# 74. Synthesis and X-Ray Structure of Bis{*S*-(1-lithio-3,3-diphenylprop-2-enyl)-*N*-methyl-*S*-phenylsulfoximine–Tetrahydrofuran (1/2)} Complemented by Model *ab initio* Calculations of α-Lithiosulfoximines

by **Jürgen F. K. Müller**[a]), **Rohit Batra**[b]), **Bernhard Spingler**[a]), and **Margareta Zehnder**[a])*

[a]) Institute for Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel
[b]) Institute for Organic Chemistry, University of Basel, St. Johanns-Ring 16, CH-4056 Basel

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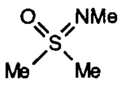
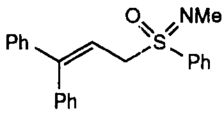
The gas-phase structure of *N,S,S*-trimethylsulfoximine **1** and of its monolithiated isomers **2**–**4** was calculated by *ab initio* methods. It was found that a Li–C–S–N four-membered chelate **2** is the most stable isomer. The second minimum **4** shows N–Li–O complexation and is only slightly higher in energy. Li-Contacts with the C(α) atom and the sulfoximine O-atom in **3** are energetically disfavored by 6.1 kcal/mol. The two transition states **5** and **6** suggest an interconversion mechanism of **2** to **3** with **4** as an intermediate. A comparison of **4** with the crystal structure of the THF solvate **7**, which was prepared by the addition of BuLi to (±)-*S*-(3,3-diphenylprop-2-enyl)-*N*-methyl-*S*-phenylsulfoximine (**8**) at low temperature in THF, demonstrates that the coordination geometry in the solid state is in good agreement with the calculated structure. The (1-lithioallyl)sulfoximine **7** crystallized as a centrosymmetric *dimeric* aggregate featuring an eight-membered ring with the atomic sequence (Li–N–S–O)$_2$. The O-atoms of two THF molecules and the sulfoximine O- and N-atoms are coordinated to the Li-atom in a *tetrahedral* orientation. After metallation, a significant shortening of the S–C(α) bond is observed. Remarkably, only one of the two possible diastereoisomeric enantiomer pairs is found in the solid state.

**Introduction.** – Sulfur-stabilized carbanions which are chiral at the S-atom such as the (lithioalkyl)sulfoximines play a significant role as intermediates in asymmetric synthesis [1]. Early structural investigations showed the anions to be pyramidal and to contain direct Li–C bonds [2][1]). Our ongoing studies have demonstrated new coordination possibilities for the Li-atom and new possibilities for the stabilization of the negative charge in such compounds. In this paper, we report model *ab initio* calculations of the gas-phase structures of *N,S,S*-trimethylsulfoximine (**1**) and the (lithiomethyl)dimethyl-



**1**



**8**

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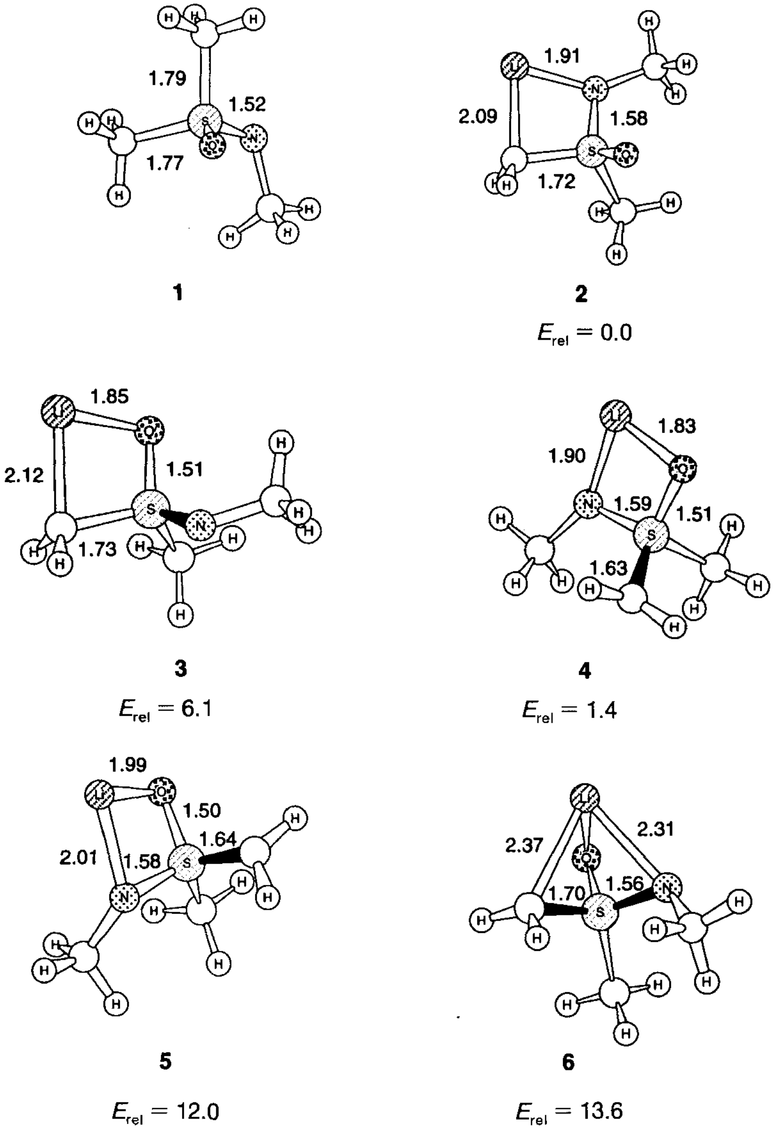
[1]) During the submission of this manuscript, the crystal structure of a solvent-separated (lithioallyl)sulfoximine was published [2d].

sulfoximine isomers **2**–**4** at the MP2/6-31 + G**//HF/6-31 + G**-level of theory[2]. An X-ray structure analysis of the 1-lithiopropenyl derivative **7** of *S*-(3,3-diphenylprop-2-enyl)-*N*-methyl-*S*-phenylsulfoximine (**8**) is also described.



**1**

**2** $E_{rel} = 0.0$

**3** $E_{rel} = 6.1$

**4** $E_{rel} = 1.4$

**5** $E_{rel} = 12.0$

**6** $E_{rel} = 13.6$

Fig. 1. *MP2/6-31 + G**//HF/6-31 + G** relative energies* $E_{rel.}$ [kcal/mol] *and bond lengths* [Å]

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[2] All calculations were carried out with Gaussian series of programms [3]. The groundstates as well as the transition states were calculated at the MP2/6-31 + G**//HF/6-31 + G** level of theory. Transition states were checked by frequency calculations. To find out whether the transition state **5** and **6** lead to the intermediates **2** and **4**, and **4** and **3**, respectively, IRC calculations were performed.

**Results and Discussion.** – *Ab initio* calculations of the lithiated dimethylsulfoximine **1** yielded three different major structural minima **2**–**4** (*Fig. 1*). Of these, **2** exhibits a Li–C–S–N four-membered chelate ring; Li–O complexation and a Li–C contact are found in **3**, whereas, quite unexpectedly, in **4** no Li–C contact occurs. There, the sulfoximine O- and N-atoms coordinate to the $Li^+$ ion in an orientation reminiscent of typical (lithioalkyl)phenylsulfones [4] [5]. The Li–N,C chelate **2** represents the structure lowest in energy, but, surprisingly, the sulfoximine O- and N-coordinated Li salt **4** is only by 1.4 kcal/mol higher in energy, whereas the Li–O,C chelation in **3** is clearly energetically disfavored by 6.1 kcal/mol compared to **2** and **4**. Lithiation of the trimethylsulfoximine **1** causes a number of distinctive structural changes: in **2**, a lengthening of the S–N (1.52 *vs.* 1.58 Å) bond is observed. Similarly, the O,C chelation in **3** lengthens the S–O bond from 1.45 to 1.51 Å, whilst in **4** with N,O coordination, both the S–N and S–O bonds are lengthened (S–N 1.59 Å, S–O 1.51 Å *vs.* S–N 1.52, S–O 1.45 Å in **1**). The C(α)–Li contact admits only a small shortening of the S–C(α) bond in **2** (1.72 Å) and **3** (1.73 Å), whereas in **4** a significant shortening of the S–C(α) bond is observed (1.63 *vs.* 1.77 Å in **1**). The anionic center in all three isomers tends towards a *pyramidal* geometry as demonstrated by the dihedral angle S–C–H–H in *Table 1*. Structure **5** shows a coordination of the $Li^+$ ion to the O- and N-atom and *can be interpreted* as the transition state between the structure minima **2** and **4**. The isomers **4** and **3** are separated by the transition state **6** by 12.2 kcal/mol. In **6**, an unsymmetrical tridentate bonding of the Li- to the O,N- and C(α) atom is found in contrast to **5** where no Li–C bonding is observed. These results suggest an interconversion mechanism of **2** to **3** with **4** as an intermediate.

Table 1. *Selected Bond Length* [Å] *and Angles* [°] *of* **1**–**6**[a])

| | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Li–N | | 1.91 | | 1.90 | 2.01 | 2.31 |
| Li–O | | | 1.85 | 1.83 | 1.99 | 1.98 |
| Li–C | | 2.09 | 2.12 | | | 2.37 |
| S–C(α) | 1.77 | 1.72 | 1.73 | 1.63 | 1.64 | 1.70 |
| S–C | 1.79 | 1.79 | 1.79 | 1.78 | 1.80 | 1.79 |
| S–N | 1.52 | 1.58 | 1.52 | 1.59 | 1.58 | 1.56 |
| S–O | 1.45 | 1.46 | 1.51 | 1.51 | 1.50 | 1.48 |
| Li–C–S | | 82 | 79 | | | 65 |
| Li–N–S | | | 104 | | | 68 |
| O–S–N | | | | 100 | 107 | 106 |
| S–C–H | 122 | 108 | | | | 112 |
| S–C–H–H | | 119 | 120 | 143 | 14 | 129 |

[a]) All calculations were carried out at the MP2/6-31 + G**//HF/6-31 + G** level of theory.

The lithiated (allyl)sulfoximine **7** was obtained by treating racemic *S*-(3,3-diphenylprop-2-enyl)-*N*-methyl-*S*-phenylsulfoximine (**8**) with BuLi at low temperatures in THF. Recrystallization of the resulting red precipitate from THF afforded red single crystals, suitable for X-ray analysis. *Fig. 2* shows the molecular structure of the Li complex **7** as a stereopicture. For comparison, the molecular structure of the educt **8** was also determined. *Table 2* summarizes all relevant distances and angles of **7** and **8** (for atom numbering, see *Fig. 3*).

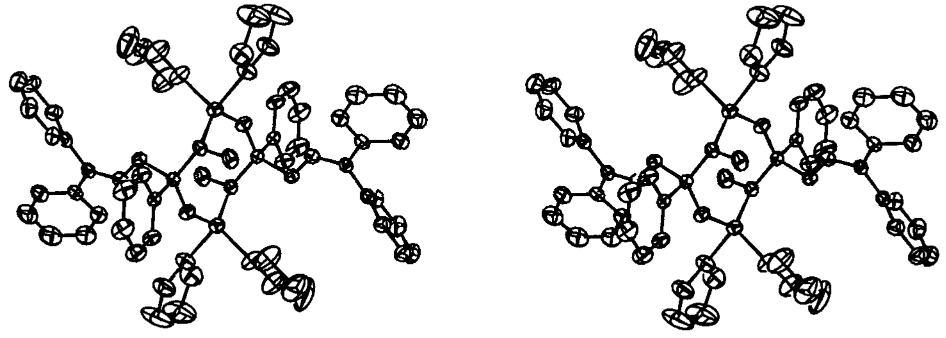

Fig. 2. *Stereopicture of Bis*{S-*(1-lithio-3,3-diphenylprop-2-enyl)*-N-*methyl*-S-*phenylsulfoximine – tetrahydrofuran (½)*} (7)

Table 2. *Selected Intramolecular Distances* [Å] *and Angles* [°] *of* 7 *and* **8**

| | Distances | | | Angles[a]) | |
|---|---|---|---|---|---|
| | 7 | **8** | | 7 | **8** |
| Li(1)–N(1) | 2.022(6) | | O(1')–Li(1)–N(1) | 119.7(3) | |
| Li(1)–O(1') | 1.914(6) | | O(1')–Li(1)–O(4) | 103.0(3) | |
| S(1)–C(1) | 1.659(3) | 1.773(4) | O(1')–Li(1)–O(5) | 102.2(3) | |
| S(1)–C(10) | 1.798(3) | 1.792(4) | S(1)–C(1)–C(2) | 120.4(3) | 109.3(2) |
| S(1)–N(1) | 1.526(3) | 1.506(3) | O(1)–S(1)–N(1) | 119.3(1) | 121.2(2) |
| S(1)–O(1) | 1.456(2) | 1.451(3) | C(1)–C(2)–C(3) | 128.6(3) | 125.1(3) |
| C(1)–C(2) | 1.402(5) | 1.494(5) | C(2)–C(3)–C(20) | 120.5(3) | 120.4(3) |
| C(2)–C(3) | 1.375(4) | 1.336(4) | C(2)–C(3)–C(30) | 121.3(3) | 122.2(3) |
| C(3)–C(20) | 1.474(5) | 1.496(5) | | | |
| C(3)–C(30) | 1.466(5) | 1.483(5) | | | |

[a]) The position of atoms marked with a prime are obtained by the symmetry operator $-x, -y, -z$.

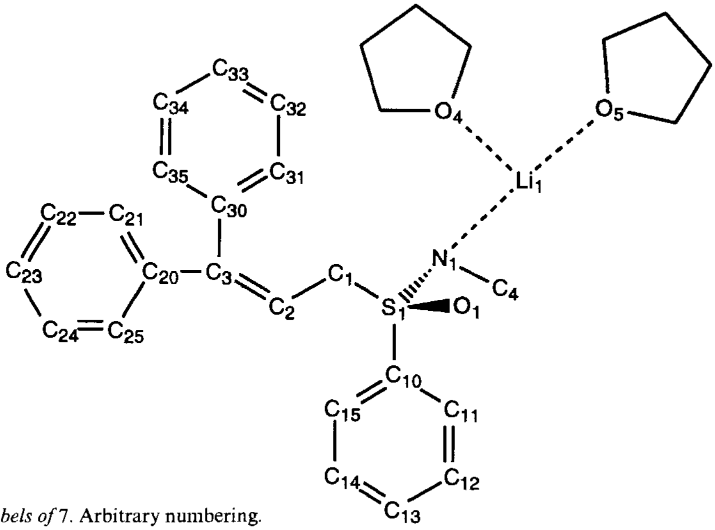

Fig. 3. *Atom labels of* 7. Arbitrary numbering.

In 7, two (lithioallyl)sulfoximine moieties with opposite chirality are linked by N–Li–O bridges to give an eight-membered ring with the atom sequence $(Li–N–S–O)_2$. Such a coordination is in good agreement with the calculated gas-phase structure **4**. In (lithioalkyl)sulfones, analogous arrangements were observed [4] [5]. In dimer **7**, the $Li^+$ ions are in a distorted *tetrahedral* environment, consisting of the O-atoms of two THF molecules and the sulfoximine O- and N-atoms. Remarkably, the Li–C bond found in all other (lithioalkyl)sulfoximines is absent [2b–d]. Apparently, the stabilization of the negative charge at the C(α) atom by conjugation with the allylic system is more favorable than forming a Li–C bond.

The *Newman* projection along the C(1)–S bond of **7** shows that C(1) is *pyramidal* in spite of the conjugation with the vinyl group, and the lone pair at C(1) is oriented in a *gauche* conformation between the O- and N-atoms of the sulfonimidoyl moiety (see *Fig. 4*). However, the allylic system is still conjugated, and the dihedral angle S(1)–C(1)–C(2)–C(3) of 166.2° allows an overlapping of the $n_C$-orbital on C(1) with the π-orbitals of the vinyl group. The (lithioallyl)sulfoximine **7** is not formally an allyllithium derivative because of the lack of direct Li–allyl interactions. However, it does contain an acceptor-substituted allyl anion with two different C–C bond lengths (1.40 Å C(1)–C(2) *vs.* 1.37 Å for C(2)–C(3)). Crystal structures which contain such a structural motif are rare, and only a few examples are known [2d] [6]. Deprotonation of **8** is accompanied by a reduction in the S(1)–C(1) bond length of *ca.* 0.11 Å; this corresponds to the situation in the calculated structures **1** and **4**. Remarkably, the central angle C(1)–C(2)–C(3) of the allylic system in **7** is increased to 128.6°, as was calculated for the allyl anion [7]. After lithiation of **8**, only one of the two possible diastereoisomeric, Li-bridged dimers was found in the crystal. NMR investigations are currently under way to determine the solution structure of this lithio compound.

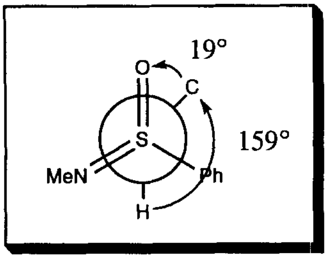

Fig. 4. Newman *projection along the S–C(1) bond of* 7

**Conclusion.** – *Ab initio* calculations on the lithiated *N,S,S*-trimethylsulfoximine system resulted in three different major energy minima where the Li–N,C chelate **2** and the sulfoximine N,O-coordinated Li salt **4** represent the most stable isomers. In contrast, Li–O,C coordination in **3** is energetically disfavored, so that N,C and N,O coordination should be preferred over O,C coordination. The transition states **5** and **6** suggest an interconversion mechanism of **2** to **3** with **4** as an intermediate. The crystal structure of the (lithioallyl)sulfoximine **7** was determined. It is a *dimeric* aggregate with N–Li–O coordination, similar to the situation found in **4**. Obviously, an individual crystal structure does not deliver sufficient information on all coordination possibilities, so the comparison of several crystal structures and the calculation of the gas-phase minima is necessary[3]) [9].

## Experimental Part

1. *Synthesis of* **7**. To a soln. of **8** (373 mg, 1.07 mmol) in $Et_2O$/THF 3:1 (4 ml), 1.51M BuLi in hexane (0.79 ml, 1.17 mmol) was slowly added at −78°. After precipitation of a red solid, the supernatant soln. was removed by decantation. Recrystallization of the solid residue from THF (2 ml) afforded red moisture-sensitive crystals of **7** (220 mg, 42%), which were suitable for X-ray analysis.

2. *X-Ray Analysis of* **7** *and* **8**. A red single crystal of **7** was sealed in a *Mark* capillary under $N_2$ and data measured at r.t. Additionally, a single crystal of **8** was measured under the same conditions. Unit-cell parameters were determined by centering 25 strong, independent reflections. The data were collected on a 4-circle *CAD4* (*Enraf-Nonius*) diffractometer and the usual corrections applied. The absorption correction was determined by psi-scans. The structures were solved by direct methods with the programme SIR92 (*C. Giacovazzo*, University of Bari, 1992) [10]. Anisotropic least-squares refinement was carried out on all non-H-atoms using the programme CRYSTALS (*D. Watkin*, University of Oxford, 1990) [11]. H-Atoms are in calculated positions with the exception of H(1) in structure **7**, which was refined isotropically while restraining the distance C(1)–H(1) to 1.0 Å [12]. Scattering factors were taken from the 'International Tables for Crystallography' (Vol. IV, Table 2.2B). Crystal data and other numerical details of the structure determination are listed in *Table 3*. *Fig. 2* was drawn with the programme SNOOPI [13].

Table 3. *Experimental Data for the X-Ray Diffraction Studies of* **7** *and* **8**

| | **7** | **8** |
|---|---|---|
| Formula | $C_{30}H_{36}LiNO_3S$ | $C_{22}H_{21}NOS$ |
| Space group | $I4_1/a$ | $P$-1 |
| a [Å] | 32.737(5) | 8.062(2) |
| $b$ [Å] | 32.737 | 9.577(2) |
| $c$ [Å] | 10.800(3) | 13.169(2) |
| $a$ [°] | 90 | 84.14(2) |
| β [°] | 90 | 83.15(2) |
| $\gamma$ [°] | 90 | 71.38(2) |
| Volume [$Å^3$] | 11574(4) | 954.4(4) |
| $Z$ | 16 | 2 |
| Crystal dimensions [mm] | 0.32 × 0.40 × 0.80 | 0.10 × 0.22 × 0.39 |
| Temperature [K] | 293 | 293 |
| $\Theta_{max}$ | 74.3 | 74.3 |
| Radiation | Cu$K_\alpha$ ($\lambda$ = 1.54178 Å) | Cu$K_\alpha$ ($\lambda$ = 1.54178 Å) |
| Scan mode | $\omega/2\Theta$ | $\omega/2\Theta$ |
| $\mu$ [$cm^{-1}$] | 11.79 | 15.19 |
| Max./min. transmission | 1/0.83 | 1/0.69 |
| No. of independent refl. | 4915 | 4160 |
| No. of refl. incl. in refinement | 3013 ($F > 3\sigma(F)$) | 2119 ($F > 3\sigma(F)$) |
| No. of parameters | 331 | 226 |
| $R$ (·100%) | 6.17 | 5.85 |
| $R_w$ (·100%) | 7.42 | 6.69 |
| $\Delta_\rho$ [e $Å^{-3}$] | 0.37/−0.38 | 0.42/−0.31 |
| Weighting scheme | $\omega \cdot (1 - (\delta F/6\sigma F)^2)^2$ | |
| $R$ value | $R = \Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert$ | |
| $R_w$ value | $R_w = \{(\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2 \cdot \omega)/\Sigma F_o{}^2 \cdot \omega\}^{1/2}$ | |

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[3]) Recently, the X-ray structure of an (1-lithiovinyl)sulfoximine was determined by our group [8].

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