122. Low-Temperature ^{13}C-NMR Spectra of ^{6}Li- and ^{13}C-Labelled Sulfur- and Selenium-Substituted Organolithium Derivatives[1][2][3]

by **Dieter Seebach***, **Josef Gabriel**[4], and **Robert Hässig**[5]

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum,
Universitätstrasse 16, CH-8092 Zürich

(22.XI.83)

Summary

The ^{13}C-NMR spectra of 19 different, singly, doubly, and triply ^{13}C-labelled α-sulfur- and α-selenium-substituted ^{6}Li-derivatives generated from methyl and phenyl thioethers, thioacetals, trithio-orthoesters and from their selenium analogues have been recorded in ethereal solutions (tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF)) at temperatures between $-30°$ and $-110°$. The effects of H/Li-exchange upon chemical shifts and coupling constants, as well as the values and multiplicities of ^{6}Li,^{13}C-coupling are interpreted in view of crystal structures of some of the same compounds. In two thirds of the cases studied, the H-decoupled ^{13}C-NMR signals observed below $-80°$ were triplets, proving that the C̦-atoms are bonded to single ^{6}Li-atoms. This is compatible either with monomeric or with dimeric, heteroatom-bridged structures. The direct ^{1}H,^{13}C- and ^{13}C,^{13}C-coupling constants (^{1}J) decrease, the ^{13}C,^{77}Se-coupling constants increase upon lithiation. More striking is that the geminal coupling ^{13}C-S-^{13}C (^{2}J) is too small to be observed in the non-metalated species, while it ranges from 3.7 to 7.5 Hz in the lithiated derivatives. These observations may be interpreted as resulting from delocalization of electron density from the carbanionic center towards the adjacent heteroatom.

A) Introduction. – In contrast to the elements of the second period, those of the third and higher periods stabilize negative charge on adjacent C-atoms. This is exemplified by the experimental observations shown in *Table 1:* Lithiation of anisol occurs in the *ortho*-position, while thioanisol furnishes the CH_2-Li derivative under the same conditions (*A*) [5]; H/D exchange is up to seven orders of magnitude faster at the C-atom with a P-, S-, or Se-substituent than with N- or O-substituent (*B*) [6] [7] [8]; pK_a-measurements show that RS-groups acidify

---

[1] See our previous full paper on ^{13}C-NMR spectra and ^{13}C,^{6}Li-coupling constants in organolithium compounds, especially in α-halogeno-substituted derivatives (carbenoids) [1].

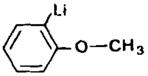
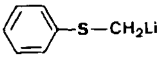
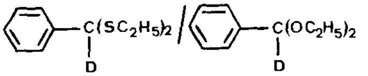
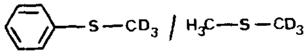
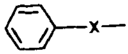
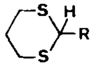
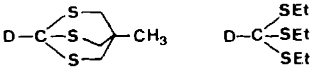
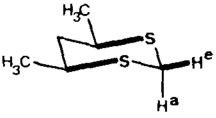
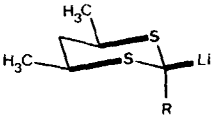
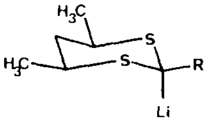
[2] The preceding paper [2] describes the preparation of ^{13}C-labelled S- and Se-derivatives used for lithiations in the present investigation.

[3] For preliminary publications describing crystal structures of 2-lithio-1,3-dithianes see [3]. The structures of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) complexes of (methylthio)- and of (phenylthio)-methyllithium are described in [4]. In a forthcoming paper we will discuss the crystal structure of the bis-sulfonium ylid **8** and of its precursor.

[4] Part of the Dissertation No. 7252, *J.G.*, ETH Zürich, 1983.

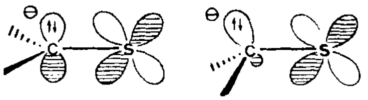
[5] *Cf.* also the Dissertation by *R.H.* (No. 7348, ETH Zürich, 1983).

Table 1. *Comparison of the Stabilization of a Negative Charge on the C-Atom in α-Position to a N-, O-, P-, S-, or Se-Atom*

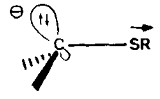
A	*ortho*-Metalation of Anisol	α-Metalation of Thioanisol
		
B	Compounds	Rel. H/D-Exchange Rates
		$4.5 \cdot 10^5 : 1$
		$3 \cdot 10^5 : 1$
	 X = CH_3N, O, CH_3P, S, Se	$1 : 40 : 3 \cdot 10^4 : 2 \cdot 10^7 : 2 \cdot 10^8$
C	Compounds	pK_a (Solvent)
	 R = H, CH_3, C_6H_5	31, 37, 28 (cyclohexylamine)
	$C_6H_5S{-}CH_2{-}C_6H_5$	30.8 (DMSO)
	$C_6H_5S{-}CH_2{-}SC_6H_5$	30.8 (DMSO)
	$C_6H_5S{-}CH(C_6H_5)_2$	26.7 (DMSO)
	$(C_6H_5S)_2CH{-}C_6H_5$	23.0 (DMSO)
	$(C_6H_5S)_3CH$	22.8 (DMSO)
	$(C_3H_7S)_3CH$	31.3 (DMSO)
D	 ratio of H/D-exchange rates $10^3 : 1$	
	 rate of abstraction of H^e/H^a *ca.* 10:1	 more stable  less stable by ≥ 6 kcal/mol

the H-atoms of the adjacent CH-moiety to the same extend as do phenyl groups (*C*) [9] [10]; both, the kinetic and the thermodynamic acidification are stronger with aryl-S than with alkyl-S groups (*B*, *C*); the effect is subject to stereoelectronic control: protons of the S-substituted CH-groups are exchanged faster if they are disposed in an antiperiplanar position with respect to a S–C bond (*D*) [7] [11]; similarly, α-S-substituted Li-derivatives are more stable with an S–C bond antiperiplanar to the C–Li bond (D) [11–13]. The metalation of thioacetals and of trithio-orthoesters [14] has led to the development of now widely used methods of reactivity umpolung [15–17].

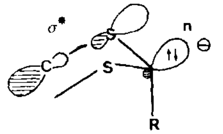
Less clear-cut than these experimental results is their interpretation. The interactions which have been discussed are shown below for S-derivatives, with omission of the counter-ions: while there seems to be no doubt that delocalization of negative charge is achieved by overlap with d-orbitals on a positively charged ($R_3S^{\oplus}$) or highly oxidized S-atom (R_2SO, R_2SO_2) [18–21], the participation of d-orbitals in derivatives of divalent sulfur is still debated [22]; instead, polarization [23] and n,σ*-delocalization (hyperconjugation) [24–26] were found by calculations to contribute most to the stabilization of S- and Se-substituted carbanions and the derived



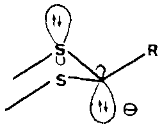
stabilization by $(n_c$- $d_s)$-π overlap



stabilization by polarization



stabilization by n_c–$\sigma^*_{c,s}$ overlap



destabilization by n_c–n_s interaction

organolithium compounds; in addition, minimalization of n_C,n_S-conjugative destabilization is an effect determining the geometry. An expert discussion is given in a recent review article [27].

We hoped that information obtained from crystal-structure analysis[3] and from NMR studies might help settling some of these questions or at least separating some of these effects from one another.

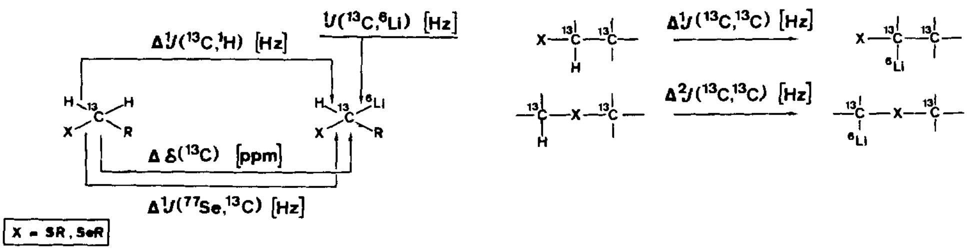
There is yet another aspect of the present investigation, and that is the nature of the C–Li bond. The conclusion from calculations is that this bond must be considered as mainly ionic ($C^{\ominus}Li^{\oplus}$) [28] or strongly polarized, with partial positive charges of 0.2–0.8 on lithium [28b] [28c]. In all of these discussions 'much depends how ionic or covalent character is defined', as *Schleyer & Pople* put it [28e]. Our previous NMR investigations of halo-lithio carbenoids [1] [29] have furnished numerous examples of strong $^{13}C,^{6}Li$-coupling (^1J), with multiplicities compatible with the presence of monomeric species. By switching to the more stable α-RS-substituted Li-derivatives we hoped to obtain the crystal structure[3] *and* NMR data ot the *same* compounds, and thus independant experimental information about the C–Li bond in these species.

B) ^{13}C-NMR Spectra of $^{13}C,^{6}Li$-Labelled Sulfur- and Selenium-Substituted Organolithium Compounds.

– The *formulae* of the investigated sulfur- (**1**–**12**) and selenium-substituted (**13**–**19**) carbanion derivatives are shown in the *Tables 2, 3* and *5,* respectively.

The preparation of the necessary ^{13}C-labelled precursors is described in the preceding paper [2]. The results are best presented by organizing the ^{13}C-NMR data according to the changes of characteristic parameters upon replacement of H by Li, *i.e.* metalation of the precursor[6][7]. The change of ^{13}C-chemical shifts is termed $\Delta\delta$(C), the change in the C,H-coupling constants Δ^1J(C,H), that in the C,Se-coupling constants

Scheme



---

[6] For the techniques used, see our previous full paper on low-temperature ^{13}C-NMR spectra of hydrocarbon-derived and α-halo-organolithium compounds [1]. In most cases, the lithiations were conducted in the NMR tube (see also *Exper. Part*).

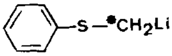
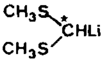
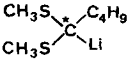
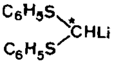
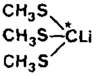
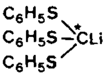
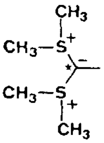
[7] The chemical shifts and coupling constants of the carbanion derivatives and of the protonated precursors were measured in the same solvent and – in most cases – also at the same temperature. The chemical shifts are slightly temperature-dependent, the coupling constants are temperature-independent.

$\Delta{}^1J$(Se,C), that in direct C,C-coupling constants $\Delta{}^1J$(C,C), and that in two-bond C,C-coupling constants $\Delta{}^2J$(C,C) (see the *Scheme*); the lithiations are all done with metalating (^{6}Li)reagents, and for the resulting ^{13}C,^{6}Li-coupling constants we use the symbol ^1J(C,Li). *In no case did we determine the sign of a coupling constant;* therefore, the signs of the ΔJ-values result from the differences of the *absolute* values of the coupling constants of the CH- and the CLi-derivatives.

Some $\Delta\delta$(C) and ΔJ(C,H) values of lithiated sulfides [30], thioacetals [11][8]) sulfoxides [30] [31], sulfones [30], and phosphonates [32], as well as of sulfur [33] [34], and phosphorous [35] [36] ylides have been reported. The $\Delta\delta$(C) values were mainly used to indicate charge distribution, the ΔJ(C,H) values were correlated with the hybridization of the C-atom *(cf. Discussion)*. J(C,Li), J(C,C), J(Se,C), and ^2J(CXC) of S- and Se-substituted carbanion derivatives have hitherto not been reported.

The *Tables 2–5* contain the values of the chemical shifts of the α-S- and α-Se-substituted organolithium compounds and of the chemical shift changes upon metalation; the ylid salt **8** is also included. In the *Tables 6–8* the coupling constants are collected.

Table 2. *^{13}C-NMR Chemical Shifts of the Labelled C-Atoms of the Open-Chain S-Substituted (^{6}Li)-Organolithium Compounds* **1**–**7** *and of the Ylid Salt* **8**. All C-atoms are shielded (negative $\Delta\delta$ values) upon replacement of H by Li.

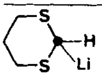
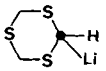
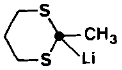
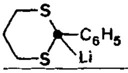
Compound			Solvent[a]	Temp. of observation	Chemical Shifts[b] [ppm]	
					δ(C)	$\Delta\delta$(C)[c]
$CH_3CH_2CH_2CH_2{-}S{-}{}^*CH_2Li$		**1**	THF/TMEDA	−110°	6.1	−8.6
	(see *Fig. 1*)	**2**	THF/TMEDA	−80°	3.0	−10.8
		**3**	THF	−90°	32.9	−7.0
		**4**	THF	−115°	35.2	−19.0
		**5**	THF	−35°	21.9	−16.4
	(see *Fig. 4*)	**6**	THF	−110°	40.0	−19.2
		**7**	MTHF	−60°	13.2	−46.9
	$B(C_6H_5)_4^{\ominus}$	**8**	acetone	+ 30°	21.0 20.1 [33]	−29.9

[a] TMEDA = *N,N,N′,N′*-Tetramethylethylenediamine; MTHF = 2-methyltetrahydrofuran.
[b] For details about the determination of these values, see *Exper. Part.*
[c] For δ(C) of the protonated precursors, see [2] and *Footnote 7*, for the definition of δ(C), see the *Scheme*.

---

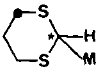
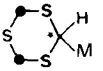
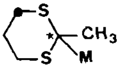
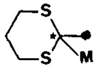
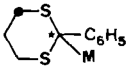
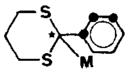
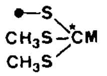
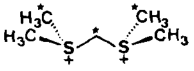
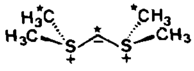
[8]) Compare also the preference for equatorial positions of the metal in 2-R_3Si-, 2-R_3Ge-, 2-R_3Sn-, and 2-R_3Pb-substituted 1,3-dithianes [37].

Table 3. *^{13}C-NMR Chemical Shifts of the Labelled C-Atoms of the (^{6}Li)Lithiodithianes* **9**, **11** *and* **12** *and of (^{6}Li)Lithiotrithiane* **10**[a]). Lithiation causes shielding of the C-atom in all cases.

Compound[b])			Temp. of observation	Chemical Shifts[c]) [ppm] δ(C)	Δδ(C)[d])
	(see *Fig. 2*)	**9**	−100°	25.8	−5.9
		**10**	−50°	27.2	−8.1
	(see *Fig. 3*)	**11**	−80°	26.2	−16.2
		**12**	−110°	42.7	−8.5

[a]) All measurements were carried out in (D_8)THF. [b]) The labelled C-atom is marked with a dot (●). [c])[d]) See *Footnotes b* and *d*, respectively, of *Table 2*.

Table 4. *^{13}C-NMR Chemical Shifts of the Labelled C-Atoms*[a]) *of the Multiply ^{13}C-Labelled Substituted (^{6}Li)Organolithium Compounds, Compared with those of the Corresponding Non-metalated Species*[a])

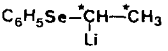
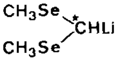
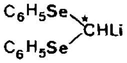
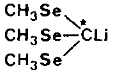
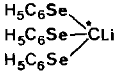
Compound			Chemical Shifts[b]) [ppm] M = H δ(C)	M = Li[c]) δ(C)	Δδ(C)
			29.8	33.8 (**9***)	+4.0
			35.3	34.6 (**10****)	−0.7
	(see *Fig. 3*)		30.9	19.8 (**11***)	−11.1
	(see *Fig. 3*)	($^{13}CH_3$)	21.2	30.6 (**11****)	+9.4
			32.1	26.9 (**12***)	−5.2
		*ipso* *ortho* *meta*	140.5 128.4 129.3	157.0 (**12****) 122.2 127.7	+16.5 −6.2 −1.6
	(see *Fig. 4*)		14.4	21.2 (**6***)	+6.8
CH_3 of:			 $2BF_4^{\ominus}$ 27.4	 (**8***) $B(C_6H_5)_4^{\ominus}$ 37.0	+9.6

[a]) The solvents and techniques are the same as indicated in *Table 2* and *3*.

[b]) The C-atom additionally labelled and marked with a dot is observed here (not the M-substituted C-atom).

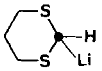
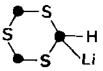
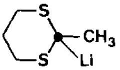
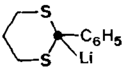
[c]) The multiply labelled carbanion derivatives have the same compound numbers as the corresponding singly labelled ones, but are distinguished by asterix.

Table 5. *^{13}C-NMR Chemical Shifts and $\Delta\delta$(C) Values of the Labelled C-Atoms of (^{6}Li)Lithio-organoselenium Compounds* **13–19**

Compound[a])		Solvent	Temp. of observation	Chemical Shifts[b]) [ppm]		
					δ(C)	$\Delta\delta$(C)[c])
CH_3–Se–*CH_2Li	**13**	MTHF	–100°		11.1	+5.7
C_6H_5–Se–*CH_2Li	**14**	THF	–80°		4.8	–1.7
 $C_6H_5Se\text{–}\overset{*}{C}H(Li)\text{–}\overset{*}{C}H_3$	**15**	THF	–100°	C–Li	17.9	–16.0
				CH_3	24.5	+0.7
	**16**	MTHF	–90°		29.9	+11.3
	**17**	THF	–100°		22.7	+3.7
 (see *Fig. 5*)	**18**	MTHF	–80°		34.5	+10.3
	**19**	THF	–100°		0.4	–28.1

[a]) The labelled C-atoms are marked with an asterix.
[b])[c]) See *Footnotes b* and *c*, respectively, of *Table 2*.

Table 6. *$^1J(^{13}C,^6Li)$ Coupling Constants from the Triplets of the Open-Chain and Cyclic Substituted (^{6}Li)-Organolithium Compounds* **1–12**[a])

Compound		Temp. of observation	Coupling Constants [Hz]		
			$^1J(^{13}C,^6Li)$	^1J(C,H)[b])	$\Delta\,^1J$(C,H)[b])
C_4H_9S–*CH_2Li	**1**	–115°	not observed	118.4	–19.2
C_6H_5S–*CH_2 Li (see *Fig. 1*)	**2**	–115°	9.2	121.4	–18.1
$(CH_3S)_2$*CHLi	**3**	–115°	8.0	143.3	–7.0
C_4H_9*$C(SCH_3)_2Li$	**4**	–110°	8.4		
$(C_6H_5S)_2$*CHLi	**5**	–120°	not observed	139.6	–13.9
 (see *Fig. 2*)	**9**	–100°	10.1	133.1	–16.4
	**10**	–100°	peak partially underneath solvent signals	*ca.* 133.0	*ca.* –18.0
 (see *Fig. 3*)	**11**	–80°	9.9	–	–
	**12**	–130°	not observed	–	–
$(CH_3S)_3$*CLi (see *Fig. 4*)	**6**	–110°	6.7	–	–
$(C_6H_5S)_3$*CLi	**7**	–130°	not observed	–	–
$(CH_3)_2\overset{\oplus}{S}\text{–}{}^*\overset{\ominus}{C}H\text{–}\overset{\oplus}{S}(CH_3)_2B(C_6H_5)_4^{\ominus}$	**8**	RT	–	190.0	+32.0

[a]) Solvents and other conditions of the measurements are identical with those stated in *Table 2* and *3*.
[b]) For ^1J(C,H) of the protonated precursor, see [2] and *Footnote 7*; for the meaning of $\Delta\,^1J$(C,H), see the *Scheme*.

Table 7. *Coupling Constants $^1J(C,C)$* [Hz] *of Direct Coupling and $^2J(C,C)$ of Geminal C–S–C Coupling of the Labelled C-Atoms in the Multiply Labelled S-Substituted Carbanion Derivatives and of their Protonated Precursors*[a])

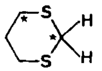
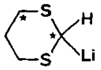
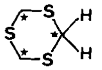
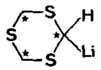
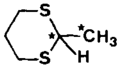
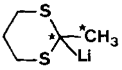
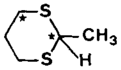
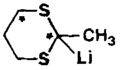
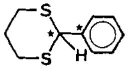
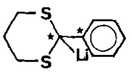
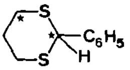
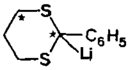
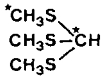
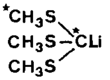
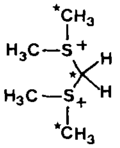
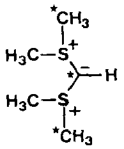
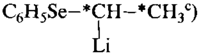
Precursor			(^{6}Li)Lithiated or Carbanionic Species		
	$^2J(C,C) \leq 0.6$			$^2J(C,C) = 5.7$	**9***
	$^2J(C,C) \leq 0.6$			$^2J(C,C) = 7.5$	**10****
	$^1J(C,C) = 34.8$	(see *Fig. 3*)		$^1J(C,C) = 28.3$	**11****
	$^2J(C,C) \leq 0.6$	(see *Fig. 3*)		$^2J(C,C) = 6.3$	**11***
	$^1J(C(2),C(1')) = 46.3$			$^1J(C(2),C(1')) = 46.8$	**12****
	$^2J(C,C) \leq 0.25$			$^2J(C,C) = 3.7$	**12***
	$^2J(C,C) \leq 0.05$	(see *Fig. 4*)		$^2J(C,C) = 6.3$	**6***
	$^2J(C,C) \leq 0.25$			$^2J(C,C) = 3.7$	**8***

Table 8. *Coupling Constants in Se-Substituted Derivatives*[a])

(^{6}Li)-Derivative		Temp. of observation	Coupling Constants [Hz]			Changes ΔJ[b]) [Hz] upon Lithiation	
			$^1J(C,Li)$	$^1J(C,H)$	$^1J(Se,C)$	$\Delta\,^1J(C,H)$	$\Delta\,^1J(Se,C)$
$CH_3Se-{}^*CH_2Li$	**13**	−120°	not observed	114.0	132.0(?)	−26.0	+71.0(?)
$C_6H_5Se-{}^*CH_2Li$	**14**	−120°	11.0	118.3	signal concealed	−23.7	–
 $C_6H_5Se-{}^*\underset{\mathrm{Li}}{\underset{\vert}{C}}H-{}^*CH_3$[c])	**15**	−100°	11.8	119.0	signal concealed	−18.0(?)	–
$(CH_3Se)_2{}^*CHLi$	**16**	−90°	10.7	134.0	159.0(?)	−20.0	+75.0(?)
$(C_6H_5Se)_2{}^*CHLi$	**17**	−120°	not observed	129.0(?)	122.2	−29.0(?)	+36.2
$(CH_3Se)_3{}^*CLi$ (see *Fig. 5*)	**18**	−80°	10.8	–	155.4	–	+57.8
$(C_6H_5Se)_3{}^*CLi$	**19**	−120°	not observed	–	98.0	–	−5.2

---

[a]) Solvents for these measurements and conditions as given in *Table 5* and *Exper. Part.* Question marks indicate values which could not be read from the spectra beyond doubt.

[b]) See also [2] for J of protonated precursors.

[c]) The $^1J(C,C)$ of $C_6H_5Se-{}^*CH_2-{}^*CH_3$ is 35.5 Hz [2], that of $C_6H_5Se-{}^*CHLi-{}^*CH_3$ 25.5 Hz ($\Delta\,^1J(C,C) = -10$ Hz).

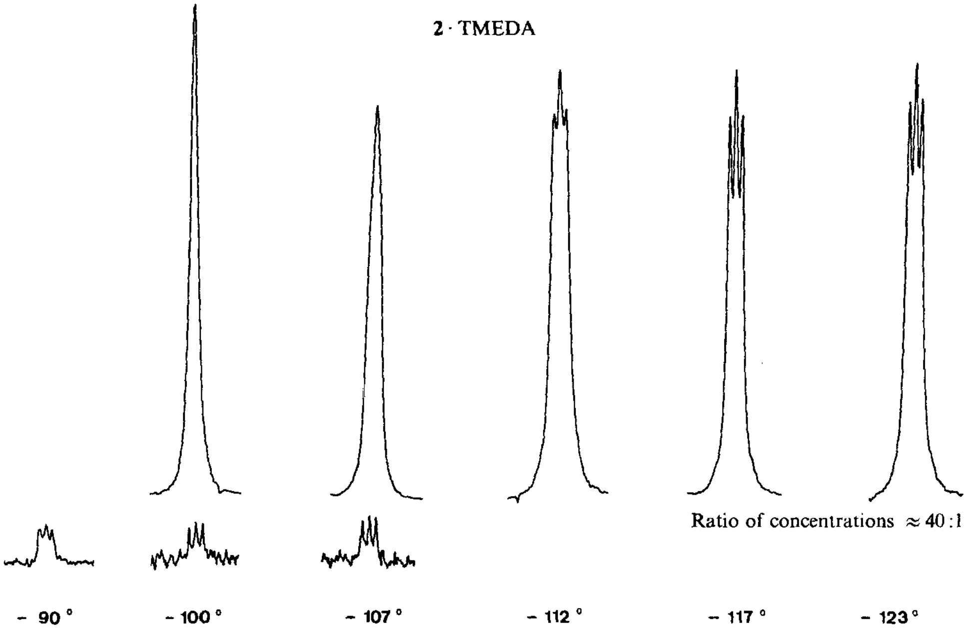


Fig. 1. *^{13}C-NMR signals of the ^{13}C-labelled ^{6}Li-substituted C-atom of (phenylthio)methyllithium* **2**. The labelled thioanisol was lithiated [38] with (^{6}Li)butyllithium [1] in neat TMEDA, crystallized from TMEDA, and the crystals dissolved in Me_2O, see also *Exper. Part.* Intensive signals (top) at $c = 0.12$M, weak signals (bottom) at $c = 0.003$M; $\delta = 3.0$ ppm, $^1J = (C,Li) = 9.2$ Hz.

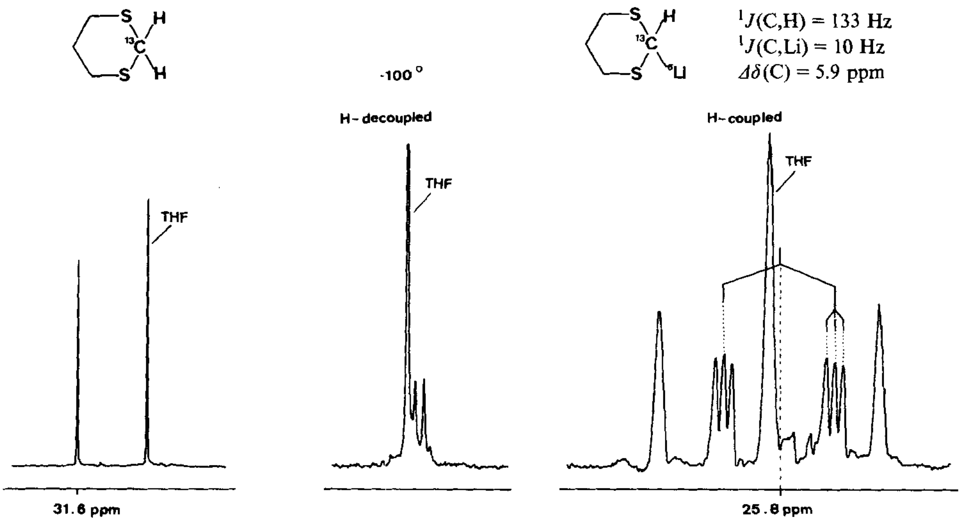


Fig. 2. *^{13}C-NMR signal of C(2) of 2-(^{6}Li)lithio[2-^{13}C]-1,3-dithiane* (**9**) *and its protonated precursor in THF at −100°*. The C,Li-coupling of **9** can be observed below −80°. The signal of ^{13}C(2) happens to have a chemical shift very close to that of C(3) of THF. By turning off the proton decoupler, ^{13}C(2) appears in a 'window', and ^1J(C,Li) and J(C,H) of **9** can easily be determined, see *Table 3* and *6*.

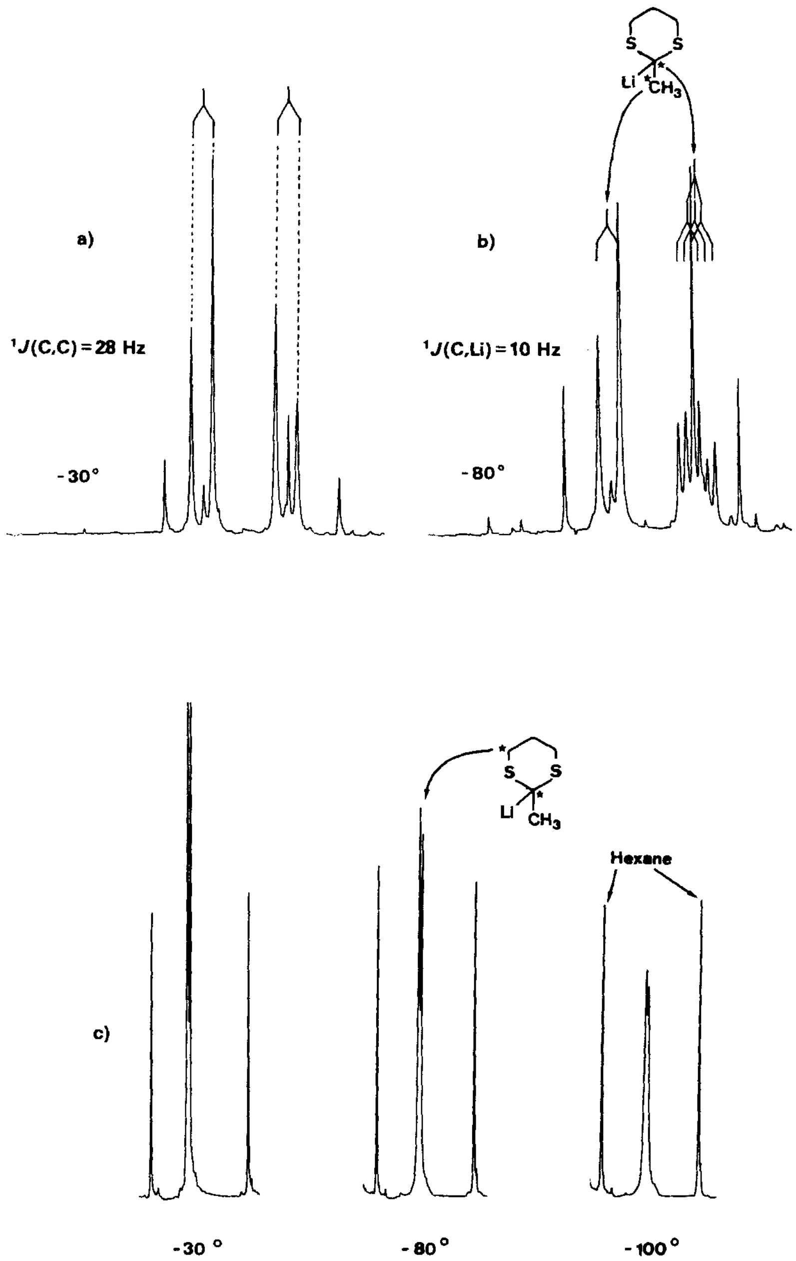


Fig. 3. *^{13}C-NMR spectra of multiply labelled 2-(^{6}Li)lithio-2-methyl-1,3-dithiane* **11**. a) At –30°, the signals of the lithiated and of the methyl C-atom of **11**** show only direct coupling (^1J(C,C)). b) At –80°, the C,Li-coupling is 'turned on', as evident from additional triplet splitting of the high-field signal of **11****. c) The signal of ^{13}C(4) of the 1,3-doubly labelled derivative **11*** is a doublet at all temperatures. We, therefore, assign the splitting to coupling (^2J(C,C) = 6.3) with the lithiated C-atom, which is *not* present in the non-lithiated precursor (see *Table 7*).

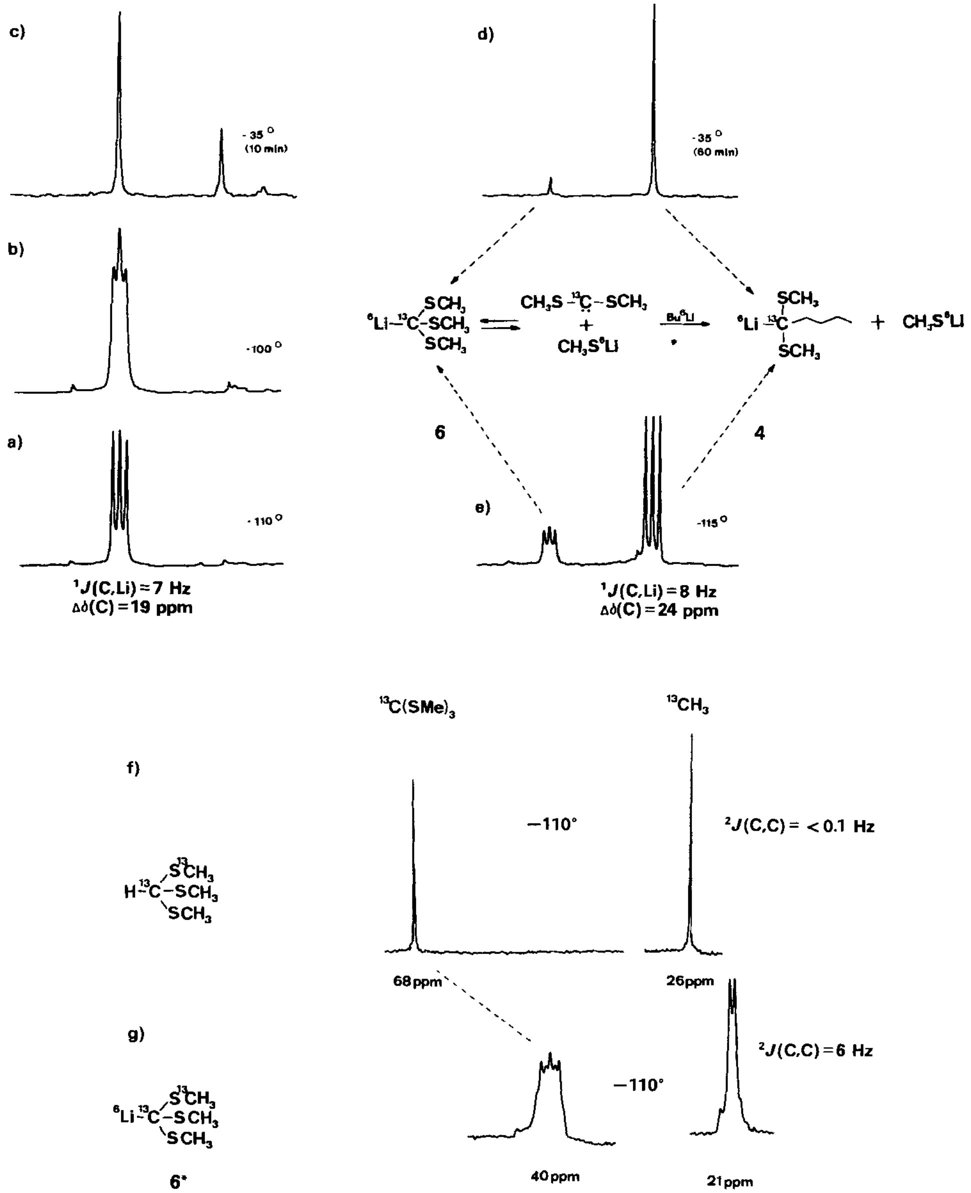


Fig. 4. *^{13}C-NMR signals of the labelled C-atoms of 4, 6, and 6**. For chemical shifts and coupling constants see also *Tables 2, 4, 6* and *7*. a) At −110°, the C,Li-coupling of $(CH_3S)_3{}^{13}C^6Li$ (**6**) is clearly visible. b) c) Upon warming, a coalescence behaviour (*cf. Fig. 1*) is observed for **b**. d) At −35°, the intensity of the singlet of **6** decreases at the expense of a new singlet at higher field, which appears only, if excess (^{6}Li)BuLi is present from the preparation of **6**, and which is assigned to the lithiated pentanal thioacetal **4**. e) On cooling, an almost baseline separated triplet results from C,Li-coupling in **4**. Note, that the chemical shift and the C,Li-coupling of **6** are not affected by the admixtures of (^{6}Li)BuLi, of **4**, and of CH_3S^6Li. f) g) Comparison shows that no coupling corresponding to ^2J(C,C) is present in the non-metalated $(^{13}CH_3S)(CH_3S)_2{}^{13}CH$, while a coupling ($^2J$(C,C) = 6 Hz) arises upon lithiation to **6***.

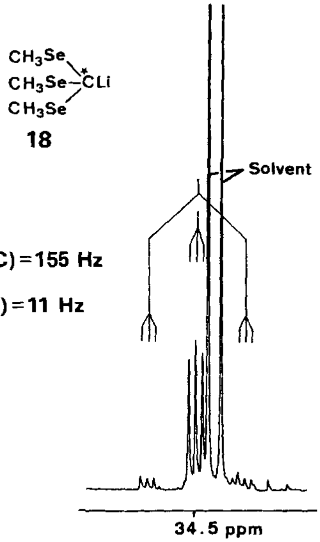


Fig. 5. *^{13}C-NMR signal of the labelled C-atom of* **18** *with natural ^{77}Se-abundance.* The satellite triplets arise from the species with one ^{77}Se-nucleus ($I = 1/2$). See *Tables 5* and *8*.

The *Fig. 1–5* show some representative ^{13}C-NMR spectra and demonstrate the quality of the corresponding data in the *Tables.*

The *chemical shifts* of the labelled C-atoms of all S-derivatives decrease upon deprotonation: the $\Delta\delta$(C)values are between −6 and −47 ppm (see *Tables 2* and *3* and *Fig. 6a*). The Se-analogues do not exhibit this uniform behaviour: H/Li-exchange causes smaller shift changes between −28 and +11 ppm (see *Table 5* and *Fig. 6*). As can be seen from *Table 4,* the non-metalated C-atoms of the S-derivatives experience yet smaller changes between −11 and +16 ppm.

Of the *coupling constants,* $^1J(^{13}C,^6Li)$ represent the most valuable information [1]: coupling is only observed at temperatures below −80°; the disappearance of coupling at higher temperatures was observed with many other Li-derivatives⁹). The mechanism of the process is still not established. For (phenylthio)[^{13}C]methyl(^{6}Li)lithium we could show by dilution experiments (see *Fig. 1*) that the rate of the process is concentration-dependant. If ^{13}C,^{6}Li-coupling can be observed at low temperatures, the multiplicity of the ^{13}C-signals is always a *triplet.* In this respect, the S- and Se-derivatives behave like the halo-carbenoids [1]. This is also true for the changes $\Delta{}^1J$(C,H) and $\Delta{}^1J$(C,C) of the coupling constants with hydrogens or carbons directly bonded to the α-S- or α-Se-C-atom: the ΔJ values are negative, *i.e.* the coupling decreases upon lithiation (see *Tables 6–8* and *Fig. 6b*). Exceptions are the labelled bis(sulfonium) salt *vs.* the ylid **8**, where the ^1J(C,H) increases by 32 Hz *(Table 6),* and the labelled 2-phenyl-1,3-dithiane *vs.* the corresponding 2-(^{6}Li)lithio-2-phenyl-1,3-dithiane **12****, where $\Delta{}^1J$(C,C) is +0.5 Hz *(Table 7).*

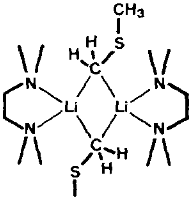
An experiment which could not possibly have been done with the halogen analogues is the measurement of the C,C-coupling across the heteroatom: as can be seen from the data in *Table 7* (see also *Fig. 3* and *4*), the corresponding coupling constants ^2J(C,C) are *zero* in the protonated precursors and 3.7–7.5 Hz in the carbanion deriva-

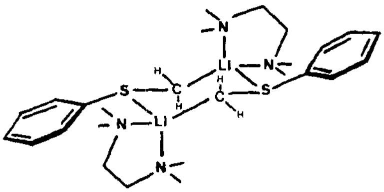
---

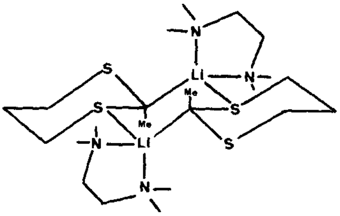
⁹) See [1] and lit. cited therein.

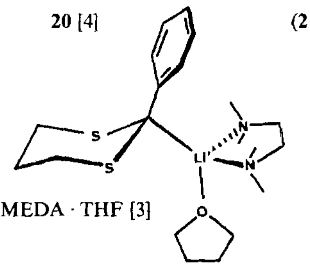
tives; the geminal coupling is 'turned on' upon lithiation or deprotonation, also in the ylid **8**. Another type of coupling which can not be observed with halogen derivatives (quadrupole effects!) is the direct coupling of the C-atom under consideration with the attached heteroatom. This was possible with the Se-substituted species, at least in some cases (see *Table 8* and *Fig. 5*): in contrast to the direct C,H- and C,C-coupling which decrease upon lithiation, the direct ^{77}Se,^{13}C-coupling increases.

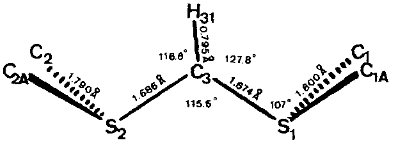
C) Discussion of the Results. – In this section, only qualitative arguments will be applied, a quantitative analysis of the NMR results must be reserved to specialists and might require further measurements such as a UV/VIS spectral comparison of the protonated with the lithiated species, or ^{6}Li-NMR measurements to determine Li-shifts.


20 [4]


(**2** · TMEDA)$_2$ [4]

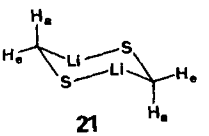

(**11** · TMEDA)$_2$ [3]


12 · TMEDA · THF [3]

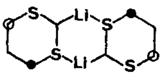


8 ($BF_4^{\ominus}$ instead of $B(C_6H_5)_4^{\ominus}$)^{3})

Aggregation of the S- and Se-Substituted Lithium Compounds. The X-ray crystal structures of the five S-substituted carbanion derivatives determined in our laboratory are of four different kinds. (Methylthio)methyllithium·TMEDA is dimeric, with C-bridging to give a four-membered ring, see **20**. Lithiated thioanisol and methyldithiane are also dimeric, but with S-bridging in a chair-like six-membered ring arrangement (see (**2**·TMEDA)$_2$ and (**11**·TMEDA)$_2$), while lithiated phenyldithiane and – not surprisingly – the ylid salt are monomeric (see **12**·TMEDA·THF and **8** (BF_4^- instead of BPh_4^-), respectively). Of the 18 S-, and Se-substituted (^{6}Li) organolithium compounds studied in the present ^{13}C-NMR investigation, 11 showed a ^{13}C-NMR signal split to a triplet by a single ^{6}Li-neighbour ($I = 1$), and 7 gave singlets even at very low temperatures. The species which give rise to triplet signals must be monomeric or aggregated through heteroatoms, *cf.* (**2**·TMEDA)$_2$, (**11**·TMEDA)$_2$, **12**·TMEDA·THF. In the cases of the lithiated thioanisol **2** and of 2-(^{6}Li)lithio-2-methyl[2-^{13}C]-1,3-dithiane (**11**), we tried to establish the presence of the same dimers in solution, which we see in the crystal (see *above*) – without success: neither did we observe two types of H-atoms (H$_a$ and H$_e$, see **21**) in the former case, nor two types of C-atoms (see ○ and ● in **22**) with



21

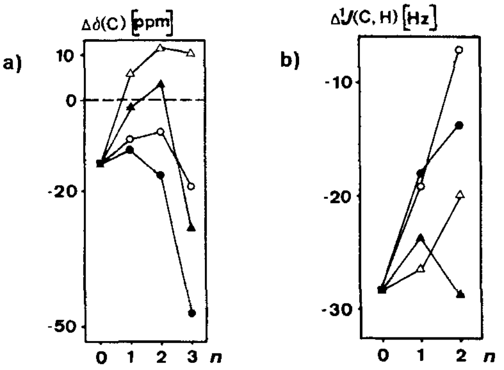


22

the latter compound *(cf. Fig. 3)*. Since it is unlikely that the two types of nuclei are accidentally isochronous, they either interchange positions rapidly on the NMR time scale even below −100° or the structures in solution differ from those in the crystalline state[10]).

Which Conclusions about the Nature of the C–Li Bond Can Be Obtained from the Data in Hand? The species of which we observe ^{6}Li,^{13}C-coupling can not be solvent-separated ion pairs: since nuclear spin-spin coupling is mediated through σ-electrons, there must be at least a contribution of covalency to these Li–C bonds. In the absence of coupling, there are either exchange processes, which are fast on the NMR time scale, or the Li–C bond is dissociated[11])[12])[13]). Although the ^{6}Li,^{13}C-coupling is not as structure-independant as in the case of halogeno-lithio-carbenoids (^1J(C,Li) = 16–17 Hz [1]), ^1J(C,Li) varies from 7 to 11 Hz in the S- and from 10 to 12 Hz in the Se-derivatives (*Tables 6* and *8*).

Chemical Shifts of the Lithiated C-Atoms and their ^{1}H,^{13}C-, ^{13}C,^{13}C-, and ^{77}Se,^{13}C-Couplings. Naively, one might expect that H/Li-exchange on a C-atom causes a shielding (negative $\Delta\delta$(C)), an upfield shift of its ^{13}C-NMR signal. This effect is observed with the S-derivatives (*Tables 2* and *3*), while the halogeno-carbenoids and all compounds with lithiated C-atoms which are part of an olefinic, acetylenic, and aromatic π-system show a strong opposite, *i.e.* deshielding effect (positive $\Delta\delta$(C), see [1] and earlier lit. cited therein). The Se-derivatives *(Table 5)* have small, mostly positive $\Delta\delta$(C)-values (see also *Fig. 6*). Since the chemical shifts depend upon hybridization,



	$(RX)_n{}^{13}CH_{3-n}{}^6Li$ *vs.*	$(RX)_n{}^{13}CH_{4-n}$	
	R	X	*n*
●	phenyl	S	1–3
○	alkyl		
▲	phenyl	Se	1–3
△	alkyl		
■	methane		

Fig. 6. *Comparison of ^{13}C-NMR shifts* (a) *and C,H-coupling constants* (b) *of open chain α-S- and α-Se-substituted organolithium compounds with those of the protonated precursors.* n = degree of substitution. For a comparison with the non-lithiated derivatives and with the corresponding halogenated methanes, see [1] [2]. Note that for both, the S- and the Se-derivatives, the $\Delta\delta$ values in the aryl series are smaller than in the corresponding alkyl series.

---

[10]) Molecular weight determinations by measuring freezing-point depressions of THF-solutions of Li-derivatives are being carried out in our laboratories. They furnish information about the major species present in solution at low temperatures.

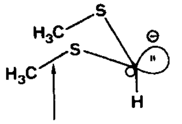
[11]) The fact *(Fig. 1)* that the disappearance of coupling upon warming is concentration-dependant proves the bimolecular nature of the process.

[12]) The chemical shifts of the signals hardly change within large temperature intervals, while the coupling appears or disappears. This suggests that the character of bonding in the observed species does not change either.

[13]) Our previous proposition [1] that contact ion pairs are indicated by the lack of coupling can not be maintained in view of our newest results[11]) [4].

charge density, inductive and steric effects, anisotropy of neighbouring groups, the heavy atom effect, *etc.*, they are most difficult to interpret with respect to structural changes. More general conclusions have been drawn from the C,H-coupling constants, which correlate with the s-character of the C–H bonds [30–36] [39]. In organolithium derivatives, a decrease of the C,H- and also of the C,C-coupling constants, as compared with the protonated analogues, is observed [1]. This is confirmed here for the S- and Se-substituted Li-compounds (see negative Δ^1J(C,H)- and Δ^1J(C,C)-values in *Table 6* and *8*). The X,C-coupling with carbanionoid C-atoms has thus far been observed for X = P [32] [35] [36]; it is strongly increased as compared with the protonated precursors just like the Se,C-coupling constants of some Se-derivatives reported here (see *Table 8*, last column).

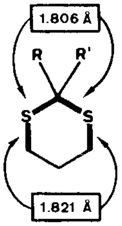
Stabilization of Carbanionic Centers by S-Substitution[14]. The different effects which supposedly contribute to the stabilization of carbanion derivatives by S and other third- and higher-row elements have been mentioned in the *Introduction*. The most recent calculations give accurate geometries of the minimum-energy structures with bond-length changes which should occur upon deprotonation [19–21] [25]. Thus, *Lehn & Wipff* calculated the bond lengthening by the n_C-σ^*_{S-C} delocalization to be 0.03 Å [25] in deprotonated thioacetals, see **23**. These predictions are now subject to comparison with our crystal structure [3] [4] and ^{13}C-NMR data.



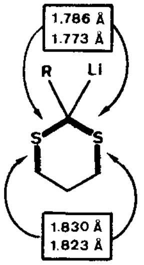
23

0.03 Å (calculated) lengthening as compared with the protonated species

From a comparison of the S–C bond lengths of some non-metalated dithianes and aryl methyl sulfides obtained from the *Cambridge Crystallographic Data File* [40] with



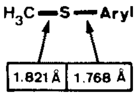
average S–C bond lengths from 5 crystal structures of non-metallated dithianes



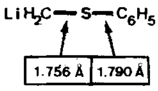
in (**11** · TMEDA)$_2$
in **12** · TMEDA · THF

in (**11** · TMEDA)$_2$
in **12** · TMEDA · THF

S–C bond lengths in (**11** · TMEDA)$_2$ and **12** · TMEDA · THF [3]



average values from 8 crystal structures



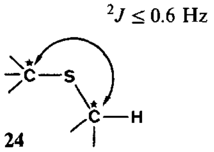
S–C bond lengths in (**2** · TMEDA)$_2$ [4]

---

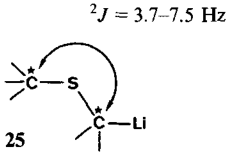
[14] The crystal structure of the ylid salt **8** will be discussed and compared with theoretical predictions in a separate paper, see also *Footnote 3*.

the S–C bond lengths in the three crystal structures of (**2**·TMEDA)$_2$, (**11**·TMEDA)$_2$, and **12**·TMEDA·THF, it appears, that the S–C bond with the carbanionoid C-atom is shortened, as expected for a partial double-bond character. Less pronounced is the change in lengths of the S–C bonds which are supposed to be σ^*-acceptors: they are lengthened to an extend which is just barely outside of experimental error.

In the ^{13}C-NMR spectra, we observed a striking effect which must be connected with bonding in these systems: the appearance of coupling (^2J(C,C)) between the lithiated (or ylidic) C-atom and its geminal partner on S, which is not observed in the



24



25

protonated precursor, compare **24** and **25** (see *Fig. 3* and *4*, and the 6 examples in *Table 7*). An admittedly speculative suggestion is that this phenomenon might result from a n_C-σ^{*}_{S-C} delocalization.

We thank Professors *J. F. M. Oth* and *R. R. Ernst* for supplying machine time on *Varian CFT 20* and *XL 100* NMR spectrometers. Discussions with Professors *E. L. Eliel, J. M. Lehn,* and *P. v. R. Schleyer* are gratefully acknowledged.

Experimental Part

1. General Remarks. – See [1] [2]. ^{13}C-NMR spectra: *Varian XL-100* (25.6 MHz) and *Varian CFT 20* (20.0 MHz) with low-temp. equipment. δ-values in ppm, related to the low-field signals of the solvents (THF: 67.96 ppm, MTHF: 75.38 ppm); resolution: ±0.024 ppm (4096 data points). Coupling constants $J(^{13}C,^{1}H)$, $J(^{13}C,^{6}Li)$, $J(^{13}C,^{13}C)$, and $J(^{77}Se,^{13}C)$ in Hz; resolution, if there is no other statement: ±0.6 Hz.

2. Preparation of the Labelled Precursors. – See [2].

3. General Procedures for the Preparation of the ^{13}C-NMR Probes (see *Table 9*). – *Method A: H,Li-Exchange with (^{6}Li)BuLi.* To a NMR tube (∅ 10 mm) containing *ca.* 0.3 mmol of ^{13}C-labelled precursor under Ar were added *ca.* 1.5 ml of solvent and 0.3 ml of (D$_8$)THF. After cooling to the appropriate temp. (see *Table 9*), 1 equiv. of (^{6}Li)BuLi in hexane was added slowly. When the reaction was completed, the ^{13}C-NMR measurement was carried out. Finally, the probe was quenched with MeOH or wet THF.

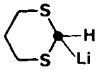
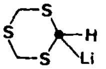
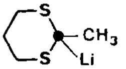
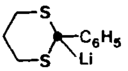
Method B: H,Li-Exchange with Lithium Diisopropylamide (LDA). A solution of LDA in 1 ml of solvent was prepared from 30.4 mg (0.3 mmol) of diisopropylamine and 1 equiv. (^{6}Li)BuLi in hexane under Ar in the NMR tube. After cooling to the appropriate temp. (see *Table 9*), a solution of the labelled compound in 1 ml of solvent [containing 0.3 ml of (D$_8$)THF] was added. The resulting lithiated compound was measured and then quenched with MeOH or wet THF.

Method C: RSe,Li-Exchange with (^{6}Li)BuLi. The procedure for this reaction is identical to *Method A*, but starts from the substrate with one additional RSe-substituent.

*(Phenylthio)[^{13}C]methyl(^{6}Li)lithium – (*N,N,N',N'*-Tetramethylethylenediamine) (2/2)* ((**2**·TMEDA)$_2$ in Me$_2$O)·Crystals of (**2**·TMEDA)$_2$ were prepared in the same way as for the X-ray analysis [4], but with ^{13}C- and ^{6}Li-label. These crystals were transfered under Ar countercurrent into the NMR tube and dissolved in *ca.* 2 ml (D$_6$)Me$_2$O.

(Butylthio)[^{13}C]methyl(^{6}Li)lithium (**1**). To 15 mg (0.13 mmol) of TMEDA in a NMR tube (∅ 8 mm) was added 1 equiv. of (^{6}Li)BuLi in hexane under Ar at 0°. On addition of a solution (33%) of 14 mg (0.13 mmol) (butylthio)[^{13}C]methane in pentane, a white precipitate was formed. The suspension was kept for 4 h at r.t. Then, the solid was dissolved by addition of 1 ml of THF (containing 0.1 ml of (D$_8$)THF) at −20°. The ^{13}C-NMR showed only a partial deprotonation under these conditions.

Table 9. *Generation of the (^6Li)Lithiated Compounds*

Compound		Method	Solvent	Reaction conditions	Lit.
$C_6H_5S*CH_2Li$	**2**	A	THF/TMEDA	10 min at r.t.	[38]
$(CH_3S)_2*CHLi$	**3**	A	THF	2.6 h at −30° to −20°	[41]
$(CH_3S)_2*C(C_4H_9)Li$	**4**	A	THF	2 h at −35° (from **6** and BuLi)	
$(C_6H_5S)_2*CHLi$	**5**	A	THF	10 min at 0°	[38]
$(CH_3S)_3*CLi$	**6**	A	THF	30 min at −78°	[42]
$(C_6H_5S)_3*CLi$	**7**	A	MTHF	10 min at −78°	[43]
	**9**	A	THF	1.5 h at −20°	[15]
	**10**	A	THF	1.5–2.5 h at 20° to −15°	[44]
	**11**	A	THF	1.5 h at −20°	[15]
	**12**	A	THF	1 h at −40°	[15]
CH_3Se*CH_2Li	**13**	C	MTHF	10 min at −78°	[45]
$C_6H_5Se*CH_2Li$	**14**	C	THF	1 h at −78°	[46]
$C_6H_5Se*CH(*CH_3)Li$	**15**	C	THF	15 min at −78°	[47]
$(CH_3Se)_2*CHLi$	**16**	C	MTHF	inverse addition 30 min at −78°	[48]
$(C_6H_5Se)_2*CHLi$	**17**	B/C	THF	1 h at −78°	[46]
$(CH_3Se)_3*CLi$	**18**	B	MTHF	30 min at −78°	[48]
$(C_6H_5Se)_3*CLi$	**19**	B	THF	warm up to −50°	[46]

REFERENCES

[1] *D. Seebach, R. Hässig & J. Gabriel,* Helv. Chim. Acta *66,* 308 (1983).

[2] *J. Gabriel & D. Seebach,* Helv. Chim. Acta *67,* 1070 (1984).

[3] *R. Amstutz, D. Seebach, P. Seiler, B. Schweizer & J.D. Dunitz,* Angew. Chem. *92,* 59 (1980), ibid. Int. Ed. *19,* 53 (1980); *R. Amstutz, J.D. Dunitz & D. Seebach,* Angew. Chem. *93,* 487 (1981), ibid. Int. Ed. *20,* 465 (1981).

[4] *R. Amstutz, Th. Laube, W.B. Schweizer, D. Seebach & J.D. Dunitz,* Helv. Chim. Acta *67,* 1100 (1984).

[5] *H. Gilman & F.J. Webb,* J. Am. Chem. Soc. *62,* 987 (1940); *H. Gilman & F.J. Webb,* ibid. *71,* 4062 (1949); *H. Gilman & J.W. Morton, Jr.,* Org. React. *VIII,* 258 (1954).

[6] *W. von E. Doering & L.K. Levy,* J. Am. Chem. Soc. *77,* 509 (1955); *W. von E. Doering & K.C. Schreiber,* ibid. *77,* 514 (1955); *W. von E. Doering & A.K. Hoffmann,* ibid. *77,* 521 (1955).

[7] *S. Oae, W. Tagaki & A. Ohno,* J. Am. Chem. Soc. *83,* 5036 (1961); *S. Oae, W. Tagaki & A. Ohno,* Tetrahedron *20,* 417 (1964).

[8] *A.I. Shatenshtein & H.A. Gvozdeva,* Tetrahedron *25,* 2749 (1969).

[9] *A. Streitwieser, Jr. & S.P. Ewing,* J. Am. Chem. Soc. *97,* 190 (1975).

[10] *F.G. Bordwell, J.E. Bares, J.E. Bartmess, G.E. Drucker, J. Gerhold, G.J. McCollum, M. Van der Puy, N.R. Vanier & W.S. Matthews,* J. Org. Chem. *42,* 326 (1977).

[11] *E.L. Eliel, A.A. Hartmann & A.G. Abatjoglou,* J. Am. Chem. Soc. *96,* 1807 (1974); *A.G. Abatjoglou, E.L. Eliel & L.F. Kuyper,* ibid. *99,* 8262 (1977).

[12] *A.I. Meyers & A.L. Campbell,* Tetrahedron Lett. *1979,* 4155; *A.I. Meyers & A.L. Campbell,* ibid. *1979,* 4159.

[13] *E.L. Eliel & S. Otsuka,* 'Asymmetric reactions and processes in chemistry', ACS-Symposium 185, p. 37ff. (1982).

[14] *J.F. Arens, M. Fröling & A. Fröling*, Recl. Trav. Chim. Pays-Bas *78*, 663 (1959); *A. Fröling & J.F. Arens*, ibid. *81*, 1009 (1962).

[15] *E.J. Corey & D. Seebach*, Angew. Chem. *77*, 1134 and 1135 (1965); ibid. Int. Ed. *4*, 1075 and 1077 (1965).

[16] *D. Seebach*, Angew. Chem. *81*, 690 (1969); ibid. Int. Ed. *8*, 639 (1969); *D. Seebach*, Synthesis *1969*, 17; *D. Seebach, K.-H. Geiss, M. Kolb & A.K. Beck*, in 'Modern Synthetic Methods 1976', ed. R. Scheffold, Sauerländer AG, Aarau, Switzerland, p. 173; *B.-T. Gröbel & D. Seebach*, Synthesis *1977*, 357.

[17] *D. Seebach*, Angew. Chem. *91*, 259 (1979); ibid. Int. Ed. *18*, 239 (1979).

[18] *D.P. Craig, A. Maccoli, R.S. Nyholm, L.E. Orgel & L.E. Sutton*, J. Chem. Soc. *1954*, 332; *D.P. Craig & E.A. Magnusson*, J. Chem. Soc. *1956*, 4895; *D.P. Craig*, Chem. Soc. (London), Spec. Publ. No. *12*, 343 (1958).

[19] *D.J. Mitchell, S. Wolfe & H.B. Schlegel*, Can. J. Chem. *59*, 3280 (1981).

[20] *R.A. Eades, P.G. Gassman & D.A. Dixon*, J. Am. Chem. Soc. *103*, 1066 (1981).

[21] *G.D. Andreetti, F. Bernardi, A. Bottoni & A. Fava*, J. Am. Chem. Soc. *104*, 2176 (1982).

[22] *S. Wolfe, L.A. La John, A. Mangini & G. Tonachini*, Tetrahedron Lett. *1983*, 3789; *S. Wolfe, A. Stolow & L.A. La John*, ibid. *1983*, 4071.

[23] *A. Streitwieser, Jr. & J.E. Williams, Jr.*, J. Am. Chem. Soc. *97*, 191 (1975); *F. Bernardi, I.G. Csizmadia, A. Mangini, H.B. Schlegel, M.-H. Whangbo & S. Wolfe*, J. Am. Chem. Soc. *97*, 2209 (1975).

[24] *N.D. Epiotis, R.L. Yates, F. Bernardi & S. Wolfe*, J. Am. Chem. Soc. *98*, 5435 (1976).

[25] *J.-M. Lehn & G. Wipff*, J. Am. Chem. Soc. *98*, 7498 (1976).

[26] *J.-M. Lehn, G. Wipff & J. Demuynck*, Helv. Chim. Acta *60*, 1239 (1977).

[27] *A. Streitwieser*, in 'Comprehensive Carbanion Chemistry', Part A, eds. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980, p. 373.

[28] a) *A. Streitwieser, Jr., J.E. Williams, S. Alexandratos & J.M. McKelvey*, J. Am. Chem. Soc. *98*, 4778 (1976); b) *M.F. Guest, I.H. Hillier & V.R. Saunders*, J. Organomet. Chem. *44*, 59 (1972); *N.C. Baird, R.F. Barr & R.K. Datta*, ibid. *59*, 65 (1973); *T. Clark, P.v.R. Schleyer & J.A. Pople*, J. Chem. Soc., Chem. Commun. *1978*, 137; *G.D. Graham, D.S. Marynick & W.N. Lipscomb*, J. Am. Chem. Soc. *102*, 4572 (1980); *G. Graham, St. Richtsmeier & D.A. Dixon*, J. Am. Chem. Soc. *102*, 5759 (1980); c) *J.D. Dill, P.v.R. Schleyer, J.S. Binkley & J.A. Pople*, J. Am. Chem. Soc. *99*, 6159 (1977).

[29] *D. Seebach, H. Siegel, K. Müllen & K. Hiltbrunner*, Angew. Chem. *91*, 844 (1979); ibid. Int. Ed. *18*, 784 (1979); *H. Siegel, K. Hiltbrunner & D. Seebach*, Angew. Chem. *91*, 845 (1979); ibid. Int. Ed. *18*, 785 (1979); *D. Seebach, H. Siegel, J. Gabriel & R. Hässig*, Helv. Chim. Acta *63*, 2046 (1980); *R. Hässig & D. Seebach*, Helv. Chim. Acta *66*, 2269 (1983).

[30] *G. Chassaing & A. Marquet*, Tetrahedron *34*, 1399 (1978).

[31] *R. Lett & G. Chassaing*, Tetrahedron *34*, 2705 (1978).

[32] *T. Bottin-Strzalko, J. Seyden-Penne, M.-J. Pouet & M.P. Simonnin*, J. Org. Chem. *43*, 4346 (1978).

[33] *G. Barbarella, P. Dembach & A. Garbesi*, Tetrahedron Lett. *21*, 2109 (1980).

[34] *G. Barbarella, P. Dembach, A. Garbesi & P. Fabbri*, Tetrahedron Lett. *23*, 763 (1982).

[35] *H. Schmidbaur, A. Schier, B. Milewski-Mahrla & U. Schubert*, Chem. Ber. *115*, 722 (1982); *H. Schmidbaur, W. Buchner & D. Scheutzow*, Chem. Ber. *106*, 1251 (1973).

[36] *K.A.O. Starzewski & H.T. Dieck*, Phosphorus *6*, 177 (1976).

[37] *G.M. Drew & W. Kitching*, J. Org. Chem. *46*, 558 (1981).

[38] *E.J. Corey & D. Seebach*, J. Org. Chem. *31*, 4097 (1966).

[39] *N. Muller & D.E. Pritchard*, J. Chem. Phys. *31*, 1471 (1959); *G.A. Olah & A.M. White*, J. Am. Chem. Soc. *91*, 5801 (1969); *G.A. Olah, Y.K. Mo & Y. Halpern*, J. Am. Chem. Soc. *94*, 3551 (1972); *G.A. Olah, G. Liang, D.B. Ledlie & M.G. Costopoulos*, J. Am. Chem. Soc. *99*, 4196 (1977); *L.J. Guggenberger & R.R. Schrock*, J. Am. Chem. Soc. *97*, 6578 (1975); *R.R. Schrock*, Acc. Chem. Res. *12*, 98 (1979); *E.O. Fischer*, Angew. Chem. *86*, 651 (1974), and references cited therein.

[40] Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, England.

[41] *M. Braun & D. Seebach*, Chem. Ber. *109*, 669 (1976).

[42] *D. Seebach, K.-H. Geiss, A.K. Beck, B. Graf & H. Daum*, Chem. Ber. *105*, 3280 (1972).

[43] *D. Seebach*, Chem. Ber. *105*, 487 (1972).

[44] *D. Seebach & A.K. Beck*, Org. Synth. *51*, 39 (1971).

[45] *D. Van Ende, W. Dumont & A. Krief*, Angew. Chem. *87*, 709 (1975); ibid. Int. Ed. *14*, 700 (1975).

[46] *D. Seebach & N. Peleties*, Chem. Ber. *105*, 511 (1972).

[47] *D. Seebach & A.K. Beck*, Angew. Chem. *86*, 859 (1974); ibid. Int. Ed. *13*, 806 (1974).

[48] *D. Van Ende, A. Cravador & A. Krief*, J. Organomet. Chem. *177*, 1 (1979).