

A ¹³C NMR STUDY OF THE STRUCTURE OF SULFUR-STABILIZED CARBANIONS

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Abstract—The structure of the lithium and potassium salts of ϕSCH_2 , ϕSOCH_2 , $\phi\text{SO}_2\text{CH}_2$, $\phi\text{SO}(\text{NCH}_3)\text{CH}_2$ has been studied by ¹³C NMR in different solvents. The results show that the metalated carbon is nearly pyramidal in and nearly planar in $\phi\text{SOCH}_2^- \text{M}^+$, whatever the solvent are cation are $\phi\text{SO}_2\text{CH}_2^- \phi\text{SCH}_2^- \text{M}^+$ and $\phi\text{SO}(\text{NCH}_3)\text{CH}_2^- \text{M}^+$ are in an intermediate hybridization state, cation and solvent dependent. For the sulfoxide, a four-center chelate is proposed, stable to strong solvating agents and only disrupted by cryptands. It is very likely responsible for the planar configuration of the anionic carbon.

The low temperature study of $\phi\text{SOCH}_2\text{Li}$ shows the existence of aggregates in THF. HMPA or external lithium salts disrupt these associations, giving rise to other species.

The ¹³C NMR parameters of the whole series of sulfur-stabilized carbanions are quite consistent with the data reported for phosphorous and arsenic ylids: the ¹J_{C-H} coupling constants appear to be a good probe of the geometry of the anionic carbon, whereas the chemical shifts are rather insensitive to its hybridization state.

Carbanions α to sulfur are important intermediates in organic synthesis and the high stereoselectivity of many reactions in which they are involved is of great utility. The origin of this stereoselectivity which has already prompted many discussions is still a matter of controversy and the problem of the structure of these carbanions is not yet solved.

The *ab initio* calculations of Wolfe, *et al.*¹ on CH_2SH , CH_2SOH , CH_2SOCH_3 , $\text{CH}_2\text{SO}_2\text{H}$ have shown that the preferred configuration of the carbanion is a pyramidal one in all cases, with the most stable orientation corresponding to the maximum of gauche interactions between lone pairs and polar bonds. In a recent study of CH_2SH and CH_2SCH_3 , Lehn and Wipff reached the same conclusion.²

As many experimental results, especially with sulfoxides are not easily rationalized by this hypothesis, it has been pointed out that the structure of the carbanions may depend on their interaction with the solvent and the cation. This is specially true for sulfoxides and sulfones where the calculated energy differences between the pyramidal and planar configurations are small, *ca.* 2–3 kcal (for the sulfide, Lehn and Wipff found a higher difference, 8–9 kcal). It is clear that experimental structural information is of the greatest interest. A few isolated NMR data have already been published,³ but the need for a more systematic study still remains. In a preliminary note, we have given some ¹³C NMR results concerning a few α lithiosulfoxides and sulfones⁴ in THF. In this paper we present a complete ¹³C NMR study which was carried out on a single family of compounds, derived from phenylmethylsulfide. We have first investigated the influence of the oxidation state at sulfur (sulfide, sulfoxide, sulfone, sulfoximine) on the structure of the corresponding carbanions and for each of them, the variations brought by a change of cation and solvent or the use of cryptand.

In a second part, we have tried, by a low temperature study on ¹³C enriched compounds, to get some information about the nature of the associations in solution (aggregates, solvates, ...).

¹³C NMR has already been largely used for studying the structure of carbanions in several series, alkyl lithium,⁵ arylmethylalkali metals,⁶ enolates.⁷ Ylids,⁸ although neutral, are also included in this discussion.

Of course, the interpretations are not always straightforward since the rationalization of coupling constants and chemical shift values of charged species raises many problems. However, from the existing experimental data, some empirical conclusions can be drawn. If the discussion of small variations must be considered with suspicion, the qualitative interpretation of large effects is possible.

Before discussing our own results, we will analyse briefly the existing data we are using in the discussion and try to evaluate the type of approximations which are made.[†]

If we consider only the "carbanions" formed from an sp³ carbon, we can distinguish three types of compounds:[‡]

(a) the alkylolithiums where the carbon remains pyramidal, (b) the arylalkylolithium, where a rehybridization of the carbon is taking place, with a p,p conjugation and (c) the heteroatoms (P, As, S) stabilized carbanions, where the mechanism of charge stabilization is still under discussion.

1 Discussion of ¹J_{C-H} of the anionic carbon

The most generally used expression of ¹J_{C-H}, in the molecular orbital formalism, is given in eqn (1):

$$^1J_{\text{C-H}} = \frac{4h}{9\Delta E} \gamma_{\text{C}} \gamma_{\text{H}} s_{\text{C}}^2 s_{\text{H}}^2 p^2 s_{\text{C}} s_{\text{H}} \quad (1)$$

$p^2 s_{\text{C}} s_{\text{H}}$, assimilated to the σ bond order between the s orbitals of C and H depends on the hybridization state of the carbon. It increases with the s character of this carbon. $s_{\text{C}}^2 s_{\text{H}}^2$, correlated with the spin density in the s orbitals of both nuclei decreases when the charge is increased. ΔE , the mean excitation energy of the molecule, is often difficult to evaluate.

(a) Methylolithium which was extensively studied by Waack *et al.*^{5a} is a good example of the first group. Its coupling constant is much smaller than that of methane ($\Delta^1J_{\text{C-H}} = -27$ Hz). This is attributed mainly to the

[†]We discuss only representative examples; a complete review of all the data is beyond our purpose.

[‡]The enolates will not be considered here.

charge effect.† The ΔE variation is generally neglected. This seems justified since there is a rough correlation in substituted methanes, including MeLi, between $^1J_{C-H}$ and the substituent electronegativity,⁹ which means that the variation of ΔE is either small or directly related to the electronegativity.

(b) A representative of the second group is diphenyl methyl lithium the metalated carbon of which must be very close to sp^2 . In this case, $^1J_{C-H}$ is increased of +15 Hz.^{6a} This is largely due to the rehybridization of the carbon (increased s character in the C-H bond) and to a decrease of ΔE due to the p-p conjugation. The charge effect is more complex to discuss.¹² If the charge is mainly concentrated in a p orbital, with a nodal plane at the nucleus, it should not affect the term $s_C^2s_H^2$, but it contributes together with the rehybridization to the variation of ΔE .‡

(c) The only available experimental data concerning the third group concern the ylids of phosphorous and arsenic. For the P ylids, a high increase of $^1J_{C-H}$ is observed. In $(CH_3)_3P=CH_2$, $^1J_{C-H} = 150$ Hz ($\Delta J = +22$ Hz with respect to the ylid methyle group, or +16 Hz with respect to the starting phosphonium salt).^{6a} An sp^2 hybridization of the ylidic carbon has been deduced from this value,§ resting on the assumption that the hybridization state remains in this case too, the dominant parameter.¶ The validity of this conclusion is strongly supported by the X-ray analysis of several ylids showing a planar carbon.¹⁴

The lithium adduct obtained by addition of LiCl to $Me_3P=CH_2$ shows a smaller coupling constant (133 Hz),^{6d} reasonably attributed to an increased sp^3 character. Likewise, in the complex $(C_6H_{11})_3PCH_2Ni(CO)_3$, whose X-ray structure indicates a distorted tetrahedral arrangement about the complexed ylid carbon, J is only 123 Hz.^{6e}

†In ethyllithium¹⁰ and cyclohexyllithium,¹¹ the metalated carbon has been shown to be pyramidal in the crystal. The hypothesis of an increased s character in the C-Li bond allowing a better overlap in the tetramer, contributing to the decrease of J has been proposed.^{3,2} The X-ray structure of EtLi gives



Li angles of 105 and 108°, but as the accuracy is unknown, it is difficult to evaluate the importance of this hybridization change.

‡The difficulty of interpreting small variations is illustrated by the discussion of the solvent effect on the spectrum of ϕCH_2Li . $^1J_{C-H}$ decreases when the polarity of the solvent decreases.^{6a} This has been attributed to a higher sp^3 character,^{6a} to an increase of ΔE ,¹² or to a greater charge concentration on the carbon when the interaction with the cation is stronger.¹³ The last two hypotheses are certainly not independent since ΔE is influenced by the charge repartition. They are more likely that the first one since the same solvent effect was also noticed with $\phi_2CHLi(Na,K)^{6c}$ where the carbon must remain nearly sp^2 in all conditions. However, the qualitative conclusion that the increase of J is related to the increase of the sp^2 character of the metalated carbon seems quite safe.

§A simultaneous increase of $^1J_{P-C}$ is observed.^{6a}

¶It is reasonable to assume that the charge effect is weak if it is concentrated in a p orbital but the variation of ΔE is very difficult to predict.

Here again, the ΔE variation is neglected.

††The reaction of MeLi on $\phi-S-CH_3$ gives besides the expected α lithio sulfide ca. 10% of the aromatic ring metalation product¹⁸ (This proportion decreases slowly with time). These two species do not interconvert at the NMR time scale and the two spectra can be observed separately.

In the arsenic ylids, J decreases slightly: $\Delta J = -5$ Hz in $\phi_2As=CH_2$ or -3 Hz in $(CH_3)_2As=CH_2$ (with respect to internal Me). This has been interpreted on the above results basis, by a much higher sp^3 character of the anionic carbon.¹³ In this case, no X-ray data are available.

2. Discussion of the chemical shift of the anionic carbon

It is well known that ^{13}C chemical shifts have a very complex origin and the discussion has to be here still more careful and qualitative.

The main contribution to the chemical shift value is the paramagnetic term which depends on the charge at the nucleus, the excitation energy and the π bond order with the neighbouring atoms.¹²

In MeLi^{3,6c} the carbon is shielded of 13 ppm with respect to CH_4 . This is due to the charge effect, the π bond order being zero.¹

In ϕ_2CHLi ,^{6c} the strong deshielding of the metalated carbon (+34,4 ppm) is due to the π bonding with the aromatic ring and to the decrease of ΔE . The charge effect producing a shielding competes with the other two parameters.

In the P ylids, the ylidic carbon is shielded.⁶ Interestingly, the shielding of this carbon is quite similar in As ylids¹⁵ although the corresponding $^1J_{13CH}$ is very different. This suggests that contrary to the case of a p-p conjugation, the chemical shift is rather insensitive to the hybridization state. It has to be noted that the theoretical expression of the paramagnetic term, σ_p ¹² has been established for molecules involving p-p overlap. It is not necessary valid for these ylids where the mechanism of charge stabilization is not clear.

The charge effect would be responsible for the observed shielding and indeed, it has been concluded^{6a} that the charge was concentrated on the C atom.

This discussion can be summarized by the following qualitative conclusions useful for the interpretation of our results: when a carbanion is formed from an sp^3 carbon, an increase of J is necessarily related to a rehybridization of this carbon and a decrease of J implies a charge increase.

The charge increase produces a shielding of the anionic carbon. The chemical shift may be insensitive to the hybridization state if the carbanion is not stabilized by p-p conjugation.

RESULTS AND DISCUSSION

It was necessary, for this study, to prepare solutions of "carbanions" free, as far as possible, of external salts. We have observed that the coupling constants are not affected by the presence of salts, but the chemical shifts may be slightly modified. Differences of ca. 1 ppm have been found at 30° for ϕSO_2CHLi . For the second part of this work (*vide infra*) the control of the salt content was of course crucial.

The lithium derivatives are prepared either with methyl lithium†† or with phenyllithium. Methyl lithium, obtained according to Waack¹⁶ by methyl iodide-butyl lithium exchange in hexane is supposed to contain less than 10% salt.

However, we observed that depending on the butyllithium batch, it may contain more important amounts. So it is better to use phenyllithium prepared by cleavage of diphenyl mercury by lithium metal in ether,¹⁷ which contains, as we have checked, less than 8% of lithium salt (LiOH and LiOEt).

The potassium derivatives of the sulfone and sulfoxide have been synthesized with KH. The sulfide does not react with KH and trimethylsilyl methyl potassium¹⁹ has been used as a base.†

I. Influence of the oxidation state of sulphur on the structure of the carbanions

The experimental results are given in Table 1. If we select in this table an homogeneous series of data concerning the lithium salts in THF/ C_6D_6 , the influence of the oxidation state of sulphur on the structure of the carbanions can be examined.

Two important features are appearing, namely a very large variation of the coupling constants and a remarkable constancy of the chemical shifts, the metalated carbon being always shielded of ca. 10 ppm.

In the α lithio sulfide an important decrease of $^1J_{\text{C-H}}$ (-18 Hz) is found as in MeLi. This allows the conclusion that the carbanion is mainly sp^3 hybridized, the charge effect being responsible for this decrease.‡

On the other hand, in the α lithio sulfoxide a large increase of $^1J_{\text{C-H}}$ (+16.5 Hz) is observed, similar to that found in $\phi\text{-CHLi}$ (+15 Hz)^{6a} or $\text{Me}_3\text{P=CH}_2$ (+22 Hz).^{6a} This means that the carbon has a high sp^2 character. The carbon is probably not completely planar since in other α lithio sulfoxides, higher values of $\Delta^1J_{\text{C-H}}$ have been

observed: +20 Hz in $\phi\text{-CHLiSOCH}_3$,⁴ +23 Hz in $\phi\text{-SO-CHLiCH}_3$.²⁰ These carbanions are probably more planar due to the additional effect of the phenyl group in the first one or to the flattening effect of the methyl (to release the steric interactions) in the second one.

The α lithiosulfone and α lithiosulfoximine both show a very similar pattern, intermediate as far as the ΔJ values are concerned, between the sulfide and sulfoxide. This probably reflects an hybridization state intermediate between sp^2 and sp^3 .

In spite of its very different hybridization state, the anionic carbon in all cases, is highly shielded. The situation is quite analogous to the one discussed above for phosphorous and arsenic ylids. This strengthens very convincingly the hypothesis according to which the chemical shift does not depend on the hybridization state when there is no p.p. conjugation, whatever the charge stabilization mechanism is. The shielding with respect to starting material may be attributed to a charge concentration on the metalated carbon.

Hence, it appears that the agreement between the experimental conclusions and the *ab initio* calculations, while adequate for the sulfide,² is not good for the sulfoxide, the sulfone representing an intermediate situation.¹

We have seen that contrary to the sulfide case, where the energy difference between the pyramidal and planar forms of the carbanion is quite high, the two forms are energetically less separated for the sulfoxide and the sulfone. The interactions with the cation and the solvent may be responsible for the observed disagreement.

The influence of these interactions on the structure and reactivity of several families of carbanions is a well documented topic.^{12,13,21} But the data are completely

†In this case, no metalation of the aromatic ring has been observed.

‡For α -lithiodithiane, we found also a ΔJ value of -15 Hz. In $\phi\text{-CHLiSCH}_3$, $\Delta J = +6$ Hz, instead of +20 Hz in $\phi\text{-CHLiSOCH}_3$.²⁰ This is probably the result of a competition between the sulfide and phenyl groups inducing respectively a pyramidal and planar configuration.

Table 1. δ and $^1J_{\text{C-H}}$ of the anionic carbon and their differences ($\Delta\delta, \Delta J$) with respect to the parent starting compound

	Solvent (b)	T(°C)	$^1J_{\text{C-H}}$	ΔJ	δ	$\Delta\delta$
$\phi\text{-S-}\overset{\omega}{\text{C}}\text{H}_2$	(a) Li ⁺ Toluene		118	-20	4.5	-10.9
	(e) THF	30°C	120	-18	4	-11.9
	THF/HMPA ^(d)		122	-16	4.4	-11.9
	K ⁺ THF	30°C	125	-13	7	-8.4
$\phi\text{-S-}\overset{\omega}{\text{C}}\text{H}_2$	Li ⁺ Toluene		153	+14	33.2	-12.2
	(f) THF	30°C	155.5	+16.5	33.5	-11.9
	THF/HMPA ^(d)		155.5	+16.5	38.15	-7.25
	THF/Crown 12-4		155	+16	34	-11.4
$\phi\text{-S-}\overset{\omega}{\text{C}}\text{H}_2$ O	THF	30°C	157	+18	36.4	-9
	K ⁺ THF/2.2.2 ^(c)	-60°C	146	+7	39.8	-2.4
$\phi\text{-S-}\overset{\omega}{\text{C}}\text{H}_2$ O	Li ⁺ Toluene		132	-6	35.4	-9
	(e) THF	30°C	139	0	35.4	-9
	THF/HMPA ^(d)		140	+1	35.9	-8.5
$\phi\text{-S-}\overset{\omega}{\text{C}}\text{H}_2$ O	THF		144	+5	35.9	-8.5
	K ⁺ THF/2.2.2 ^(c)	30°C	149	+10	37	-7.4
$\phi\text{-S-}\overset{\omega}{\text{C}}\text{H}_2$ O N-CH ₃	Li ⁺ THF	30°C	137	-2	33.8	-10.8
	(e)					

(a) 90% enriched in ^{13}C . (b) 1M solution in a 1/3 benzene-solvent mixture. (c) addition of 1 eq of cryptand (2.2.2). (d) addition of 1.4 eq HMPA. (e) addition of 2 eq HMPA. (f) prepared with CH_3Li . δ in ppm from TMS using THF (C_6 , 68.1 ppm/TMF C_6 , 26 ppm/TMS) as an internal standard. Accuracy: ± 0.2 ppm in the absence of external lithium salts. J: ± 1 Hz.

lacking for the sulfur-stabilized anions we are discussing here. Independently of the problem of theoretical calculations, it was interesting to investigate this point.

Influence of the associated cation and of the solvent

The lithium salts were studied in solvents of increasing polarity: $C_6H_5CH_3$; THF- C_6D_6 ; THF- C_6D_6 -HMPA and the potassium salts in THF- C_6D_6 . The influence of added cryptand [2.2.2] to the latter was also examined. The results are given in Table 1.

With the sulfide, the variations of $^1J_{C-H}$ are small, the extreme values, between the Li^+ salt in toluene and the K^+ salt in THF, differing only of 7 Hz.

With the sulfone, the trend is the same, but the variation is more pronounced, the extreme values under the above set of conditions reaching 12 Hz. When cryptand [2.2.2] is added to the K^+ salt, $^1J_{C-H}$ is further increased of 5 Hz.[†]

With the sulfoxide, the situation is quite different. The influence of a change of solvent and cation is very weak, only 4 Hz between the Li^+ salt in toluene and the K^+ salt in THF. But when cryptand [2.2.2] is added to the K^+ salt, a large decrease of J is observed.[†]

Hence, the variation of $^1J_{C-H}$ produced by the cryptation of the cation is in opposite directions for the sulfoxide and the sulfone.[‡]

It has to be pointed out that the $\Delta\delta$ value vary only weakly through the whole set of conditions.

We propose the following interpretation. The variations of $^1J_{C-H}$ brought by modification of the anion-cation interaction may be due either to an hybridization change or to a charge variation. We think that the first factor is the predominant one. If the charge was the determining parameter, it would be difficult to explain why in the cryptated species, $^1J_{C-H}$ varies in opposite directions for the sulfoxide and the sulfone. Moreover, if we assume that the chemical shift of the metalated carbon is charge-sensitive, the relative constancy of the $\Delta\delta$ values, reveals small charge variations.[§]

On the other hand, the hypothesis of an hybridization change is quite consistent. The increase of J , for the sulfide and the sulfone, when the solvent polarity increases or when Li^+ is replaced by K^+ , that is when the anion-cation interaction becomes looser,[¶] may be due to a flattening of the anionic carbon (increased s character in the CH bond). In the sulfide, it remains strongly pyramidal (high negative ΔJ values). In the sulfone, the

high positive ΔJ value in the cryptated species (+10 Hz) must be due to a rehybridization, with a high sp^2 character.

In the sulfoxide, the anionic carbon is nearly planar whatever the solvent and the cation are. The important finding that J decreases in the cryptated potassium salt that is, that it becomes much more pyramidal, indicates that the planar configuration is stabilized by the interaction with the cation. It is reasonable to assume a chelated structure (Fig. 1) which is possible because of the high charge density beared by the oxygen.^{22,23} This internal chelate must be very strong even with K^+ . It is not destroyed by a polar solvent like HMPA or a crown ether, as shown by the constancy of $^1J_{C-H}$ values. Only a very powerful chelating agent such as a cryptand is able to disrupt it.

If the planar configuration of the anionic carbon in α metalated sulfoxides is mainly induced by their chelated structure, the difference with α metalated sulfones is not unexpected: the S \rightarrow O bond in sulfones being much less polar,^{22,23} such a chelation is not possible or much weaker.

It is interesting to point out that according to the ΔJ values, the geometry of the carbanions in the cryptated species, which may be considered as a good approximation for the free ions, is quite similar for the sulfoxide and the sulfone, probably intermediate between sp^2 and sp^3 .

It has also to be noticed that on all the spectra described in Table 1, no appreciable charge delocalization in the aromatic ring has been observed (estimated from the para carbon shielding).^{¶¶}

II. Nature of the species in solution

It is well known^{16,24,25} that in solution alkyllithium forms stable aggregates, with a high covalent character. These have been studied by several techniques, including NMR. For instance, the low temperature 7Li ¹⁶ spectrum of a mixture $^{12}MeLi$ and $^{13}MeLi$ demonstrated, through the C-Li coupling pattern, its tetrameric structure, and the slow exchange with external lithium salts or another alkyllithium, with formation of mixed aggregates have been observed. The ^{13}C - 7Li coupling has also been detected on the ^{13}C spectrum of $tBuLi$.^{5b} In a recent very thorough 1H NMR study of racemic 2-methylbutyllithium,²⁶ the rate of interaggregate exchange of RLi moieties could be calculated, by line-shape analysis. On the other hand, more ionic compounds like benzylic or allylic lithium compounds exist as solvated ion pairs and no C-Li couplings have been detected by NMR.^{6a,b}

Nothing is known concerning the heteroatom stabilized

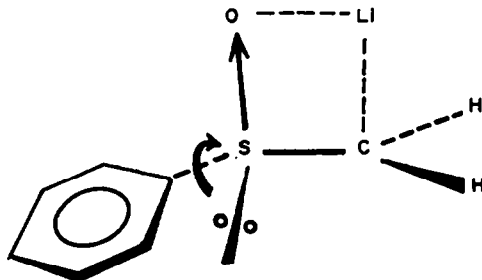


Fig. 1.

[†]In the presence of cryptand, a single signal is observed for the metalated carbon, as well for $\phi SOCH_2K$ as for ϕSO_2CH_2K . We do not know if it represents a single cryptated species or a fast equilibrium, with an unknown constant, between the cryptated and non-cryptated species. Hence, the observed Δ^1J_{C-H} values are minimal values.

[‡]It was not possible to record the spectrum of ϕSCH_2K in the presence of cryptand [2.2.2]. The cryptated salt is a very reactive species which cleaves instantaneously the tetrahydrofuranne, to give the starting sulfide.

[§]The greatest variation is found in the cryptated α potassio sulfoxide. However, it is not the shielding expected for a charge increase, but a deshielding. We do not attempt to interpret it.

[¶]In the absence of data on the nature of ion pairs in this type of compounds, it was difficult to predict how the interaction varies by changing Li^+ for K^+ . The fact that J increases, as in polar solvents, shows that it is indeed looser.

^{¶¶}For the sulfone, the aromatic carbons have not been studied. Because of the insolubility of the salts only the metalated carbon has been observed on ^{13}C enriched samples.

carbanions and it would be interesting for the understanding of their reactivity to get information on this point. It was useful to check if the values of J and δ reported in Table 1, obtained at 30° and necessarily averaged, depend on the temperature, that is on the association and solvation state.

That is why we have carried out a low temperature study with compounds 90% enriched in ^{13}C .

α -Lithiosulfoxide. The ^1H decoupled spectra are shown in Fig. 2. With the THF/ C_6D_6 solution of the α lithiosulfoxide, the single line observed at 30° gives a broad massif A where several lines can be detected, by lowering the temperature (curve a). This proves that several species are present in the solution, very likely diastereomeric or polymeric aggregates.[†]

Addition of increasing amounts of HMPA produces a progressive deshielding and sharpening of the peak. With only 0.25 eq., a single broad line is obtained. With 2 eq. the peak corresponds to (H) and no change is observed by further addition.

Addition of increasing amounts of LiBr (or Li I, LiOH \ddagger) to the THF/ C_6D_6 solution results in a decrease of the high field broad resonance (A) and another species (S), in slow exchange with (A), appears. These signals coalesce by increasing the temperature. (S) must represent a very stable association for its concentration is appreciable after addition of a small amount of salt (curve b). It is the only species when 1–1.5 eq. are added.

Compared to (A), signal (S) is very sharp. It probably corresponds to a monomeric structure $\phi\text{SOCH}_2\text{Li}$ (LiBr), more likely involving a $\text{S}\rightarrow\text{O}\dots\text{LiBr}$ interaction. \S

Addition of 0.3 eq. of HMPA to a solution containing solely (S) results only in a slight deshielding. In (S), LiBr is probably coordinated to $\text{S}\rightarrow\text{O}$ and addition of small

amounts of HMPA brings only and additional solvation of Li^+ , without breaking the $\text{S}\rightarrow\text{O}$, Li^+ association.

On the other hand, if 0.3 eq. of LiBr are added to a solution containing (H) as the single species, (S) appears in slow exchange with (H) (curve c). It may be assumed that in (H), HMPA solvates Li^+ and that LiBr can still associate to $\text{S}\rightarrow\text{O}$ to form HMPA solvated (S).

The ^1H coupled spectra of all these species have been recorded and the $^1J_{\text{C-H}}$ are always the same, within the accuracy of the measurements (± 1 Hz). The chemical shift variations which appear on Fig. 1 are also small. The extreme values differing of only 3.9 ppm. As small variations of δ were not taken in account in the above discussion, we can conclude that the data of Table 1 concern really the monomer structure and are not affected by the presence of aggregates.

The stability of aggregates in organolithium compounds seems to require strong C–Li interactions (alkyllithium are more aggregated than arylmethyl-lithium) and a concomitant C–Li coupling is generally found.^{5a,b,c} It is interesting to point out that in $\phi\text{SOCH}_2\text{Li}$, there is no C–Li coupling although aggregates are present.

This is consistent with the four-center chelated structure we propose (Fig. 1) where the Li cation is tightly bound, but where the C–Li bond can be loose enough to prevent the coupling.

α -Lithiosulfide and sulfone. With these two derivatives, a temperature decrease (until -60°) produces a broadening of the $-\text{CH}_2\text{Li}$ signal. The absence of decoalescence may be due to a smaller chemical shift difference between the different species, compared to the sulfoxide case. It more probably reflects the greater mobility of the lithium cation.

The explanation should be provided by the ^7Li study we are undertaking.

CONCLUSION

In this study, we have brought some experimental evidence on the structure of sulfur-stabilized carbanions. We have shown that the metalated carbon is nearly pyramidal in $\phi\text{SCH}_2\text{M}^+$ and nearly planar in $\phi\text{SOCH}_2\text{M}^+$, whatever the cation and the solvent are $\phi\text{SO}_2\text{CH}_2\text{M}^+$ and $\phi\text{SO}(\text{NCH}_3)\text{CH}_2\text{M}^+$ are in an intermediate hybridization state, cation and solvent dependent. For the sulfoxide, a four-center chelate has been proposed, stable to strong solvating agents and only disrupted by cryptands. This chelate is very likely responsible for the planar configuration of the anionic carbon. Other NMR results which are not discussed here^{3d,4,20,27} show that these conclusions are probably quite general for non benzylic or allylic carbanions. For these, the conjugation increases the planar character.

The very self-consistent set of results we have obtained bring new useful data for the empirical discussion of the ^{13}C NMR of heteroatom-stabilized carbanions. The similarity with the behaviour of P and As ylids is particularly interesting. $^1J_{\text{C-H}}$ appears to be a good probe of the geometry of the anionic carbon. But contrary to the case of carbanions stabilized by p-p overlap, the chemical shift is rather insensitive to the hybridization state.

The low temperature study of $\phi\text{SOCH}_2\text{Li}$ has shown the existence of aggregates in THF. HMPA or external lithium salts disrupt these associations giving rise to other species. In a forthcoming paper²⁷ we will show how these results contribute to the rationalization of the

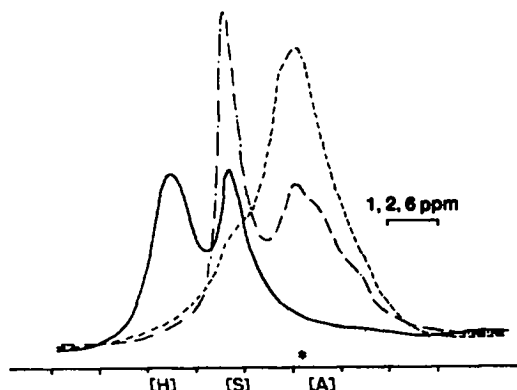


Fig. 2. ^1H decoupled spectrum of the metalated carbon in a 90% ^{13}C enriched sample of $\phi\text{SO}^{13}\text{CH}_2\text{Li}$ at -60°C ($\pm 5^\circ\text{C}$). *HMPA signal, omitted on the figure. — (a) 1 M solution in THF, C_6D_6 3/1 containing 0.1 e.g. of LiOH; ---- (b) Addition of 0.35 eq. of LiBr to solution (a); — (c) Addition of eq. HMPA and 0.3 eq. LiBr to solution (a).

[†]The aggregation forces may be either lithium multicenter bonds, as in the alkyllithium³ or intermolecular $\text{S}\rightarrow\text{O}\dots\text{Li}^+$ interactions. It is difficult to make a comparison with the results concerning alkyllithium where aggregates were essentially studied by ^7Li NMR.

[‡]With LiClO_4 , higher amounts are necessary to produce the same effect.

[§]A very symmetrical structure, or an exchange faster than in (A), could also be invoked, but they are less probable.

stereochemistry of the reactions in which these intermediates are involved.

EXPERIMENTAL

NMR spectra were recorded on a Varian CFT-20 spectrometer. Glc were performed on a Girdel 3000 instrument.

Reagents. Hexane was dried over Na. The other solvents were distilled over sodium benzophenone ketyl, just before use. MeLi was obtained from BuLi and MeI.¹⁶ ϕ Li was prepared¹⁷ by reaction of Li metal on ϕ_2 Hg in ether.

Three titrations have been used. The organolithium was determined by titration with *s*-BuOH in the presence of *o*-phenantroline.²⁸ The total alkalinity by acidimetry and the total amount of Li by flame spectrophotometry (UNICAM SP90A).

Preparation of the lithio derivatives. They were generated in the NMR tube stopped with a rubber septum. 10^{-3} Mole of starting compound dissolved in 250 μ l THF was introduced through a syringe under Argon, at -78° . 1.1 eq. of a THF soln of MeLi or ϕ Li was then added. Then, the temp was slowly raised to room temp. With MeLi the reaction was followed by CH₄ evolution.

The soln was then either concentrated under vacuum or diluted with THF (depending on the titre of the base soln) to an approximate volume of 750 μ l. Then, 250 μ l benzene was added.

Preparation of the potassio derivatives

With KH, ca. 1.5 eq of an homogenized 50% suspension of oily KH was introduced under argon in a centrifuge tube and washed 3 times with 2.5 ml hexane. 1 eq. of sulfoxide or sulfone dissolved in 750 μ l THF was then added. With the sulfone, the reaction was rapid at room temp. With the sulfoxide, it was necessary to warm ($40-45^\circ$) for 1 hr (the reaction was followed by NMR). With the sulfide, no trace of carbanion was detected after 48 hr at 45° .

The soln was centrifuged and the supernatant liquid was transferred by means of a syringe to the NMR tube.

With Me₂Si-CH₂K, ca. 1.2 eq. of Me₂Si-CH₂-Hg-CH₂SiMe₂, prepared¹⁹ from Me₂Si-CH₂Cl (Fluka), was introduced under argon to a centrifuge tube containing ca. 20 m^o K previously washed 3 times with 2.5 ml hexane. The tube was shaken vigorously with a Wortex until a black amalgam was obtained. This amalgam was washed with hexane. The washing solvent was checked by vpc (1/8 in. \times 5 ft. 10% SE-30 on 80/100 Mesh Chromosorb WHMDS column at 80°) until all the hexane soluble (Me₂Si-CH₂)₂Hg had reacted. The neat sulfide was then added and the tube stirred again, until a dry powder was obtained. 750 μ l of THF was introduced at -78° . After warming at room temp, the tube was centrifuged and the soln introduced in the NMR tube.

Quenching with methyl iodide. After the spectra had been recorded, the tube content was alkylated with Me₃I. The recovered product (85-90% yield) was analyzed by NMR showing quantitative methylation.

With the sulfide, a mixture of phenylethyl sulfoxide with variable amounts of *o*-methylphenyl methyl sulfide was formed.

REFERENCES

- S. Wolfe, A. Rauk and I. G. Csizmadia, *J. Am. Chem. Soc.* **91**, 1567 (1969); S. Wolfe, A. Rauk and I. G. Csizmadia, *Ibid.* **89**, 5710 (1967); S. Wolfe, A. Rauk, L. M. Tel and I. G. Csizmadia, *Chem. Comm.* **96** (1970); A. Rauk, S. Wolfe and I. G. Csizmadia, *Can. J. Chem.* **47**, 113 (1969).
- J. M. Lehn and G. Wipff, *J. Am. Chem. Soc.* **98**, 7498 (1976).
- H. Kloosterziel, *Chem. Comm.* 1330 (1968); ^bS. Bradamante, F. Gianni and G. A. Pagani, *Ibid.* 478 (1976); ^cE. L. Eliel, *Tetrahedron* **30**, 1503 (1974); ^dR. Lett and A. Marquet, *Tetrahedron Letters* 1579 (1975).
- R. Lett, G. Chassaing and A. Marquet, *J. Organometal. Chem.* **111**, C17 (1976).
- L. D. McKeever, R. Waack, M. A. Doran and E. B. Baker, *J. Am. Chem. Soc.* **91**, 1057 (1969); ^bL. D. McKeever and R. Waack, *Chem. Comm.* 750 (1969); ^cS. Bywater, P. Lachance and D. J. Worsfold, *J. Phys. Chem.* **79**, 2148 (1975) and refs cited.
- R. Waack, M. A. Doran, E. B. Baker and G. A. Olah, *J. Am. Chem. Soc.* **88**, 1272 (1966); ^bL. D. McKeever and R. Waack, *J. Organometal. Chem.* **28**, 145 (1971); ^cR. Waack, L. D. McKeever and M. A. Doran, *Chem. Comm.* 117 (1969); ^dJ. P. C. M. van Dongen, H. W. D. van Dijkman and M. J. A. de Bie, *Rec. Trav. Chim. Pays-Bas* **93**, 29 (1974); ^eK. Takahashi, Y. Kondo and R. Asami, *Org. Magn. Resonance* **6**, 580 (1974); ^fD. H. O'Brien, C. R. Russell, A. J. Hart, *J. Am. Chem. Soc.* **98**, 7427 (1976); ^gD. H. O'Brien, A. J. Hart, C. R. Russell, *Ibid.* **97**, 4410 (1975).
- H. O. House, A. V. Prabha and W. V. Phillips, *J. Org. Chem.* **41**, 1209 (1976); R. Meyer, L. Gorrichon and P. Maroni, *J. Organometal. Chem.* **129**, C7 (1977).
- K. A. O. Starzewski and M. Feigl, *Ibid.* **93**, C20 (1975); ^bH. Schmidbaur and W. Tronich, *Chem. Ber.* **101**, 3556 (1968); ^cH. Schmidbaur and W. Tronich, *Ibid.* **101**, 595 (1968); ^dT. A. Albright and E. E. Schweizer, *J. Org. Chem.* **41**, 1168 (1976); ^eF. Heydenreich, A. Molibach, G. Wülke, H. Dreeskamp, E. G. Hoffmann, G. Schroth, K. Seevogel and W. Stempf, *Isr. J. Chem.* **10**, 293 (1972); ^fH. Schmidbaur, W. Richter, W. Wolf and F. H. Köhler, *Chem. Ber.* **108**, 2649 (1975); ^gH. Schmidbaur, W. Buchner and D. Scheutzw, *Ibid.* **106**, 1251 (1973); ^hT. Bottin-Strzalko, J. Seyden-Penne and M. P. Simmonin, *Chem. Comm.* 905 (1976).
- N. A. Werstiuk, R. Taillefer, R. A. Bell and B. A. Soyer, *Can. J. Chem.* **51**, 3010 (1973); A. W. Douglas, *J. Chem. Phys.* **45**, 3465 (1966).
- Von H. Dietrich, *Acta Cryst.* **16**, 681 (1963).
- R. Zerger, W. Rhine and G. Stucky, *J. Am. Chem. Soc.* **96**, 6048 (1974).
- J. B. Stothers, *Carbon-13 NMR spectroscopy* (Edited by A. T. Blomquist and H. Wasserman), Academic Press, New York (1972).
- J. R. Murdoch and A. Streitwieser, *Intra-Sci. Chem. Rept.* **7**, 45 (1973).
- J. C. Bart, *J. Chem. Soc. (B)*, 350 (1969); and refs cited.
- Y. Yamamoto and H. Schmidbaur, *Chem. Comm.* 668 (1975).
- L. D. McKeever, R. Waack, M. A. Doran, E. B. Baker, *J. Am. Chem. Soc.* **90**, 3244 (1968).
- G. Wittig, F. J. Meyer and G. Lange, *Liebigs Ann.* **571**, 167 (1951).
- D. A. Shirley and B. J. Reeves, *J. Organometal. Chem.* **16**, 1 (1969).
- A. J. Hart, D. H. O'Brien and C. R. Russell, *Ibid.* **72**, C19 (1974).
- G. Chassaing, unpublished results.
- J. Smid, *Angew. Chem. Internat. Edit.* **11**, 112 (1972).
- H. H. Szmant, *Sulfur in Organic and Inorganic Chemistry* (Edited by A. Senning), Vol 1 p. 142, Decker, New York (1971).
- H. H. Szmant and J. J. Rigau, *J. Org. Chem.* **31**, 2288 (1966).
- L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.* **80**, 2174 (1966).
- R. Waack, M. A. Doran and E. B. Baker, *Chem. Comm.* 1291 (1967).
- G. Fraenkel, W. E. Beckenbaugh and P. P. Yang, *J. Am. Chem. Soc.* **98**, 6878 (1976).
- G. Chassaing, R. Lett and A. Marquet, *Tetrahedron Letters*, 471 (1978).
- S. C. Watson and J. F. Easthan, *J. Organometal. Chem.* **9**, 165 (1967).