

Structure of Radical Anions in Solution as Deduced from Paramagnetic Solvent Nuclear Magnetic Resonance Shift Measurements. 1. Molar Paramagnetic Solvent Shifts as Molecular Parameters for Understanding Structure, Reactivity, and Solute-Solvent Interactions in Ketyl Anion Solutions

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The molar paramagnetic solvent shifts of the aromatic ketyl anions $(\text{Ph}_2\text{C}=\text{O})\cdot\text{M}^+$ ($\text{M} = \text{Li}, \text{K}$), $(\text{Fl}=\text{O})\cdot\text{M}^+$ ($\text{Fl}=\text{O} = \text{fluorenone}$, $\text{M} = \text{Li}, \text{Na}, \text{K}$), $(1\text{-C}_{10}\text{H}_7\text{COPh})\cdot\text{M}^+$ ($\text{M} = \text{Li}, \text{K}$), and $(2\text{-C}_{10}\text{H}_7\text{COPh})\cdot\text{Li}^+$ have been measured in tetrahydrofuran (THF), at $35 \pm 1^\circ\text{C}$, and with respect to both the α and β proton bands of THF. These parameters appear to be characteristic of the anion-cation pair in a given solvent and at a given temperature. The two molar paramagnetic solvent shifts, referred to the two bands of THF solvent, $\Delta\nu_m^\alpha$ and $\Delta\nu_m^\beta$ are not equal, as they should be if the observed shifts were arising from bulk paramagnetic effects. The difference between the two molar shifts, which ranges from about -10 to $+10\%$, has been accounted for on the basis of Fermi contact interactions. This interpretation requires the acquisition of a larger positive spin density by the β protons of the THF solvent. It has been observed that addition of a strongly cation complexing agent may or may not "eliminate" the contact shift. Thus, although tetramethylethylenediamine (TMEDA) can "take up" or "eliminate" the contact shift when added to lithium benzophenone ketyl in THF, it has no effect on the shift in the case of lithium fluorenone ketyl in THF. Shifts larger than those predicted by Langevin's expression for bulk paramagnetic solvent shifts have been measured, e.g., in $(\text{Fl}=\text{O})\cdot\text{K}^+$, 180 Hz/mol vs. the "theoretical" value of 153 Hz/mol at 35°C . It has been concluded that the contact or any microscopic magnetic interactions between the odd electron of the anion and the solvent molecules are transmitted through the mediation of the cation. Other conclusions drawn from molar paramagnetic solvent shift parameters are that in fluorenone ketyl anions covalency decreases in the order $\text{Li}, \text{Na}, \text{K}$ and that benzophenone and fluorenone ketyl anions do not tend to undergo disproportionation at high concentrations. Using potassium benzophenone ketyl as a paramagnetic probe it was decided that 18-crown-6 does not produce a "naked anion" by complexing with the potassium cation. A quantitative expression of the effect of added cosolvent on aromatic ketyl anion structure in solution has been derived. It is based on comparisons of initial slopes of shift vs. concentration relationships in mixtures of THF and the poorly solvating cosolvents dioxane and triethylamine. It appears that in the presence of these cosolvents a fraction of the paramagnetic species undergoes some transformation to diamagnetic species. This effect is more pronounced in lithium benzophenone ketyl than in lithium fluorenone ketyl.

We have been using an adaptation of an NMR method¹ for measurements of kinetics and equilibria of reactions in which a stable radical anion is involved either as a reactant or product.² This method is based on observing solvent shifts in the NMR caused by the paramagnetic solute and it is applicable to concentrations comparable to those of the preparative reactions, i.e., 1 M or so. We now report the application of this method to structural problems of radical anions in solution at such concentrations.

Most of the reported studies concerned with the structure of radical anions in solution were based on either UV-visible or ESR spectrometric techniques.³ Both methods, however, are applicable to very dilute solutions of radical anions. This is so because of the very high molar extinction coefficients of the radical anions or the necessity to work with dilute solutions in order to obtain good resolution in the ESR spectra. The fact, however, that the structure of radical anions, and particularly of the ketyl anions, is concentration dependent⁴ calls for studies of ketyl anions at concentrations comparable to those of the

preparative reactions. Studies under these conditions are expected to yield more realistic information, directly applicable by the organic chemist who deals with the chemistry of radical anions. Moreover, structure and reactivity of radical anions in solution should be related and, therefore, the reactivity of radical anions should be, and in fact is,⁵ concentration dependent. Perhaps, the only available information concerning the structure of radical anions in solution at high concentrations has been derived from alkali metal NMR studies by de Boer's laboratory.⁶

This paper, more specifically, (a) is concerned with the relationship between shift of the α and/or β proton NMR bands of tetrahydrofuran (THF) and the concentration of certain ketyl anions; (b) it is intended to show that the molar paramagnetic solvent shifts of ketyl anions can be useful molecular parameters, characteristic for a particular anion-cation pair in a particular solvent and at a given temperature; (c) it attempts to provide evidence that the molar paramagnetic solvent shifts can yield information concerning structure, reactivity, and solute-solvent interactions in radical anion solutions.

We have employed a dual external marker technique in order to measure simultaneously the shift induced on the two bands of THF by a radical anion dissolved in this solvent. The ^1H NMR bands of ethylene chloride and *tert*-butyl bromide served as external markers. Ethylene

(1) Evans, D. F. *Proc. Chem. Soc.* 1958, 115; *J. Chem. Soc.* 1959, 2003.

(2) (a) Screttas, C. G. *J. Chem. Soc., Chem. Commun.* 1972, 869; (b) *J. Chem. Soc., Perkin Trans. 2* 1974, 745. (c) Screttas, C. G.; Georgiou, D. G. *Tetrahedron Lett.* 1975, 417. (d) Screttas, C. G.; Cazianis, C. T. *Tetrahedron* 1978, 34, 933. (e) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* 1978, 43, 1064.

(3) See, e.g.; Hirota, N. In "Radical Ions"; Kaiser, E. T., Kevan, L., Eds.; Interscience: New York, 1968; p 35.

(4) Smid, J. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed., Wiley-Interscience: New York, 1973; Vol. 1, p 146.

(5) Reference 2c.

(6) Sommerdijk, J. L.; de Boer, E. In ref 4, Chapter 8. de Boer, E. "Ions and Ion Pairs and their Role in Chemical Reactions"; Smid, J., Ed., Pergamon Press: Oxford, 1978; p 73.

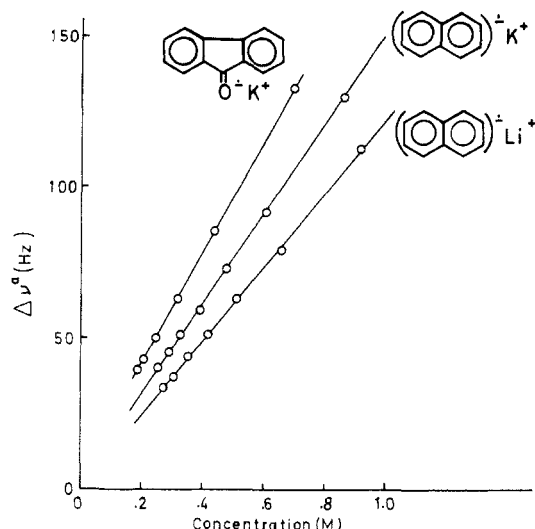


Figure 1. Relationship between shift induced to the α proton band of THF and concentration in solutions of potassium fluorenone ketyl, potassium naphthalene radical anion, and lithium naphthalene radical anion.

chloride (40% v/v) and *tert*-butyl bromide (40% v/v) containing 20% (v/v) benzene exhibit sharp singlets at ca -5 Hz from the α and β bands of THF, respectively. In the presence of a radical anion the THF bands lose their fine structure and are shifted to higher fields. The shift is linearly related to the concentration of the radical anion. In Figure 1 is given the shift induced to the α band of THF by potassium fluorenone ketyl, potassium naphthalene radical anion, and lithium naphthalene radical anion, as a function of concentration. We see that in all cases the shift depends linearly on the concentration.⁷ These types of relationships are useful because they can serve as working curves for the estimation of concentrations of radical anions by measuring solvent shifts. We notice that radical anions which have either a common cation, as in the case of potassium fluorenone ketyl and potassium naphthalene radical anion, or a common anion, as in the case of lithium and potassium naphthalene radical anions, exhibit different dependencies of shift on concentration. In other words, the slopes of the lines, which are proportional to the concentration of the radical anion, are not equal. By extrapolation to the concentration of 1.0 M one obtains the so-called molar paramagnetic solvent shift which we designate as $\Delta\nu_m^\alpha$ and $\Delta\nu_m^\beta$ for the two bands of THF, respectively (see also the Experimental Section). Obviously the $\Delta\nu_m^\alpha$ values are characteristic for a particular anion-cation pair in a given solvent and at a given temperature. Thus, the values of molar paramagnetic solvent shifts reported in this paper, Table I, are referred to tetrahydrofuran solvent and the temperature of $35 \pm 1^\circ\text{C}$, at 60 MHz.

In Figure 2 the line marked by α represents the relation between the shift induced to the α proton band of THF by lithium benzophenone ketyl vs. concentration of the ketyl. The line marked by β relates the shift of the β proton band of THF and the concentration of lithium

(7) It might seem surprising that the shift vs. concentration plot is linear even in the case of ketyl anions. Metal ketyls in solution may contain a multitude of species which differ in the degree of association, the type of ion pairing, the magnetic state,³ and the reactivity.^{2c} Solvent shifts "feels" the paramagnetic species (one or more) collectively. The linearity then could mean that under these conditions the concentration of the diamagnetic species (if any), being at equilibrium with the paramagnetic species, is very small compared to the concentration of the latter one(s).

Table I. Molar Paramagnetic Solvent Shifts (Hz/mol) of Certain Aromatic Ketyl Anions in Tetrahydrofuran at $35 \pm 1^\circ\text{C}$ and 60 MHz

entry	ketyl	$\Delta\nu_m^\alpha$	$\Delta\nu_m^\beta$	$\frac{\Delta\Delta\nu_m^{\alpha\beta}}{100} \times$
1	(Ph ₂ CO) ⁻ ·Li ⁺	84 ^a	77 ^a	8.3
2	(Ph ₂ CO) ⁻ ·Li ⁺	85 ^b	77 ^b	9.4
3	(Ph ₂ CO) ⁻ ·K ⁺	129 ^a	117 ^a	9.3
4	(Ph ₂ CO) ⁻ ·K ⁺	130 ^b	116 ^b	10.8
5	(FlO) ⁻ ·Li ⁺	112 ^a	107 ^b	4.5
6	(FlO) ⁻ ·Li ⁺	110 ^b	104 ^b	5.5
7	(FlO) ⁻ ·Na ⁺	162 ^a	155 ^a	4.3
8	(FlO) ⁻ ·Na ⁺	163 ^b	157 ^b	3.7
9	(FlO) ⁻ ·K ⁺	180 ^a	173 ^a	3.9
10	(FlO) ⁻ ·K ⁺	180 ^b	173 ^b	3.9
11	(1-C ₁₀ H ₇ COPh) ⁻ ·Li ⁺	24 ^a	27 ^a	-11.1
12	(1-C ₁₀ H ₇ COPh) ⁻ ·K ⁺	23 ^a	23 ^a	0
13	(2-C ₁₀ H ₇ COPh) ⁻ ·Li ⁺	61 ^a	57 ^a	6.6

^a The ketyl was prepared by direct reaction of equivalent amounts of the ketone and the alkali metal. ^b The ketyl was prepared from the dianion of the ketone and the neutral ketone.

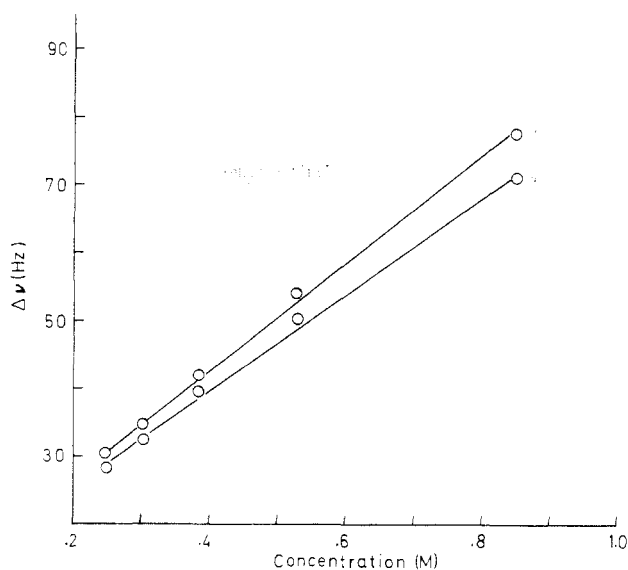


Figure 2. Shift vs. concentration referred to the α and β proton bands of THF in solutions of lithium benzophenone ketyl.

benzophenone ketyl. As can be readily seen the two lines have different slopes and, therefore, yield different values of molar paramagnetic solvent shifts. This is usually the case, i.e., $\Delta\nu_m^\alpha > \Delta\nu_m^\beta$, with the only exception encountered so far in the case of lithium 1-naphthylphenyl ketyl anion, for which $\Delta\nu_m^\alpha < \Delta\nu_m^\beta$; see value of $\frac{\Delta\Delta\nu_m^{\alpha\beta}}{100} \times 100$, entry 11, Table I. The inequality between the two molar shifts would seem unexpected if the observed shifts were due to the bulk paramagnetic effects. An explanation of this phenomenon can be given on the basis of the pioneer work of de Boer and co-workers.⁸ They noticed that on adding a strongly cation complexing agent such as tetraglyme to a solution of sodium triphenylene or sodium coronene radical anions in THF, the THF resonance bands were shifted to higher fields to an extent that corresponded to the shift expected on the basis of the bulk paramagnetism of the solution. They also observed a shift to lower fields of the resonances of the complexed to cation tetraglyme measured from the relevant bands of the uncomplexed ligand. They interpreted this downfield as arising from contact shift interactions between the unpaired electron

(8) de Boer, E.; Smid, J. *J. Am. Chem. Soc.* 1970, 92, 4742. de Boer, E.; Grotens, A. M.; Smid, J. *J. Chem. Soc. D* 1970, 1035.

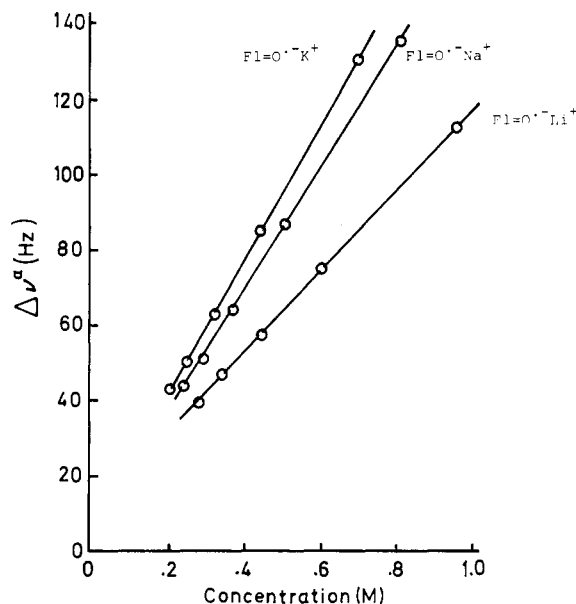


Figure 3. Relationship of shift vs. concentration (see caption for Figure 1) in solutions of potassium, sodium, and lithium fluorenone ketyls in THF.

and the complexed to cation tetraglyme molecule(s). They concluded that the observed solvent shift in the absence of added ligand is consistent of one paramagnetic (upfield) component arising from bulk magnetic effects and a downfield component, obviously of a smaller magnitude, due to Fermi contact (microscopic) interactions between the odd electron and the solvent molecule. This interpretation requires that the protons of THF molecules acquire a positive spin density, hence the shift to lower fields. From this information one can also conclude that addition of a strongly complexing agent "takes up" or "eliminates" the contact shift, which now no longer can be felt by the solvent molecules, hence the elimination of the downfield shift and the enlargement of the observed shift.

It is felt that one can reasonably interpret the inequality between the two molar shifts by assuming that the two types of THF protons acquire different values of positive spin densities. A larger value of positive density at the β protons than at the α protons can explain a larger contact shift and therefore a smaller overall solvent shift exhibited by the β protons. Thus the first practical application of molar paramagnetic solvent shifts is that their relative values reflect the magnitude of the contact shift. According to ref 8 the solvent shift should be given by eq 1 (C = concentration) in the case where no contact shifts were operable.

$$\delta_s = (-2\pi/3)10^3 \frac{N\beta_e^2}{kT} C \quad (1)$$

In Figure 3 are given the relationships of shift vs. concentration, with respect to the α protons of THF, for solutions of potassium fluorenone ketyl, sodium fluorenone ketyl, and lithium fluorenone ketyl. These lines yield the following $\Delta\nu_m^\alpha$ values, respectively: 180, 162, 112 Hz/mol. The "theoretical" value according to eq 1 should be 2.55 ppm, or 153 Hz at 60 MHz. We notice that the $\Delta\nu_m^\alpha$ values for sodium and potassium fluorenone ketyls are larger than the "theoretical" one. One then is forced to conclude that either eq 1 does not predict correctly the shift of the solvent due to bulk magnetic effects or that there are induced negative as well as positive spin densities on the protons of the THF solvent molecules by the contact

mechanism. We assume that the first hypothesis is correct, namely, that eq 1 does not predict correctly the bulk shift. The most important feature of Figure 3 is that the lines lead to different values of $\Delta\nu_m^\alpha$, in spite of the fact that all three ketyl anions have a common anion. Since the differences in the underlying diamagnetism in these three ketyls should be very small, we are led to the conclusion that the different contributions of contact shifts to the overall solvent shifts are mainly cation dependent. One then can arrive at the following conclusion: the contact interactions or any microscopic magnetic interactions between the odd electron and the solvent molecules are transmitted through the mediation of the cation. Alkali metal magnetic resonance studies⁶ have shown that the magnetic nuclei of the alkali metals may exhibit contact shifts in radical anion solutions. On the basis of this information we can visualize the interaction between the unpaired electron of the anion and the solvent molecules as follows. Odd electron induces a spin density at the nucleus of the cation which, in turn, induces a spin density on the magnetic nuclei of the molecules of its coordination or solvation sphere. Rapid exchange between the molecules in the solvation sphere with the molecules of the bulk solvent creates the conditions so that the microscopic magnetic interactions can be felt by all solvent molecules and not only by those found in the coordination sphere of the cation. Thus, the molar paramagnetic solvent shifts of lithium, sodium, and potassium fluorenone ketyls can be rationalized as follows. In the absence of any contact interactions all three ketyl anions of fluorenone with lithium, sodium, and potassium should exhibit (approximately) equal molar paramagnetic solvent shifts. The fact that the $\Delta\nu_m^\alpha$ values decrease in the order K, Na, Li indicates that the magnitude of the negative contribution by contact interactions increases in the order K, Na, Li. This requires an increase of the positive spin density at the α protons of THF molecules forming the coordination sphere of the cation. It is reasonable to expect that the higher the spin density at the nucleus of the cation, the higher the spin density induced on the nuclei of the solvent molecules which are coordinated with the cation. Therefore, the spin density at the nucleus of the cation should be in the order $K < Na < Li$. ESR measurements showed this to be true in the case of *o*-dimesitylbenzene ketyl anion.⁹

Since the exhibition of hyperfine interactions in general, and contact interactions in particular, is a manifestation of covalency¹⁰ we can readily see a practical utility of the $\Delta\nu_m$ values. Namely, they can yield information concerning bonding situations in the anion-cation pair. Thus, from the observed order of $\Delta\nu_m^\alpha$ for lithium, sodium, and potassium fluorenone ketyls we conclude that covalency decreases in the order Li, Na, K. There are, however, cases, e.g., like those in entries 11 and 12, in which the unusually small molar shift could arise by some effect other than contact shifts, for example, spin pairing. In such a case the magnitude of the molar solvent shift could not be taken as evidence for extensive covalency. Noteworthy could be the difference in the molar paramagnetic solvent shifts of the two isomeric naphthylphenyl ketylolithiums, entries 11 and 13 in Table I. It is tempting to associate the small molar shift of 1-naphthylphenyl ketylolithium with perhydrogen interactions, which are not possible in the case of the 2-naphthyl isomer.

(9) Herold, B. J.; Correia, A. F. N.; Veiga, J. S. *J. Am. Chem. Soc.* **1965**, *87*, 2661. Herold, B. J.; Novais, H. M.; Lazana, M. C. L. R.; Correia, P. *B. Rev. Port. Quim.* **1971**, *13*, 78.

(10) Owen, J.; Thornley, J. H. M. *Rep. Progr. Phys.* **1966**, *29*, 675.

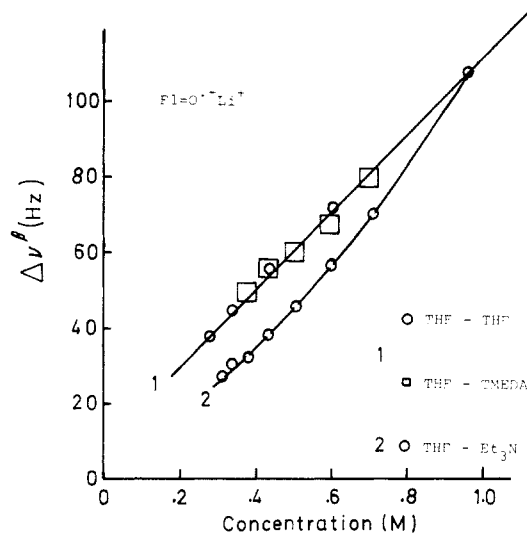
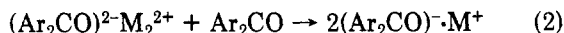


Figure 4. Line 1: shift (induced to β proton band of THF) vs. concentration in THF (circles) and in mixtures of THF and TMEDA (squares). The latter points were obtained by diluting 0.50 mL of 0.96 M lithium fluorenone ketyl in THF with 0.15, 0.30, 0.45, 0.60, and 0.75 mL of TMEDA and recording the shift due to the β protons of THF. Line 2: β proton shift vs. concentration relationship in solution of lithium fluorenone ketyl in mixtures of THF and Et_3N . Points were obtained by diluting 0.50 mL of a 0.96 M solution of lithium fluorenone ketyl in THF with 0.15, 0.30, 0.45, 0.60, 0.75, 0.90, and 1.05 mL of Et_3N .

We have employed two different methods for the preparation of the ketyl anions. The first involved the direct reaction of equivalent quantities of the aromatic ketone and the alkali metal in THF. In the second method, eq 2, the reverse disproportionation reaction was employed.



In the case where the radical anion tends to undergo disproportionation, reaction 2 should yield the equilibrium mixture. In such a case, namely, in a case where the solution contains a considerable amount of dianion, the shift that will be observed will be smaller, because the dianion does not contribute to the shift, due to its diamagnetic nature. Thus, we confirmed that was already known for dilute solutions of ketyl anions, namely, that they do not tend to undergo disproportionation.¹¹ For example, solutions of lithium benzophenone ketyl, prepared by the two methods, gave the $\Delta\nu_m^\alpha$ values of 84 and 85 Hz/mol and $\Delta\nu_m^\beta$ values of 77 and 77 Hz/mol, respectively. Similarly, solutions of potassium benzophenone ketyl, prepared according to the two methods, gave values $\Delta\nu_m^\alpha$ of 129 and 130 Hz/mol and $\Delta\nu_m^\beta$ values of 117 and 116 Hz/mol, respectively; see also relevant entries 5–8, Table I.

We decided to use tetramethylethylenediamine (TMEDA) as a lithium cation complexing agent in order to observe shifts analogous to those reported in ref 8. In Figure 4, line 1 represents the shift induced on the β proton band of THF by lithium fluorenone ketyl in THF (circles) and mixtures of THF–TMEDA (squares). Evidently TMEDA failed to cause any shifts like those reported by de Boer and co-workers.⁸ TMEDA acted simply as a diluent. In Figure 5 lines 1 and 4 represent the shift of the β proton bands of THF vs. concentration relationships of solutions of lithium benzophenone ketyl in pure THF (line 1) and in mixtures of THF and TMEDA (line 4). We notice that in the case of lithium benzophenone ketyl TMEDA causes shifts analogous to those of ref 8. Since there is no obvious

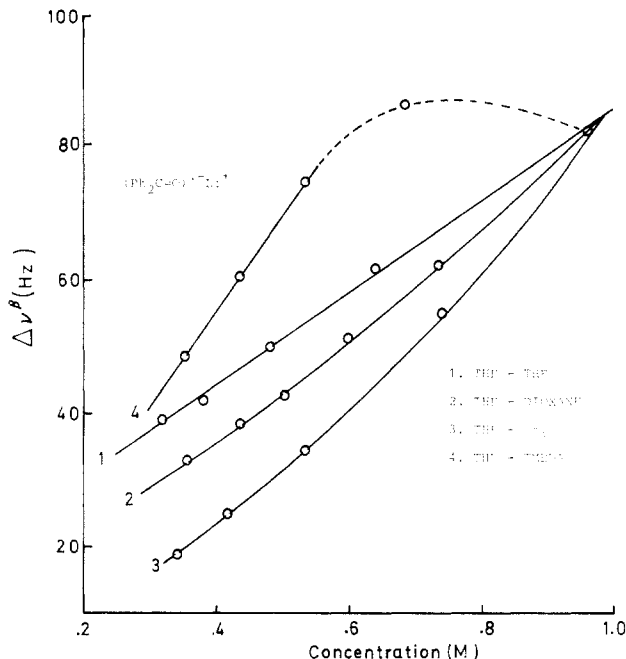


Figure 5. Relationship between β shift of THF and concentration of lithium benzophenone ketyl: line 1, in THF; line 2, in THF–dioxane (points were obtained by diluting 0.50 mL of 0.96 M lithium benzophenone ketyl in THF with 0.15, 0.30, 0.45, 0.60, and 0.80 mL of dioxane); line 3, in THF– Et_3N (points in the curve correspond to dilutions of 0.50 mL of 0.96 M lithium benzophenone ketyl with 0.15, 0.40, 0.65, and 0.90 mL of Et_3N); line 4, in THF–TMEDA (points on line correspond to dilutions of 0.50 mL of 0.96 M lithium benzophenone ketyl with 0.20, 0.40, 0.60, and 0.85 mL of TMEDA).

reason why TMEDA does not complex with lithium cations in lithium fluorenone ketyl solutions, we are forced to conclude that strong cation complexation could be a necessary but not sufficient condition in order to observe “elimination” of the contact shift. This conclusion was further supported by the following experiment. We added 18-crown-6, in excess, to a solution of potassium benzophenone ketyl. Although this crown ether is an effective complexing agent for potassium cation, it actually acted as a diluent. Similarly, with potassium fluorenone ketyl and 18-crown-6 were obtained the same results; namely, no shifts like those of ref 8 were observed. It should be, however, noted that in the latter case the measurements were somewhat ambiguous due to precipitation to a small extent, caused by the crown ether. The results with potassium benzophenone seem to disagree with the picture of the “naked anion” created by complexation of the cation by the crown ether. Again, since there is no obvious reason that the crown ether did not complex the potassium cation, we can exclude the formation of a “naked anion” on the grounds that in such a species there would be no contact interactions between the paramagnetic ion and the solvent molecules, due to the lack of the covalency.¹⁰ There could be, however, a possibility that the “naked anion” can interact with the solvent molecules by some sort of charge-transfer-to-solvent mechanism.¹²

The reason that strong cation complexation may or may not cause shifts of the type reported in ref 8 is not understood. Perhaps this has to do with the ability of the coordinated ligand to undergo a more or less rapid exchange with uncomplexed ligand and/or the solvent molecules.

(11) Reference 3, p 57.

(12) Platzman, R.; Frank, J. In “L. Farkas Memorial Volume”; Research Council: Jerusalem, Israel, Special Publication, 1952; No. 1.

Table II. Effect of Added Cosolvent on the Shift vs. Concentration Relationship for Lithium Benzophenone Ketyl and Lithium Fluorenone Ketyl and THF^a

entry	ketyl	cosolvent-solvent	initial slope ($\Delta\nu^\beta/\Delta c$), Hz/mol	$\Delta(\Delta\nu^\beta/\Delta c)$ $\times 100$	$\Delta\nu_m^\beta$
1	(Ph ₂ C=O) ⁻ ·Li ⁺	THF-THF	69	0	77
2	(Ph ₂ C=O) ⁻ ·Li ⁺	Dioxane-THF	86	25	
3	(Ph ₂ C=O) ⁻ ·Li ⁺	Et ₃ N-THF	124	80	
4	(Fl=O) ⁻ ·Li ⁺	THF-THF	102	0	107
5	(Fl=O) ⁻ ·Li ⁺	Dioxane-THF	113 ^b	11	
6	(Fl=O) ⁻ ·Li ⁺	Et ₃ N-THF	138	35	

^a The data were derived from the relevant curves in Figures 4 and 5. ^b Slope. The relationship between shift and concentration in this case is linear.

We have studied the effect of poorly solvating cosolvents on solvent shifts in solutions of lithium benzophenone and fluorenone ketyls in THF. Line 2, Figure 4, represents the relation between the shift of the β proton band of THF and the concentration of lithium fluorenone ketyl in THF and triethylamine mixtures. It is noted that the relationship is no longer linear, but it exhibits an upwards concavity. This means that the shift drops more rapidly on diluting with triethylamine than on diluting with THF. Even more pronounced is the effect of added dioxane (line 2, Figure 5) to a solution of lithium benzophenone ketyl in THF. Again an upwards concavity is observed, which becomes more evident in line 3, Figure 5, on adding triethylamine to lithium benzophenone ketyl in THF. We interpret this phenomenon as arising from changes in the structure of the ketyls in solution, caused by added cosolvent. It appears reasonable to assume that poorly solvating solvents, such as dioxane and triethylamine, partially destroy the "structure" of the THF solvent, which no longer can stabilize the paramagnetic species of the ketyls. Thus a fraction of the paramagnetic species (P) undergo some transformation to diamagnetic species (D). This process is shown schematically in eq 3. Only spec-



ulations can be made about the structure of the diamagnetic species. The simplest possibilities are the dianion of the ketone, which can result from disproportionation of the radical anion, or a pinacolate dianion resulting from spin pairing.

By measuring the initial slopes of the line 2, Figure 4, and the lines 2 and 3 in Figure 5, one can have, perhaps for the first time, a quantitative expression for the effect of added cosolvent. Table II summarizes these results. In the table are given the ketyl anion, the cosolvent and solvent, the initial slope (or the slope) of the shift vs. concentration relationship with respect to the β proton band of THF, the percent difference of the slopes in pure and the two-component solvent system, and, in the last column, the molar paramagnetic solvent shifts with respect to the β proton band of THF in pure THF. The following conclusions can be drawn from the data in Table II. Dioxane appears to be less effective than triethylamine in bringing about changes in the structure of the ketyl anions in solution. This can become apparent by comparing the $\Delta(\Delta\nu^\beta/\Delta c) \times 100$ values in entries 2 and 3 and 5 and 6. A given cosolvent, e.g., triethylamine, appears to be more structure destructive in the case of lithium benzophenone ketyl than in the case of lithium fluorenone ketyl; compare entries 3 and 6, Table II. Thus lithium fluorenone ketyl appears to be considerably more stable than lithium benzophenone ketyl, with respect to solvent changes. We are tempted then to assume that the $\Delta\nu_m^\beta$ values reflect the stability of the particular radical anion. Since a larger value of $\Delta\nu_m^\beta$ means a greater ionic character in the O-Li



Figure 6. Arrangement for replacing the air inside the NMR tube by argon (see Experimental Section).

bond of Ar₂C-OLi (see previous discussion), we wish to compare these parameters with another parameter which expresses the ability of the respective Ar₂C-OH to dissociate into ions, namely, pK_a values. The $\Delta\nu_m^\beta$ values are 77 and 107 Hz/mol, respectively, for lithium benzophenone ketyl and lithium fluorenone ketyl, whereas the pK_a values of the relevant Ar₂C-OH acids are 9.2 and 6.3,¹³ respectively. We notice that on the basis of either criterion fluorenone ketyl appears to be more ionic.

Experimental Section

A Varian A60A NMR spectrometer was used for the solvent shift measurements. A mixture of ethylene chloride (40% v/v), *tert*-butyl bromide (40% v/v), and benzene (20% v/v) was sealed in thin-walled capillaries and served as a dual external marker. The role of added benzene was to cause an upfield shift of the ethylene chloride and *tert*-butyl bromide resonances and bring them to within -4.5 ± 0.5 Hz from the corresponding bands of THF, due to the α and β protons, respectively. These two bands of THF served as internal references. Figure 6 shows the arrangement for replacing the air inside the NMR tube by pure argon. The capillary with the external markers was placed in an ordinary NMR tube, which then was stoppered with a rubber septum. The septum was secured in place with parafilm, pierced with a fine hypodermic needle, and placed in a larger tube, which was part of a vacuum-argon line. Several cycles of vacuum-argon secured the complete removal of the air and its replacement by argon. Finally, the system was filled with argon to a slight positive pressure, the large tube was disconnected from the vacuum line, and the needle was removed from the septum. Solutions of ketyl anions were standardized by standard acid titration of hydrolyzed aliquots. This agreed with the double titration, using ethylene bromide,^{2b} provided that the THF is absolute and the metal free of surface oxides. The standard

solutions of the ketyl anions were handled with microsyringes lubricated with paraffin oil and previously flashed with argon and the ketyl solution. The difficulty of reading accurately the volume of dark solutions was overcome by measuring the length of the plunger of the syringe with a pair of calipers, preset when the syringe was empty.

The shift vs. concentration relationships have been determined as follows. An aliquot of the ketyl solution, 0.50 mL, was added to the NMR tube containing the capillary with the external markers and having been filled with argon. The resonances due to the markers and the two THF bands were recorded at 35 ± 1 °C. In order to observe solvent resonances in concentrated solutions it was necessary to apply very fast spinning to the sample, otherwise the signals were too broad to be seen. Dilution of the sample with argon-saturated solvent (or cosolvent), by adding 100-300 μ L at a time, and recording the respective shift gave the data points from which the curve shift vs. concentration could be constructed. Molar paramagnetic solvent shifts were calculated by analytical extrapolation, using the shift vs. concentration linear regression equations. These equations had a correlation coefficient better than 0.998. The reported $\Delta\nu_m^\alpha$ and $\Delta\nu_m^\beta$ values have been corrected for the difference in the chemical shifts between the external marker and the THF bands. Namely, there was sub-

tracted from the α shift 4.5 Hz and from the β shift 5.0 Hz.

Tetrahydrofuran was purified as described previously.²⁶ Dioxane, triethylamine, and TMEDA were distilled from lithium aluminum hydride under argon shortly before use. Benzophenone and fluorenone were products of Merck, 99% pure, and were used after recrystallization from ethanol. The naphthyl phenyl ketones were prepared from the corresponding naphthyl bromides via naphthyllithium and naphthylphenylcarbinol. Finally the carbinols were oxidized with potassium permanganate in benzene, using tetrabutylammonium bromide as a phase-transfer catalyst.¹⁴ The ketones after two recrystallizations from hexane melted as follows: 1-naphthylphenyl ketone, 74-76 °C (lit.¹⁵ mp 75.5-76 °C); 2-naphthylphenyl ketone, 80-81 °C (lit.¹⁵ mp 82 °C).

Registry No. 1-Naphthyl phenyl ketone, 642-29-5; 2-naphthyl phenyl ketone, 644-13-3; (Ph₂CO)⁻Li⁺, 16592-10-2; (Ph₂CO)⁻K⁺, 4834-86-0; (FIO)⁻Li⁺, 34474-11-8; (FIO)⁻Na⁺, 34474-12-9; (FIO)⁻K⁺, 34474-13-0; (1-C₁₀H₇COPh)⁻Li⁺, 75973-37-0; (1-C₁₀H₇COPh)⁻K⁺, 75975-38-1; (2-C₁₀H₇COPh)⁻Li⁺, 75975-39-2.

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Theoretical Study of the Methylsilyl and Silylmethyl Cations and Anions

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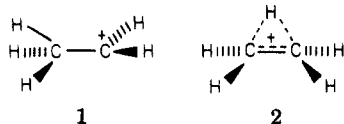
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Ab initio molecular orbital calculations with a double- ζ basis set have been used to optimize geometries for methylsilane, the methylsilyl and silylmethyl anions and cations, and their carbon analogues. Silicon is more effective than carbon at supporting both positive and negative charges. There is a barrier of ~ 60 kcal/mol to the interconversion of the methylsilyl and silylmethyl anions while on the CSiH₅⁺ surface only the methylsilyl cation is at a minimum at the highest level of calculation. In carbenium ions the α -silyl group is stabilizing relative to hydrogen but destabilizing relative to an α -methyl group. In carbanions the α -methyl group is weakly destabilizing while the α -silyl group is strongly stabilizing. An α -methyl group destabilizes both methyl and silyl anions relative to hydrogen but stabilizes both the methyl and silyl cations. Inclusion of polarization functions (d orbitals on Si and C, p orbitals on H) does not significantly change the results.

The structure of the ethyl cation, C₂H₅⁺, has been the subject of considerable experimental^{1,2} and theoretical³⁻⁷ investigation. Ab initio molecular orbital calculations with small basis sets predict the ion to have the classical primary carbenium structure 1, while inclusion of d functions



on the carbon atoms results in the nonclassical bridged structure 2 being the more stable. Inclusion of correlation energy corrections results in a further relative stabilization of 2. Calculations on the vinyl cation, C₂H₃⁺, have produced similar conclusions, with small basis set calculations favoring the classical or open cation and the bridged nonclassical ion becoming progressively more stable as the basis set is improved and correlation effects are included.^{3-5,8}

There have been few reports of calculations on the analogous CSiH₅⁺ and CSiH₃⁺ surfaces,⁹⁻¹² even though CSiH₅⁺ is a well characterized ion in the gas phase.^{13,14}

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