Another explanation would be the possible formation of dimers,[52] but the work of Eliel[11] discussed earlier rules out this possibility. Work is currently under way to extend these T_1 studies to a wider variety of carbanions.

INDO MO Calculations. It has been well established that there is a linear relationship between ^{13}C chemical shift and charge density as calculated by SCF MO[12,13,53,54] (dividing the charge by the number of carbons in symmetrical carbanions[9]), by HMO,[56] or by CNDO.[24,57] The proportionality constants have varied from an average value of 161 ppm/charge of an electron[9,12,13,55,56,57] to as high as 316 ppm/charge of an electron for hydroxycarbenium ions.[24] The studies mentioned deal only with π electron densities and generally involve compounds with extensive charge delocalization in which there is little question as to where the charge is located or what the hybridization states of the carbons are. For example, $C_5H_5^-$, C_6H_6, $C_7H_7^+$, and $C_8H_8^{2-}$ and similar compounds were investigated by Spiesecke and Schneider[13] and by O'Brien.[9] When the correlations of the ^{13}C chemical shifts of substituted benzenes[12,57] or benzyllithium and di- and triphenyllithium[53] with charge density were performed, only the para[12] or ortho, meta, and para[57] carbons were considered. The present study used both σ and π charge densities and considered the α-carbon and ipso-carbons as well as the aromatic carbons. This evaluation is also different than any previously reported in that the correlations consider all the carbons within one molecule and use variations in slope between differing compounds to gain additional information about hybridization and charge delocalization in these molecules.

Theoretical treatments of carbon-13 shifts for aromatic hydrocarbons,[58] substituted benzenes,[59] and heteroaromatics[20,60] have shown that it is critical to take into account the σ electron density and polarization of the σ framework by heteroatoms as well as the charge density in the π system. Since these considerations are even more important when a full charge is present, there is a need to extend the relationship between carbon-13 shifts of carbanions and $\sigma + \pi$ charge density. We have used INDO calculations[31] to reinvestigate benzyllithium and to calculate charge densities for (biphenylylmethyl)lithium and fluorenyllithium. Calculations were also done for benzyllithium with the anion orthogonal to the phenyl ring with sp^3 or sp^2 hybridization for the α carbanion. The results of these calculations showing π and $\sigma + \pi$ charge densities can be seen in Table VII. The correlation of carbon-13 shifts with charge density for various carbanions is found in Table VIII.

Our experimental data for carbanions generated in the same solvent and with the same cation at 25 °C and at similar concentrations should allow the best estimates of the sensitivity of chemical shift to charge density. (Biphenylylmethyl)lithium had the best correlation (see Figure 2). (Biphenylylmethyl)lithium appears to be more delocalized and sp^2 in character than the much studied benzyllithium, given the chemical shifts of para carbons and α-carbons (see earlier discussion). The fluorenes, which are known to be sp^2 hybridized, have a good fit for the α-carbanion. The points for the α-carbanion were low for the other compounds, especially for the dithianes, which are sp^3 hybridized. This is reasonable since the change in chemical shift due to changes in hybridization is not taken into account in the INDO calculations. The α-carbons were therefore omitted from the calculations of all slopes in Table VIII. Given variations in the hybridization of the α-carbon, position of the lithium cation, type of ion pairing, and steric interactions, the fact that the α-carbon correlates for any of the compounds is encouraging. When more compounds are evaluated the degree of deviation of the α-carbon can presumably be used to determine the hybridization of the carbanion if other factors are relatively constant. In some correlations the ipso carbons were more deshielded than the calculated charge density indicated. This was especially evident for the 10, 13, and 11, 12 carbons of fluorene and the ipso carbons in 2-biphenylyl-1,3-dithiane. There have been similar problems in calculating the charge densities of these types of carbons in neutral

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aromatic compounds.[60c] Two different correlations were done for the substituents in Table VIII, one without α- and one without α- or ipso carbons for comparison. The same trends can be seen in either correlation. The anions which have a large amount of delocalization of charge into the phenyl rings show larger slopes. Benzyl anion, biphenylylmethyl anion (Figure 2), and fluorenyl anion have slopes equal to 172, 151, and 163 ppm/charge of an electron, respectively, for the sp^2-hybridized carbanion. These slopes are essentially the same within experimental error.

When the benzyl anion is twisted so that the p orbital of the α-carbon is orthogonal to those of the phenyl ring in the MO calculation and the charge densities so obtained are plotted relative to the chemical shifts of the 9-phenyl substituent of fluorene, the slope drops to a value of 88 ppm/charge of an electron. In the case of 9-phenylfluorene, the 9-phenyl substituent is twisted out of the plane of the fluorene due to steric interaction with the 1 and 8 hydrogens so that its p orbitals are orthogonal to those of the carbanion. Little or no delocalization of charge is possible. The INDO calculation is apparently accurately assigning charge density resulting from an inductive effect since the linear fit for correlation is very good. The decrease in slope is obviously due to the fact that the C-9 carbon does not have the full negative charge assumed in the INDO calculation. If we correct for this, the slope becomes a minimum of 149 ppm/charge of an electron.

Slopes of 128 and 110 ppm/charge of an electron are seen for 2-phenyl- and 2-biphenyl-1,3-dithianyl anions. These are even lower (55 and 19) when the unusually large ipso-carbon chemical shifts are removed from the correlation. These smaller slopes indicate a smaller degree of charge delocalization into these aromatic rings than for the fully delocalized cases. In these cases, the calculated charge density in the aromatic ring is larger than is actually occurring in the substituted dithianes. This will result in a slope of less than 160 ppm/charge of an electron. Each sulfur atom in dithiane offers about the same stabilization as a phenyl ring (a decrease of 10 pK_a units for each sulfur adjacent to a carbanion[26]). Apparently the stabilization of being adjacent to 2 sulfurs is sufficient to decrease the delocalization of charge into the phenyl or biphenylyl substituent. 7-Phenylnorbornyl anion is also somewhat intermediate in its slope with a value of 120 ppm/charge of an electron.

In general the use of $\sigma + \pi$ charge densities gives a better fit in these correlations than with π charge density alone. The α-carbons do not fit at all when only π charge densities are used. The ipso carbons also correlate better with the use of $\sigma + \pi$ charge densities. Changing the hybridization of the α-carbon from sp^2 to sp^3 in the INDO MO calculation did not have a large effect on the charge densities. This can be seen in the similarity of the slopes for sp^2 vs. sp^3 which vary less than 10%. Obviously the largest change seen was for twisting the phenyl group out of the plane of the carbanion.

Conclusions

The present work reaches several significant conclusions. It is clear that the $\Delta\delta$ for the α-carbon can be used to evaluate charge density and hybridization when similar compounds are compared under the same conditions, provided that enough examples are available. Carbon-13 NMR spectra of carbanions that set limits of $\Delta\delta_\alpha$ and $\Delta\delta_{para}$ for maximal charge delocalization for an sp^2-hybridized substituted methyllithium ((biphenylylmethyl)lithium) and the least stabilization by a phenyl on an sp^2 carbanion (9-phenylfluorene) have been obtained. The results (both $\Delta\delta_\alpha$ and $\Delta\delta_p$) for the (biphenylylmethyl)lithium show that the negative charge in benzyllithium is not completely delocalized and support earlier propositions that benzyllithium is between sp^2 and sp^3 in hybridization. Comparing the data obtained in Tables I–III with chemical shifts in the literature (Table IV) one can see that carbanions α to sulfides as well as carbanions of sulfones, sulfoxides, and silanes are sp^3 hybridized and localized. Since these moieties are widely used to stabilize carbanions in synthetic applications, the knowledge that adjacent phenyls are acting mainly in an inductive manner has important ramifications in the design of these alkylating reagents.

We report for the first time the σ and π electron densities calculated by INDO for phenyl and biphenylyl substituents in several structural variations adjacent to sp^2 and sp^3 carbanions. Given the wide range of compounds that have these substituents, these results will be useful in many other correlations, such as in allowing estimates of steric twisting of phenyl rings and the many effects of charge density on reactivity. The linear relationship of charge density and chemical shift within a molecule offers a new method for examining the structure of similar carbanions. As additional correlations for carbanions become available, a quantitative calculation of the degree of sp^2 character in the carbanion should become possible.

The T_1 measurements acquired for 2-substituted 1,3-dithianes are among the first to be reported for carbanions. It is expected that as the T_1 values of more carbanions are obtained for comparison, they will offer valuable information as to the dynamic properties and steric interactions of carbanions. It is important to emphasize that the new technique developed to generate the carbanions studied did not require a vacuum line or glovebox. The carbanions formed by this method gave consistent spectra which corresponded well to spectra obtained from carbanions prepared by more elaborate methods in cases where comparison was possible. The carbanion preparations were also quite stable. The time and effort involved in taking spectra of the anions was thus cut considerably. This technique can easily be extended to other reactive species.

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Registry No. 1, 505-23-7; **1** lithium salt, 36049-90-8; **1** (^{13}C enriched), 88157-07-7; **2**, 6007-26-7; **2** lithium salt, 27969-97-7; **3**, 5425-44-5; **3** lithium salt, 53178-41-9; **3** anion, 88157-06-6; **3** (d_2), 14664-88-1; **4**, 54527-55-8; **4** lithium salt, 88157-01-1; **4** anion, 88157-05-5; **4** (d_2), 27969-97-7; **5**, 86-73-7; **5** lithium salt, 881-04-9; **5** anion, 12257-35-1; **6**, 2523-37-7; **6** lithium salt, 19219-11-5; **7**, 789-24-2; **7** lithium salt, 733-88-0; **8**, 644-08-6; **8** lithium salt, 68695-93-2; **8** anion, 88157-04-4; **9**, 3901-32-4; **9** lithium salt, 88157-02-2; benzyl anion, 18860-15-6; 7-phenylnorbornyl anion, 77938-35-3; 1,3-propanedithiol, 109-80-8; benzaldehyde, 100-52-7; acetaldehyde, 75-07-0; *p*-biphenylcarboxaldehyde, 3218-36-8; 9-hydroxy-9-phenylfluorene, 25603-67-2; 9-hydroxy-9-methylfluorene, 6311-22-4.

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