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^{1}H AND ^{13}C NMR STUDY OF THE STRUCTURE OF α-LITHIO THIACYLOHEXANE 1-OXIDES

A PLANAR METALLATED CARBON

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Abstract—The lithiospecies deriving from the *cis* and *trans* 4-t-butyl thiacyclohexane 1-oxides are studied by ^{1}H and ^{13}C NMR. Their structure is discussed mainly by examination of H–H and ^{13}C–H coupling constants. Pyramidal α-sulfinyl carbanions are definitely rejected on the basis of these NMR data and half-chair structures with a planar metallated carbon are proposed.

Carbanions α to sulphur are important intermediates in organic synthesis. They have interesting stereochemical properties, shown for example by the highly stereoselective electrophilic substitutions of 2-lithio m-dithianes[1] or α-lithio sulfoxides.[2-4]

In previous work from our group on 4-t-butylthiane oxides, we showed that methylation of the α-lithio carbanions with MeI occurs always *trans* to the S→O bond with a high stereoselectivity (Scheme 1), even in highly crowded compounds.[4]

Theoretical calculations optimizing the geometry of α-sulfinyl carbanions were done by Wolfe *et al.*, according to which the carbanion would be pyramidal, the most stable configuration would have the electron pair *gauche* both to the S→O bond and the lone pair of sulphur.[5] These results were at the origin of the "gauche effect" concept, developed and generalized by Wolfe *et al.*,[6] and raised much experimental work to test their conclusions.

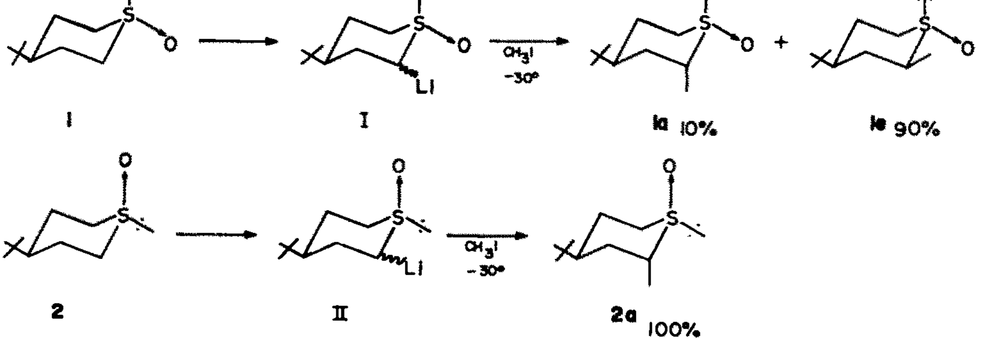
However, the above results[4] and, more generally, many experimental data for α-sulfinyl anions[7-12] cannot be rationalized by the "gauche effect". Therefore, for interpreting our results, we tried to get stereo-chemical informations on the lithio derivatives themselves, by NMR, in the same conditions as those of the electrophilic reactions.

In a preliminary communication, we showed by an ^{1}H NMR study that the possibility of a planar metallated carbon had to be considered for the α lithiosulfoxides (I and II).[13] We wish to present here a more thorough discussion of these results with ^{13}C NMR data which are in good agreement and give convincing evidence of the planar structure of these lithiospecies in solution.

The lithioderivatives of the two 4-t-butylthiacyclohexane 1-oxides were generated in the NMR tube with MeLi (1.1 eq) in THF-d_8 at −78°, under argon. These species, (I and II), are quite stable, even at room temperature for several hours. A particularly striking feature is the fine structure of their ^{1}H spectra (Figs. 1 and 2), a careful integration of which shows that, in each case, a monolithiated species is formed.[a] Consistently, under the conditions described in the Experimental, no trace of starting sulfoxide, or dianion is observed, either by ^{1}H or by ^{13}C NMR. After the spectra were recorded, the lithio derivatives were always reacted with methyl iodide and it was secured that the only reaction occurring was a quantitative methylation.[b]

^{1}*H NMR*

In order to make the analysis of these complex systems easier, I-γd_1 and II-γd_1 were synthesized, since the separation of the {αβ} and {α′β′} moieties greatly



Scheme 1.

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[a] The slight excess of MeLi is observed at highfield.

[b] The lithio derivatives start to give side reactions after 3–4 hr at 30°, particularly if they are generated in the presence of a methyllithium excess.

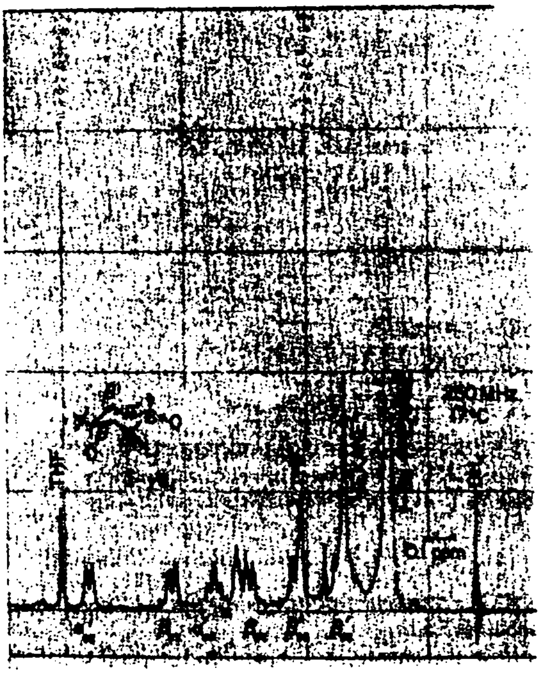


Fig. 1.

simplifies the spectra. I-$\beta\beta'd_4$ and II-$\beta\beta'd_4$ were also prepared to check independently some assignments based on selective ^1H double irradiation. The synthesis of the deuterated compounds is reported in the Experimental.

The assignments are discussed in appendices A and B. The chemical shifts and the coupling constants are given in Tables 1 and 2.

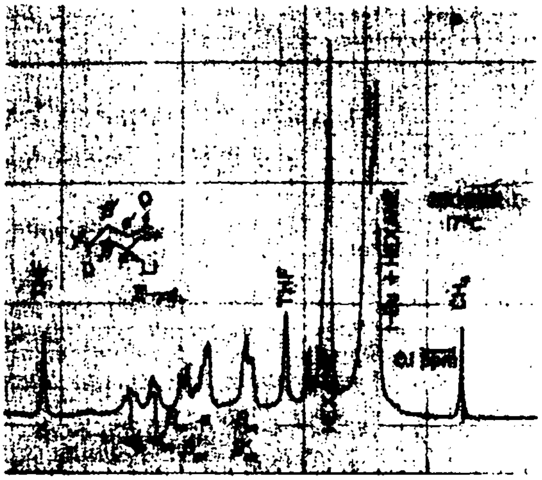


Fig. 2.

DISCUSSION

The most important result is that the HαHβ couplings are of about 5 Hz or less as well in I as in II.

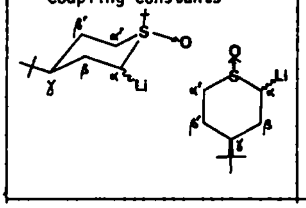
As all the values of the coupling constants between the hydrogens in each moiety, $\{\alpha\beta\gamma\}$ and $\{\alpha'\beta'\gamma\}$, have been determined[c] (Tables 1 and 2), it is possible to discuss the structure and the geometry of the lithio derivatives (I and II), provided that that these values correspond to a unique or a quasi-unique species in an almost completely shifted equilibrium.

In order to examine the possibility of an equilibrium between several species, the spectra were run at variable temperatures, from −40°[d] to +50°. The spectra were also run in different solvents (THF or variable mixtures of THF[e]-1/1 to 1/3 in v/v- with pyridine, benzene, toluene and cyclohexane).

The main result is that no solvent or temperature effect on the magnitude of the coupling constants and only very weak chemical shift variations (less than 0.1 ppm) were observed.

Only a continuous broadening of the multiplets and of the t-Bu signal occurred when the temperature was lowered, with respect to the sharp methane resonance as an internal reference. The broadening of the multiplets

Table 1. ^1H Chemical shifts and coupling constants of 2-lithio 4-t-butylthiacyclohexane *trans* 1-oxide

δ/CH$_4$ int.	α	βax	βeq	α'ax	α'eq	β'ax	β'eq	γ
	1.97	2.50	1.86	2.16	3.19	1.09	1.49	1.36
coupling constants 	βaxβeq = −13.9 Hz αβax = 5.4 Hz αβeq = 4.5 Hz			α'axα'eq = −12.5 Hz* β'axβ'eq = −13.5 Hz α'axβ'ax = 13.0 Hz α'axβ'eq = 3.0-3.5 Hz α'eqβ'ax = 3.5 Hz α'eqβ'eq = 3.0 Hz				βaxγ ~ 12-13 Hz βeqγ ~ 4.5 Hz β'eqγ ~ 3.5-4 Hz β'axγ ~ 12.5 Hz

δ/CH$_4$ int. : tBu 0.73 ; CH$_3$Li (+ 1.98) ; THF (1.44 ; 3.42) ; hexane (0.72 and 1.09) (traces dues to the preparation of CH$_3$Li).

* $^2J_{\alpha'ax\alpha'eq}$ = −12.2 Hz (I-ββ'd$_4$).

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[c] When not determined with precision, due to the complexity of the spectrum (as in II), the order of magnitude of the couplings is however known by comparison with the spectra of the (γ-d_1) and ($\beta\beta'$-d_4) species, and double irradiation experiments (Appendices A and B).

[d] Precipitation occurs at lower temperatures in the described conditions.

[e] A minimal amount of THF is necessary, I and II being not soluble in pure hydrocarbons or aromatic solvents.

and of the t-Bu singlet also increases qualitatively with the polarity of the medium. Very interestingly, this broadening is always larger for the axial sulfoxide (II) than for the equatorial sulfoxide (I), in the same conditions of concentration, solvent and temperature (Figs. 1 and 2).[f] Consistently, whereas no variation at all of δ and J is noticed for I, a weak chemical shift effect (less than 0.1 ppm) is measured for Hα' in II, but with no appreciable variation of the coupling constants at 250 MHz.

The origin of these very weak chemical shifts variations and broadening effects may be attributed to solvation equilibria and (or) dissociation of a polymeric lithio species aggregate, equilibria which might have different positions for I and II.

As no variations of the coupling constants have been observed, we shall discuss the ^{1}H NMR results for I and II in terms of a ***unique or a quasiunique, configurationnally homogeneous lithiospecies,***[g] ***independently*** of the problem of the nature of their solvation state and (or) aggregation that we may take up afterwards.[14,15]

The results may be discussed by postulating either a pyramidal or a planar metallated carbon. In each hypothesis, all the basic conformations have to be examined *a priori* and we shall compare the set of observed vicinal H–H coupling constants with the values expected by a *qualitative* application of the Karplus curve,[16] for the whole cyclic framework.

Hypothesis of a planar metallated carbon[h]

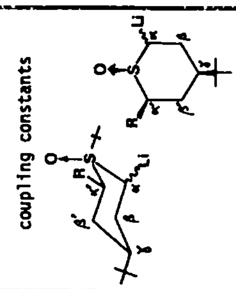
The magnitude of the $\alpha\beta$ couplings excludes the chair with a planar Cα having an equatorial t-Bu, where Hα and Hβ eq are nearly eclipsed since this should result in a large ^{3}J value very different from the coupling between Hα and Hβax which have a dihedral angle of about 120°.

The chairs having an axial t-Bu and all the boat conformations, very unlikely on the basis of the interactions, are rigorously eliminated for the values of the $\alpha\beta$ and $\alpha'\beta'$ couplings.

The two twist conformations of CαCβ' axis and the two half-chairs having a pseudo-axial t-Bu are also excluded since they are incompatible with the magnitudes of the $\alpha'\beta'$, $\beta\gamma$ and $\beta'\gamma$ couplings considered together. A half-chair conformation (Cβ, Cα, S, Cα' coplanar), having a pseudo equatorial t-Bu, can be rejected on the basis of the $\alpha\beta$ couplings because it implies $\alpha\beta$ dihedral angles of about 30° and 80° which should result in very different coupling constants.

All the values are in good agreement with conformations I' and II', where Hα approximately bissects the angle between the β protons and the other dihedral angles are consistent with the $\alpha'\beta'$, $\beta\gamma$ and $\beta'\gamma$ couplings.

Table 2. Chemical shifts and coupling constants of 2-lithio 4-t-butylthiacyclohexane *cis* 1-oxides (II) and (III)

δ/CH_4 int.	α	βax	βeq	α'ax	α'eq	β'ax	β'eq	γ
II : R = H	2.10	2.26	~ 1.76	2.66	2.55	2.12	~ 1.76	1.16
III : R = CH_3	2.32	2.38	1.68 or 1.84	2.64	$CH_3\alpha'$eq:1.16	1.92	1.68 or 1.84	1.12
coupling constants 	βaxβeq = -13.5 Hz αβax = 2-3 Hz αβeq = 5-5.5 Hz			α'axα'eq = - 12.0 Hz* β'axβ'eq = - 13 Hz α'axβ'ax = 12-13 Hz α'axβ'eq = 3 Hz α'eqβ'ax = 3 Hz α'eqβ'eq = 3 Hz				βaxγ ~ 13.5-14 Hz βeqγ ~ .4-5 Hz β'eqγ ~ 4-5 Hz β'axγ ~ large

δ/CH_4 int. tBu : 0.78 (R=H) ; 0.95 (R=CH_3)

* $^2J_{\alpha'_{ax}\alpha'_{eq}}$ = -12.0 Hz (II - ββ'd_4)

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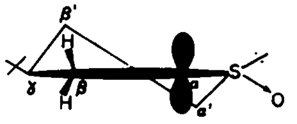
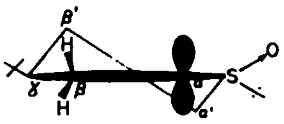
[f] For example, in the same conditions at 30°, if the half-height width is 0.6 Hz for the methane resonance, that of the t-Bu is 2 Hz for I and 15 Hz for II.

[g] ^{13}C NMR of ^{13}Cα, α' enriched I and II shows no variation at all of $^1J_{^{13}C-H}$, each of these lithio derivatives behaving like a single species having always the same geometry of the metallated carbon, from room temperature to −60° in THF–benzene (4/1 in v/v), thus validating the discussion.

[h] Cα being assumed to be planar, two chairs, six boats, two twists (CαCβ' axis) and four half-chairs have to be examined *a priori*. Other basic conformations having 5 atoms coplanar are not considered in this discussion.



I'



II'

Hypothesis of a pyramidal metallated carbon

In this hypothesis, the ring conformation and the orientation of the C–Li bond have both to be determined.

By examination of Dreiding models, the whole set of vicinal couplings determined for the two moieties $\{\alpha\beta\gamma\}$ and $\{\alpha'\beta'\gamma\}$- or, at least, their order of magnitude allow to exclude all the conformations and configurations other than those reported in Fig. 3.[i]

Among the chair conformations, as all the HαHβ couplings are of about 5 Hz or less, as well in I as in II, only structures Ia and IIa are consistent with the data.[j] In order to discuss the remaining boat conformations, it is necessary to consider the fact that the results are quite similar for II and III, as well for the chemical shifts as for the magnitude of all the $\{\alpha\beta\gamma\}$ and $\{\alpha'\beta'\gamma\}$ coupling constants, showing that the lithio species (II and III) have the same structure.

Conformation $\mathrm{III_B}$ would imply a strong 1-2 interaction between eclipsed Me-α' and S→O. Structure $\mathrm{III_{B'}}$, would involve very large interactions between Meα'/CβHβax and Me-α'/*t*-Bu.[k] Therefore conformations $\mathrm{III_B}$ or $\mathrm{III_{B'}}$ should be very highly destabilized and we may exclude these structures for III, and by analogy $\mathrm{II_B}$ and $\mathrm{II_{B'}}$ for II because of the quite similar results between II and III (Table 2).

We think also that structures $\mathrm{I_B}$ and $\mathrm{I_{B'}}$, which cannot be rigorously excluded on the basis of the coupling constants, are made highly improbable by the large steric interactions which would be involved and should be at least as severe, if not more, as those in $\mathrm{II_B}$ and $\mathrm{II_{B'}}$ respectively.

Moreover, a large chemical shift variation should be expected for Hγ in conformations $\mathrm{I_B}$ and $\mathrm{I_{B'}}$, due to a *syn-axial* effect of the S→O bond,[20] in contrast with the observed δHγ which are almost the same as in the starting sulfoxides.[4b]

Therefore the discussion sums up the choice between the half-chair structures (I' and II') in the planar hypothesis and the chair conformations (Ia and IIa) which may represent the structures of the lithio derivatives (I and II) in the pyramidal hypothesis, either as a single species, or in equilibria Ia⇌Ie, IIa⇌IIe highly shifted towards Ia and IIa respectively, if pyramidal inversion of the carbanion occurs.

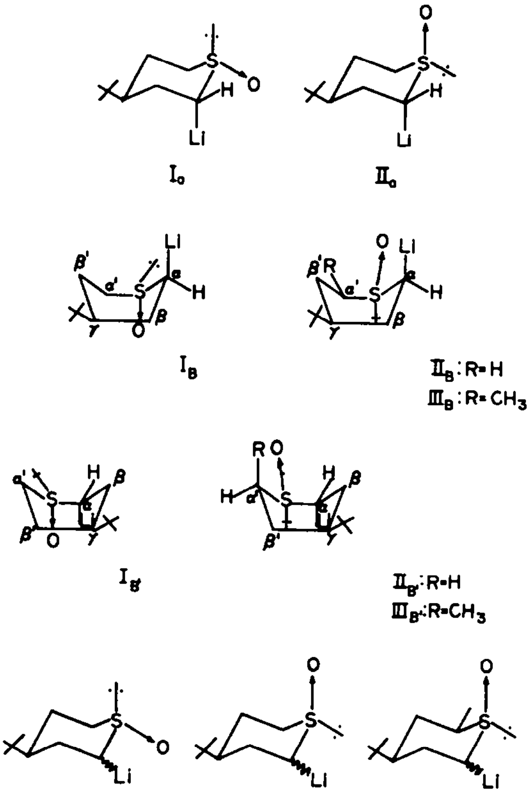
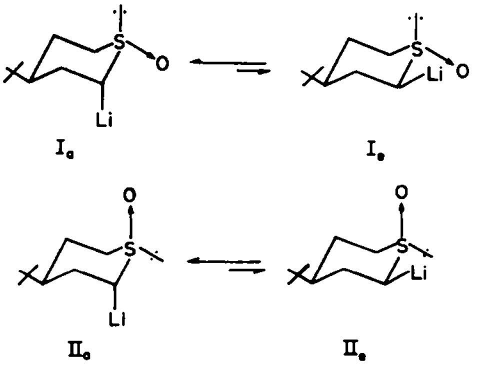


Fig. 3. Possible structures of I and II according to ^{1}H NMR vicinal coupling constants.



Some of the ^{1}H NMR data are however difficult to rationalize with the hypothesis of a pyramidal metallated carbon:

(1) The Hβ are at very similar fields in I and II, while

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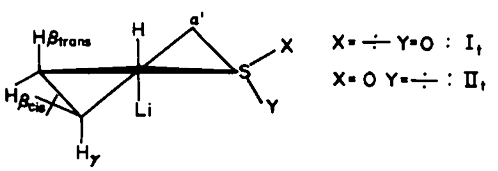
[i] It is worth to note that a twist conformation of αβ' axis (It, IIt) with a pyramidal Cα, which is very close to the half-chairs I' and II' having a planar Cα, can be rigorously eliminated because one large and one medium HβHγ couplings are observed (Tables 1 and 2), whereas a nul or very weak HγHβ *cis* coupling should be expected for a dihedral angle being nearly 90° in contrast with another large HγHβ *trans* constant in an antiperiplanar situation in It and IIt.



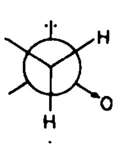
[j] A large coupling HαHβ of about 15 Hz should be observed in an antiperiplanar situation.[17-19]

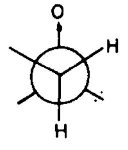
[k] This interaction is well shown by examination of Framework, or better, CPK molecular models.

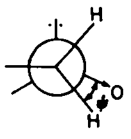
they are very different in the starting sulfoxides, due to the "syn-axial effect".[4b] These striking changes in δ may reflect an important ring deformation.

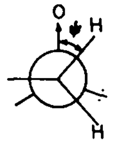
(2) No long-range ^{4}J coupling could be detected at 250 MHz in I[l] where all the hydrogens are well separated, whereas a ^{4}Jαα′ of about 2 Hz is always observed between Hα eq and Hα′ eq in a chair conformation.[21]

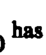
(3) ^{2}Jα′axα′ eq is the same for I and II (12.2 ± 0.2 Hz). This value is consistent with an equatorial S→O bond or any arrangement like i, whereas it should be about 14.5–15 Hz for an axial S→O (as in IIa) or any conformation corresponding to ii.[20]


i

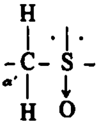

ii


iii


iv

J gem of a methylene α to the S has been shown to be very sensitive to the orientations of the C–H bonds relatively to the sulfinyl group and to be a reliable criterion in conformational analysis of cyclic sulfoxides.[20] Therefore, ***structure IIa is definitely excluded*** on the basis of the observed value of $^2J_{CH_{2\alpha'}}$,[m] which is much too low (12.0 Hz) for an axial type orientation of the S→O bond.

The identical values observed for I and II may reflect nearly same arrangements


$$-\underset{\alpha'\ \ H}{\overset{H}{C}}-\underset{O}{\overset{\cdot\,|\,\cdot}{S}}-$$

and are consistent with the half-chairs I′ and II′.[n] Conformations I′ and II′ are also consistent with the nearly identical chemical shifts of the β hydrogens in I and II because they have symmetrical situations with respect to the sulfinyl group and are relatively far from substituents at sulfur.

^{13}C NMR

In order to gain some more evidence about the hybridization of the metallated carbon, the lithiospecies (I and II) were studied by ^{13}C NMR.

^{13}C NMR has proved to be very successful for arylmethyllithio derivatives[24] and phosphorous ylides.[25] The conclusions of these studies are in very good agreement with X-ray results,[26,27] thus validating the $^1J_{C^{13}-H}$ coupling constant of the metallated carbon as a reliable criterion for the discussion of variations of hybridization.

In contrast, the ^{13}C chemical shifts are too complicated to discuss and there is no simple consistent interpretation of the shieldings experienced by the metallated carbon for the whole set of ^{13}C data on organometallics.

The ^{13}C NMR results for the lithiospecies (I and II), and the initial sulfoxides are reported in Table 3.

Consistently with the absence of significant variations in ^{1}H NMR with the temperature for I and II, no variation of the $^1J_{C_\alpha-H}$ coupling constant and single C_α and $C_{\alpha'}$ resonances were observed for $^{13}C_{\alpha,\alpha'}$ enriched I and II, when lowering the temperature to *ca.* −60°. These results validate the hypothesis of a unique or a quasi-unique lithio species[o] in each case.

$^1J_{C_\alpha H_\alpha}$ *coupling constant*

The results are consistent with those we already reported, in a preliminary communication, for the lithio derivatives of t-butylmethylsulfoxide, benzyl methyl and benzyl t-butylsulfoxides.[29]

$^1J_{C_\alpha H_\alpha}$ is increased by + 19 Hz in I and II, which is more than for t-butylmethylsulfoxide (+ 10 Hz) and nearly the same as for a benzylic lithiated carbon in benzylmethyl (+ 20 Hz) or benzyl t-butyl (+ 23 Hz) sulfoxides.

Whatever the lithio derivative, the ^{1}J coupling is always increased with respect to the initial sulfoxide. As an increase of negative charge on the carbon results in a decrease of the ^{1}J coupling constant, for a given hybridization state, the significant larger values of ^{1}J have to reflect a rehybridization.[p]

The variations are about the same as that observed in trimethylmethylene phosphorane[25] for which the planar configuration of the methylene carbon has been established;[25,27a] these variations are also greater than in diphenylmethyllithium for which all the results are consistent with a nearly sp^2 hybridization state of the benzylic carbon.[24,26]

These results are a strong indication for a planar or a nearly planar C_α and they are in good agreement with the ^{1}H NMR data for I and II.

In I and II, $^1J_{C_{\alpha'}H_{\alpha'}}$ is the same as in the initial sulfoxide, which shows that there is no perturbation and modification of the C–H bonds on that moiety by generating the lithio species on the C_α.

^{13}C *chemical shifts*

The variations of chemical shifts are difficult to discuss like in other organometallics,[30] as we already pointed out for simple sulfoxides and sulfones[29] and has been more thoroughly analyzed recently.[14]

Examination of the ^{13}C chemical shifts shows that the variations with respect to the starting compound[q] are almost negligible for $C_{\alpha'}$ in I, C_α and $C_{\alpha'}$ in II. In contrast, there is a large shielding effect of 12.3 ppm for C_α in I, which is the order of magnitude usually observed for the metallated carbon α to sulfur (–CH$_2$Li or –CHLi–R, R = alkyl).[14,29] Therefore the weak shielding of C_α in II (~ 3.2 ppm) may be the result of opposite effects—metallation and δ variation due to a confor-

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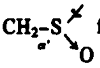
[l] The spectrum of II is too complex, even at 250 MHz, to be able to detect long range couplings.

[m] It is reasonable to assume that no modifications of the bonding properties occur in the CH_2–S fragment by metalation of the C_α carbon on the other moiety, since rigorously the same values of $^1J_{C_{\alpha'}H_{\alpha'}}$ are measured for II and the initial sulfoxide. As a consequence, the value of $^2J_{CH_{2\alpha'}}$ should not be affected by other factors than conformational variations in the lithio species (II).

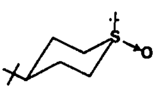
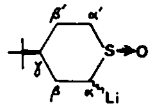
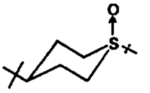
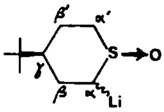
[n] In I′ and II′, the relative orientations correspond to iii and iv respectively (ψ ~ 30°). A coupling of 11.4 Hz has been measured in an orientation corresponding to iii by Fraser and Schuber.[22] Geminated couplings of 12.0 to 13.5 Hz have also been observed in eclipsed situations in the bicyclo[2.2.1] system.[23]

[o] Considered as a monomer, independently from the problem of its possible involvement in a polymeric lithioaggregate for which we have no evidence.

[p] If variations of mean excitation energy are neglected.

[q] The variations of ^{13}C chemical shifts are also weak or negligible for the β, β′ and γ carbons for I and II; they may be due mainly to the change of conformation.

Table 3. ^{13}C Chemical shifts and coupling constants

 †	 ≠ I	 †	 ≠ II
$C\alpha = 53.0 \pm 0.15^*$ ${}^1J_{^{13}C-H} = 139$ Hz	$C\alpha$ $40.7 \pm 0.2^*$ ${}^1J_{^{13}C-H} = 158$ Hz $C\alpha'$ $52.25 \pm 0.95^*$ ${}^1J_{^{13}C-H} = 139$ Hz.	$C\alpha$ $47.07 \pm 0.06^*$ ${}^1J_{^{13}C-H} = 138$ Hz	$C\alpha$ 43.9 ${}^1J_{^{13}C-H} = 157$ Hz $C\alpha'$ $50.6 \pm 0.3^*$ ${}^1J_{^{13}C-H} = 138$ Hz
$C\beta$ 24.24		16.83	
$C\gamma$ 46.35		47.01	
tBu(CH_3) 27.37		27.20	
C 32.09		32.76	

≠ Spectra recorded on enriched $^{13}C\alpha,\alpha'$ sulfoxides.

† These values are in good agreement with those of G.W. BUCHANAN and T. DURST (28).

* A weak chemical shift variation is observed with the concentration or added lithium salts.

mational change, going from the sulfoxide to the α-lithiosulfoxide, that is a chair to a half-chair.[r] The different shieldings experienced by C_α in I and II may be due to the different orientations of the S→O bond in the two compounds,[28] like in the starting sulfoxides (SO eq: C_α 53.0 ppm; SO ax C_α 47.1 ppm).

The very similar values of ^{13}C chemical shifts observed for the homologous carbons in I and II, together with the identical ${}^1J_{C^{13}-H}$ couplings, are in very good agreement with the same basic conformation for the two species such as in I′ and II′.

CONCLUSIONS

The ^1H and ^{13}C NMR results of this study allow us to definitely reject pyramidal species and are consistent with an almost similar structure with a planar metallated carbon for the α-lithiosulfoxides (I and II).

On the basis of the ^1H NMR data, we assign them half-chair conformations I′ and II′ respectively. In a forthcoming full paper, we shall propose an interpretation of the stereoselectivities of the electrophilic substitutions of these planar species (I and II), showing the contribution of the cation to the stereochemistry of the methylation.[15,31]

We want also to point out that our results and conclusions may not be extrapolated to α-sulfinylanions involved in H/D exchanges in protic media.

EXPERIMENTAL

Proton NMR spectra were obtained with a Varian HA-100, locked on internal benzene-h_6 or TMS, operating in the frequency sweep mode and a Cameca 250 MHz (C.W.) in field sweep (HR). Fourier transform ^{13}C spectra were recorded with a Varian CFT-20 (16 K) spectrometer, locked on internal benzene-d_6.

All the lithio derivatives were handled under Argon U; the glassware, NMR tubes and the syringes were dried and flushed with Argon, according to usual techniques.[32] Gas-tight Hamilton syringes were used for the titration of the nBuLi or MeLi solutions, and for the preparation of the NMR samples. NMR tubes were sealed with small rubber septums (5 mm and 10 mm) and parafilm. All the solvents were dried with the usual agents (CaH_2, Na, sodium ketyl). The sulfoxides, which are highly hygroscopic, were thoroughly dried first as a soln over Na_2SO_4 and then by evaporating 3 portions of anhydrous benzene over them under vacuum.

Reagents. MeLi was prepared by the procedure of Waack *et al.* from nBuli/hexane (Merck) and an equimolecular amount of dry MeI.[24b] Precipitated MeLi was centrifuged and washed with anhyd hexane; the white powder was dried by flushing with a stream of Argon.

MeLi–THF-d_8 NMR solns were prepared, starting from 4 mmoles of nBuLi and MeI; 2.0 ml of the THF-d_8 (Merck sealed tubes) were opened and added to the dry white powder, at −78°, and the mixture was allowed to warm up slowly in *ca.* 15 mn to room temp., giving a clear colourless soln.

MeLi was titrated with a standard 0.1 M soln of 2-BuOH in anhyd benzene in the presence of traces of *o*-phenantroline.[33] Quite satisfactory reproducible titrations, with a dispersion of the results inferior to 5%, were secured on 200 μl samples of the soln (usually 1.0–1.5 M), provided that some precautions were taken: oven-dried erlenmeyer of 10 ml containing a magnetic bar and traces of *o*-phenantroline, sealed afterwards

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[r] In ^1H NMR, the large deshielding of one Hβ (ax) in I and of one Hα′ (ax) in II and III have to be noted. These striking changes in δ may reflect an important ring deformation, because near eclipsing angles or eclipsing situations have dramatic, although non predictable effects for hydrogens α to the sulfoxide group.[20] All the other hydrogens of the αβ and α′β′ moieties, Hγ and the t-Bu do not experience important δ changes with respect to the initial sulfoxide. The comparison of the lithio-species with the initial sulfoxide also shows that the shielding experienced by the α proton in I, II, III is much weaker than in simple alkyllithium compounds.[13]

with a rubber septum and parafilm, filled under vacuum and flushed with Argon; gas-tight syringes of 250 μl and 2.0 ml for adding the MeLi soln and the s-BuOH/Benzene solns respectively; benzene distilled over calcium hydride. Total alkalinity was determined with a standard soln HCl 0.1 N with phenolphtaleine as indicator.

NMR samples. For ^{1}H NMR, a 5 mm NMR tube is sealed with a Kontess rubber septum and parafilm. Vacuum is established with a pump through a needle which is removed afterwards. The tube is then filled and flushed with Argon, using 2 needles. 1.1 eq MeLi/THF-d$_8$ (2.2×10^{-4} mole) is introduced with a gas-tight syringe, and then 50 μl of benzene-h$_6$ (or TMS) for locking the spectrometer. The spectrum having been checked, the tube is cooled at −78° and the pressure of argon allowed to reach its equilibrium through a needle. A soln of 2×10^{-4} moles of sulfoxide in the desired volume of co-solvent is added drop by drop with a syringe. Reagents are mixed carefully to prevent any bumping of the solution, methane evolving instantaneously at −78° and being flushed away with a stream of Argon, using two needles. The tube is then allowed to warm up to room temp, degased with argon and centrifuged with the sealed end downwards in a test tube, at 2000–2500 rpm.

The ^{1}H spectra which are shown were obtained in the following conditions, unless otherwise stated: 2×10^{-4} moles sulfoxide; 1.1 eq CH_3Li/THF-d$_8$ (250–300 μl); 200 μl benzene; +30°.

^{13}C NMR spectra were obtained with 8 mm or 10 mm tubes. The standard conditions being: 2 mmoles of sulfoxide (C ~ 0.8 M); 1.1 eq CH_3Li/THF; THF/C_6D_6 = 4/1; room temp.

Specifically labelled 4-t butylthiacyclohexane cis *and* trans *1-oxides*

We used a scheme analogous to that of Purdum and Berlin,[34] starting with diethyl isopropylidene malonate.[35]

Diethyl t-butyl d$_1$-*malonate* prepared in 95% yield by 1–4 addition of MeMgBr in the presence of cuprous iodide,[36] with a high deuterium incorporation (better than 95%) by hydrolysis of the intermediate cuprate adduct with D_2O (99.85%-CEA) (50 ml for 0.05 mole), followed by the usual work up with ammonium chloride.

2-*t-Butyl*-1,3 *d$_4$ propane diol* obtained in 85% yield by reduction with LAD (1.5 eq) (Merck, 98% at least) in anhydrous ether, as described.[34]

2-*t-Butyl*-1,3-*propane diol dimethane sulfonate* prepared in 88% yield with 4 eq methane sulfonyl chloride in anhyd pyridine, the addition being done between −20° and −15°. The mixture is then allowed to warm up slowly and kept at room temp for *ca.* 10 hr. The crude is carefully poured over ice and triturated; the dimesylate (F = 76°) precipitates progressively and is separated by filtration, without any extraction.

3-*t-Butyl*-1,5 ^{13}C *pentane dinitrile.* The dimesylate (1 mmole) was added to 7.5 eq (15 mmoles) K ^{13}CN (85–90% isotopic purity-CEA) in 25 ml anhyd DMSO (dried over CaH_2). The mixture was stirred at 100°C and followed by TLC (benzene/MeOH 9/1). With an efficient stirring, the reaction was finished after 1.5 hr. After cooling, the almost solid residue was dissolved in water and extracted with ether. The combined extracts were thoroughly washed with several portions of water, dried over Na_2SO_4 to afford the dinitrile as an oil, in an almost quantitative yield, which was used without further purification.

3-*t-Butyl*-2,4 *d$_4$ pentanedioic acid.* Dinitrile (1 mmole) was added to 5 ml dimethoxyethane and 10 ml D_2O/NaOD (~ 10 N), prepared from D_2O (99.85%-CEA) and Na. The heterogeneous mixture was boiled 2 hr with a good magnetic stirring (an homogeneous soln was observed after *ca.* 1 hr). After acidification to pH ~ 2 with conc. HCl, extraction by CH_2Cl_2 afforded the diacid (95%) (F = 146°). D_2O/NaOD was necessary, since an almost complete H/D exchange occurs with KOH/H_2O/dimethoxyethane.

The diacid was quantitatively esterified with an ethereal soln of diazomethane. Reduction of the diester with LAH in ether[34] afforded the 3-t-butyl-1,5 pentanediol in 81% yield.

3-*t-Butyl*-1,5 *pentanediol dimethane sulfonate.* The solution of 875 mg of diol in 150 ml anhyd pyridine was cooled and stirred at −15°C. Methanesulfonyl-chloride (1.9 ml) was added dropwise and the mixture allowed to remain afterwards 1 hr at −15°. Conc HCl was then added (160 ml), keeping the temp lower than +10°, and the whole was extracted by *ca.* 400 ml ether. The combined extracts were thoroughly washed with brine till pH ~ 6 and dried over Na_2SO_4 to afford 1.45 g of the dimesylate as a viscous oil (85% yield), used without further purification.

4-*t-Butylthiacyclohexane* was prepared according to Johnson *et al.*[37] We noted that the sulfide was easily lost if solns in hexane, benzene or alcohols were evaporated, or in the presence of traces of water.

4-*t-Butylthiacyclohexane* cis *and* trans 1-*oxides.* The *cis*-oxide was prepared stereospecifically by oxidation of the sulfide with tBuOCl in MeOH, according to Johnson *et al.*;[37] tBuOCl was at best prepared according to Ref. 38 and distilled before use. A very pure reagent was necessary to avoid mixtures of *cis* and *trans* oxides, and α-halogenation. We noted also that the nature of the base in the work up (anhyd Na_2CO_3) was determinant for a clean stereospecific oxidation.

The *trans* oxide was prepared by inversion of the *cis*-oxide with Meerwein's salt according to Johnson *et al.*[39]

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APPENDIX A

Analysis of the ^{1}H NMR *spectrum of 2-lithio 4-t-butylthiacyclohexane trans* 1-*oxide* (*I*)

The two independent systems $\{\alpha\beta\}$ (3H) and $\{\alpha'\beta'\}$ (4H) are very easily identified in I-γd_1 by double irradiation, because each well separated multiplet corresponds to one single hydrogen (Fig. 1).

$\{\alpha\beta\}$ part. This three protons system is analyzed as an ABX at 250 MHz. Only one large coupling (13.9 Hz) is observed

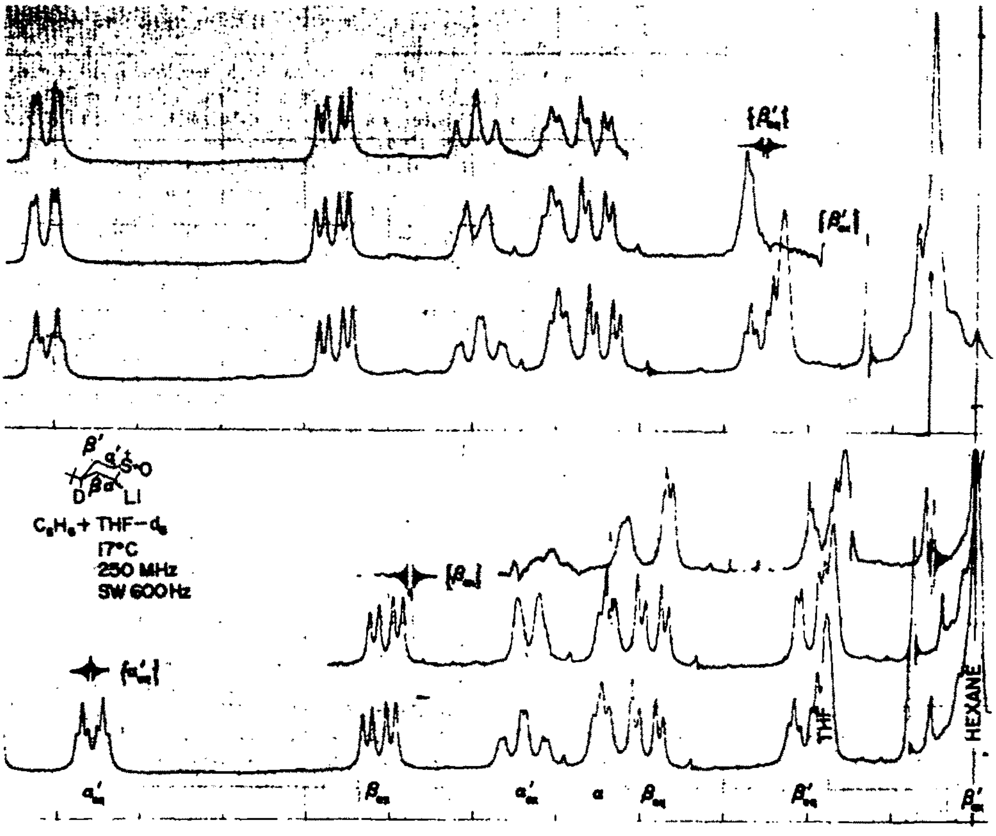

Fig. 4.

which is necessarily the gem coupling between the two β hydrogens. Different solutions are possible *a priori* and the definite assignment given in Table 1 is based on the fact that there is a large negative $^2J_{\beta ax\beta eq}$ and the two other vicinal couplings $^3J_{\alpha\beta}$ have to be positive.[s,t] The calculated couplings HαHβax and HαHβeq are respectively 5.4 Hz and 4.5 Hz, Hβax and Hβeq being assigned by comparison of the spectra of I-γd$_1$ and I-γH.

{α'β'} *part.* Hα'eq ($\delta = 3.19$) is identified by the characteristic shape of its multiplet and its chemical shift (δHα' eq = 2.90 for the starting sulfoxide in benzene). The other protons of this part are assigned on the results of selective double irradiation of α'eq, β'eq and β'ax which are inambiguous (Fig. 4).

An independent verification of the α' and β' protons is given by the spectrum of (I-ββ'd$_4$). A definite choice of Hβ'ax and Hβ'eq is given by I-γH (Fig. 5), in which a larger width of one proton is observed while the other one has a much weaker coupling.[u]

APPENDIX B

Analysis of the ^{1}H NMR *spectrum of* 2-*lithio* 4-*t*-*butylthiacyclohexane* cis 1-*oxide* (II)

The spectrum of II is much more complicated. Assignments are based on the comparison of the spectra of II, II-γd$_1$ and II-ββ'd$_4$, on selective double irradiations which together then lead to the only remaining possible assignment given in Fig. 2, of all those which had to be considered *a priori*. The spectrum of II-ββ'd$_4$ shows an AB part with a J gem = 12.0 Hz (α' hydrogens: A, B) and a singlet which is the α proton (E). Selective double irradiations of each multiplet in the spectrum of II-γd$_1$ allow to assign the {αβ} (3H) and {α'β'} (4H) systems:

Irradiation of A[v] eliminates a large coupling in D and perturbs (F, G), probably by suppression of a weak coupling. C is not affected at all[w] (Fig. 6).

Irradiation of (D, E) perturbs very much A and (F, G) by suppression of large couplings; B looses a coupling of about 3–4 Hz (Fig. 7).

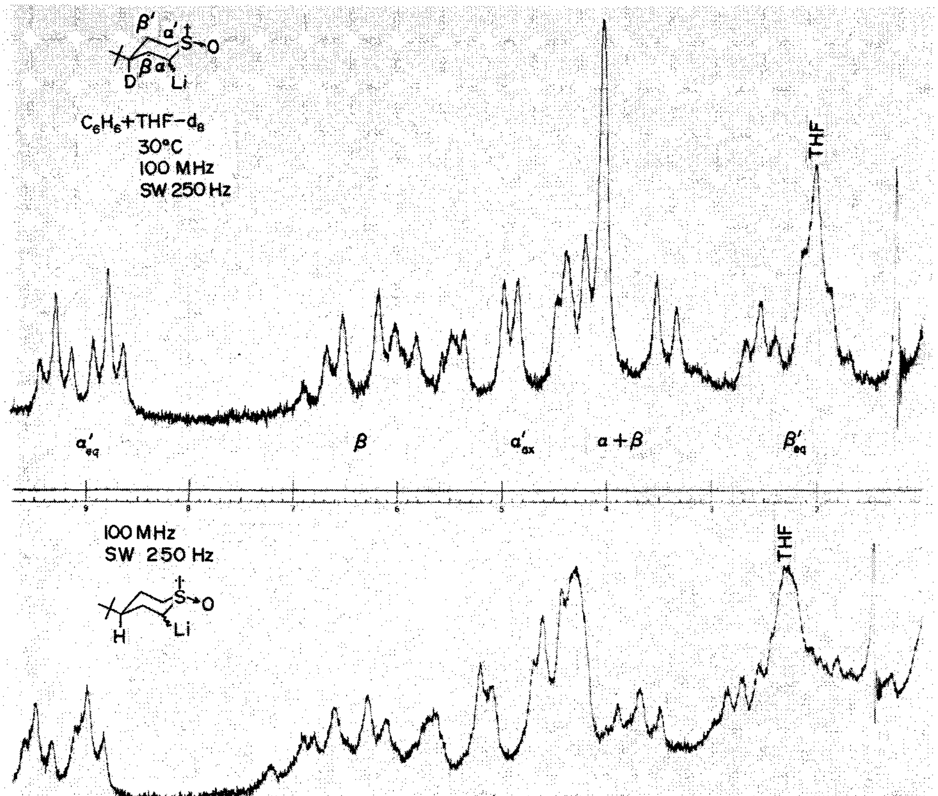

Fig. 5.

Irradiation of B eliminates a weak coupling in the (F, G) part; C, D and E are not affected at all (Fig. 6).

Irradiation of the whole (F, G) multiplet suppresses the large coupling in C which gives then a broad singlet; the whole group (D, E) is very perturbed by elimination of a large coupling with the set (F, G). Weak couplings of about 3 Hz are also suppressed for A and B (Fig. 7).

Irradiation of C suppresses a large coupling in the (F, G) group and does not affect A at all.[x]

These irradiations allow the conclusion that the two hydrogens F and G belong to the two separated moieties {αβ} and {α'β'} (Fig. 7).

Comparison of the spectra of II and II-γd$_1$—and also irradiation of Hγ in II—show then an important modification of the C and (D, E) multiplets while A is not modified at all (Fig.

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[s] Some weak negative vicinal couplings have been reported in dihalogeno 1,2 propanes or tetrahalogeno ethanes, but are dubious according to Jackmann and Sternhell.[16]

[t] *Ab initio* Calculations for cyclohexyllithium vicinal coupling constants,[19]

[u] Due to the great complexity of the whole spin system, it is not possible to extract more than an order of magnitude for the couplings Hβ'Hγ (Table 1).

[v] A has the same chemical shift ($\delta = 2.66$/CH$_4$ int.) as Hα'ax of the methine in III ($\delta = 2.64$/CH$_4$ int.).

[w] The decoupling of the geminated proton B cannot be observed, being too proximate.

[x] B is at most very slightly perturbed, but may be due to the proximity with C; D and E cannot be observed.

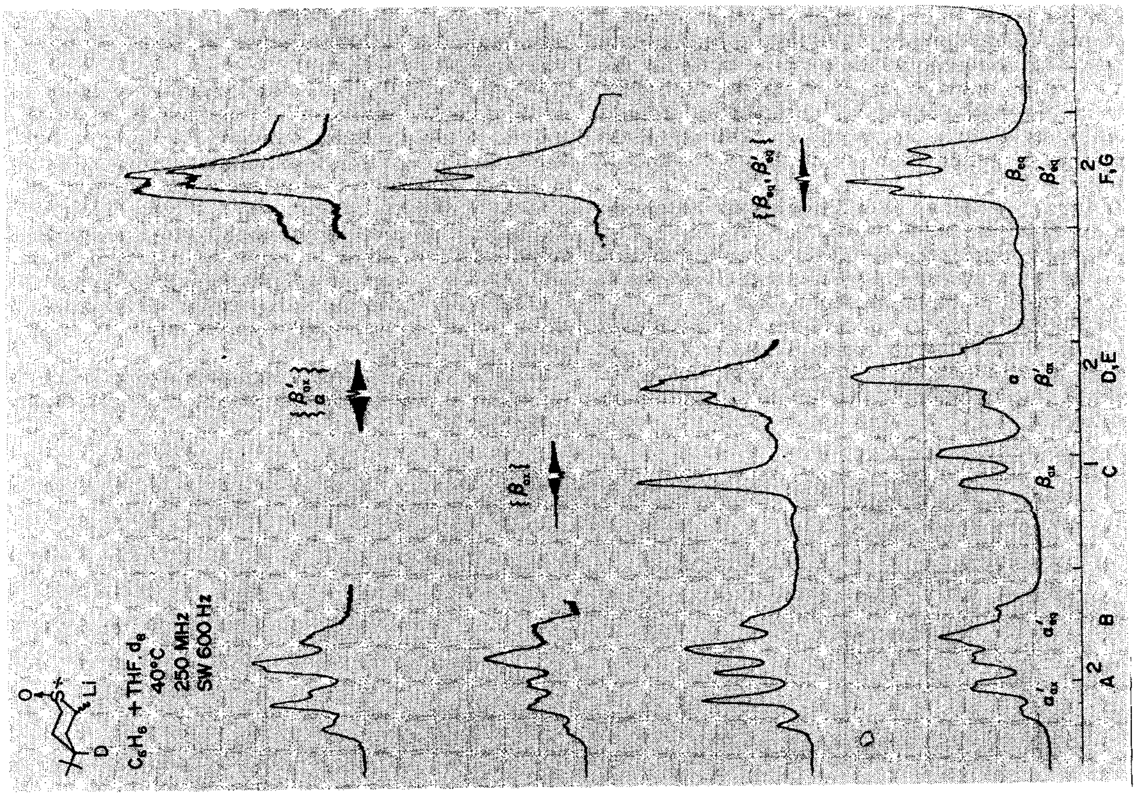
O
S
Li
D
C6H6 + THF, d8
40°C
250 MHz
SW 600 Hz
{β'ax α}
{βax}
{βeq, β'eq}
α'ax
α'eq
βax
α
β'ax
βeq
β'eq
2
A
B
1
C
2
D,E
2
F,G

Fig. 7.

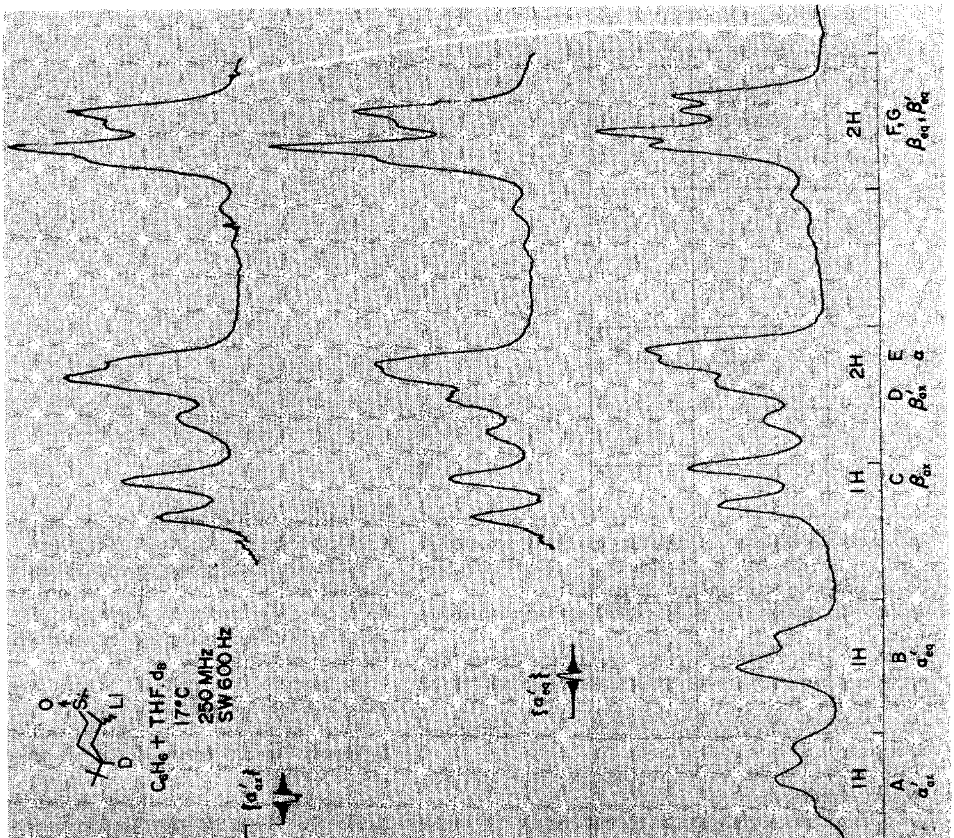
O
S
Li
D
C6H6 + THF, d8
17°C
250 MHz
SW 600 Hz
{α'ax}
{α'eq}
1H
A
α'ax
1H
B
α'eq
1H
C
βax
2H
D
β'ax
E
α
2H
F,G
βeq, β'eq

Fig. 6.

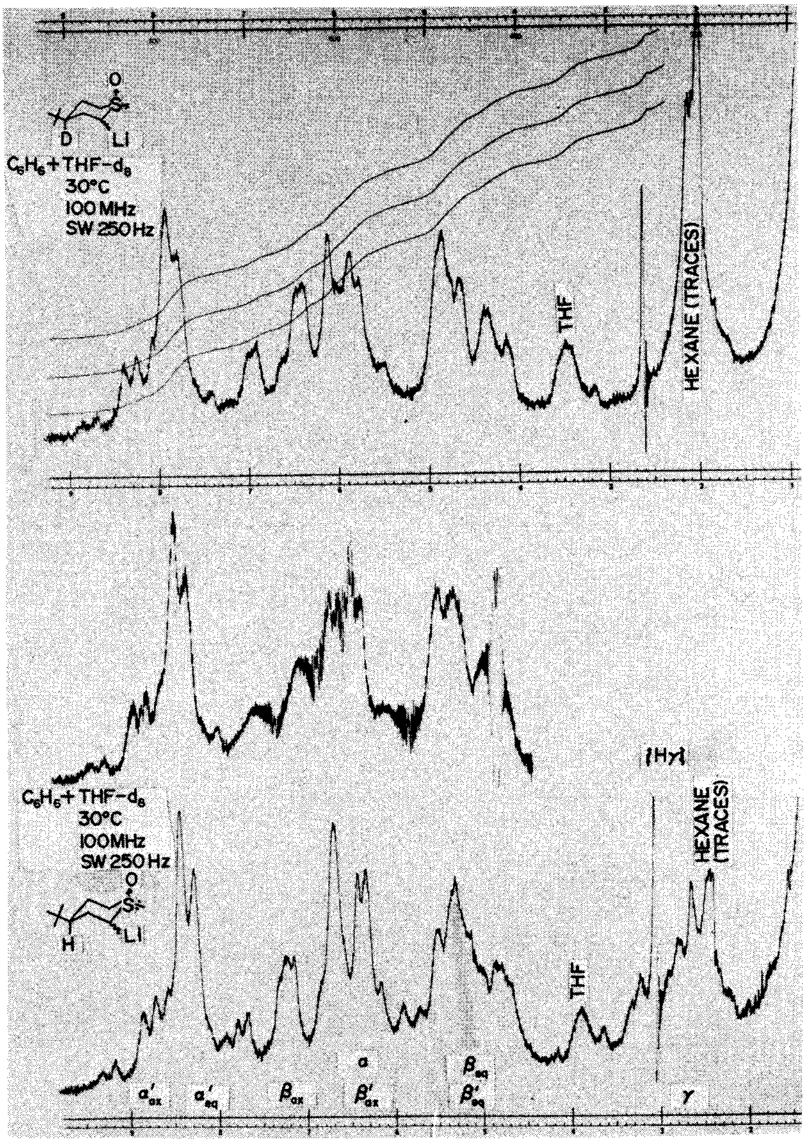

Fig. 8.

8). The main result is the existence of a coupling of about 13–14 Hz between Hγ and C. Hence C has to be Hβax or Hβ'ax and as it is not coupled at all with A or B (α' hydrogens), C has to be Hβ. The same comparison or irradiation of Hγ[y] show weak or medium coupling constants between Hγ and (F, G) and a very weak perturbation of B by Hγ. Therefore it is possible to make a definite and inambiguous assignment as in Fig. 2.

---

[y] A precise and complete decoupling gives a superposable spectrum of II-{Hγ} and (II-γd_1), thus validating the irradiation conditions and the real chemical shift of Hγ.