CHIMIA 1999, *53*, No. 5

Chimia 53 (1999) 215–216

ISSN 0009–4293

Chiral Sulfur-Stabilized Lithium Compounds: Solid-State Structures and *Ab Initio* Calculations

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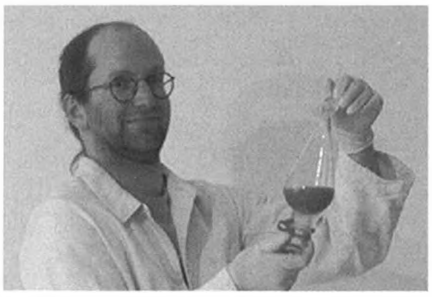
Abstract. The common structural features of monolithiated sulfoximines are presented. A comparison of solid-state and gas-phase structures of lithiated *N*,*S*,*S*-trimethylsulfoximines showed a good agreement, and theoretical studies based upon model compouds lead to a better understanding of the system.



Jürgen Müller studied chemistry at the University of Freiburg i. Br. and completed his doctoral studies at the University of Basel in 1993 under the guidance of *C. Bolm*. In 1994, he worked as a post-doctoral fellow with *M.A. Tius* at the University of Hawaii in the field of marine chemistry. He is currently a habilitand in the Institute of Inorganic Chemistry. Further details of his research interests are to be found at http://crystal.chemie.unibas.ch/xtl/projects/lithium.html.

Sulfur-stabilized organolithium compounds which bear a chiral sulfur-based auxiliary, such as the lithiosulfoximines, play a significant role as reagents in asymmetric synthesis [1]. Early structural investigations showed the anions to be pyramidal and to contain direct Li–C bonds [2]. Our ongoing studies have demonstrated new possibilities for the coordination of lithium and the stabilization of the negative charge in such compounds. We have crystallized several monolithiated sulfoximines and shown that they contain either C–Li or exclusively Li–heteroatom-bonds depending on the substituents at the C(α)-atom [3].

Racemic lithiated allyl or benzyl sulfoximines adopt structural motifs where two sulfoximine units with opposite chirality are linked by N–Li–O bridges to give eight-membered rings **A** with the atom sequence $(Li–N–S–O)_2$. With alkyl or alkenyl substituents, dimeric aggregates bridged through Li–sulfoximine-O bonds, giving two eight-membered rings with atomic sequences $(Li–O–S–N)_2$ and $(Li–O–S–C)_2$, respectively, are formed.

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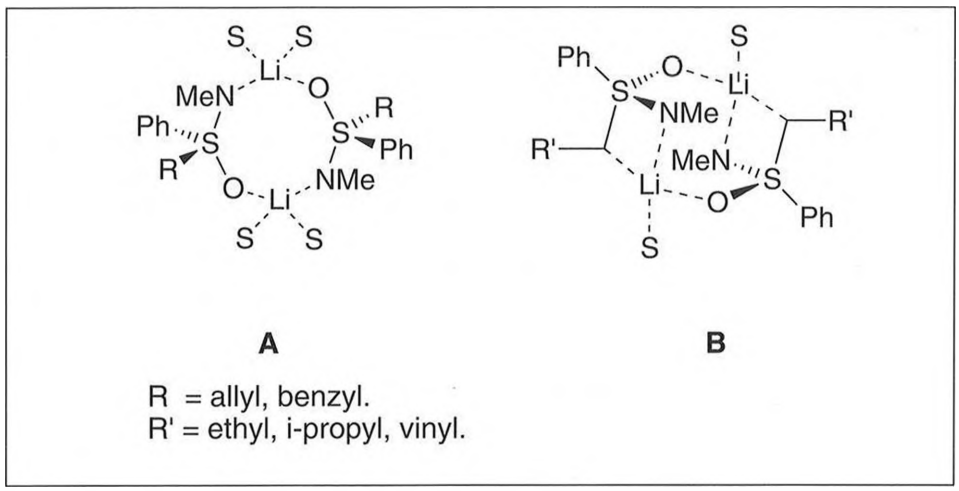

The Li–C contact distance of ≈2.21 Å together with the coordination to the sulfoximine-N-atom leads to arrangement **B**. Model *ab initio* calculations of the gas-phase structures of lithiated (*N*-methyl)dimethylsulfoximine at the MP2/6-31+G**//HF/6-31+G**-level yielded three different major structural minima **1–3** (*Fig.*) [3].

Of these, **1** exhibits a Li–C–S–N four-membered chelate ring; Li–O bonds and a Li–C contact are found in **3** whereas in **2** there is no Li–C contact. The chelate **1** represents the structure lowest in energy, but **2** is only 1.4 kcal/mol higher in energy, whereas the Li–O chelation in **3** is energetically disfavoured by 6.1 kcal/mol. Structure **4** can be interpreted as the transition state between the minima **1** and **2**. The isomers **2** and **3** are separated by transition state **5** which lies 12.2 kcal/mol above **2**. In **5**, an unsymmetrical tridentate bonding of the lithium to the O-, N-, and C(α)-atom is found. These results suggest an interconversion mechanism for **1** to **3** with **2** as an intermediate

Received: February 26, 1999

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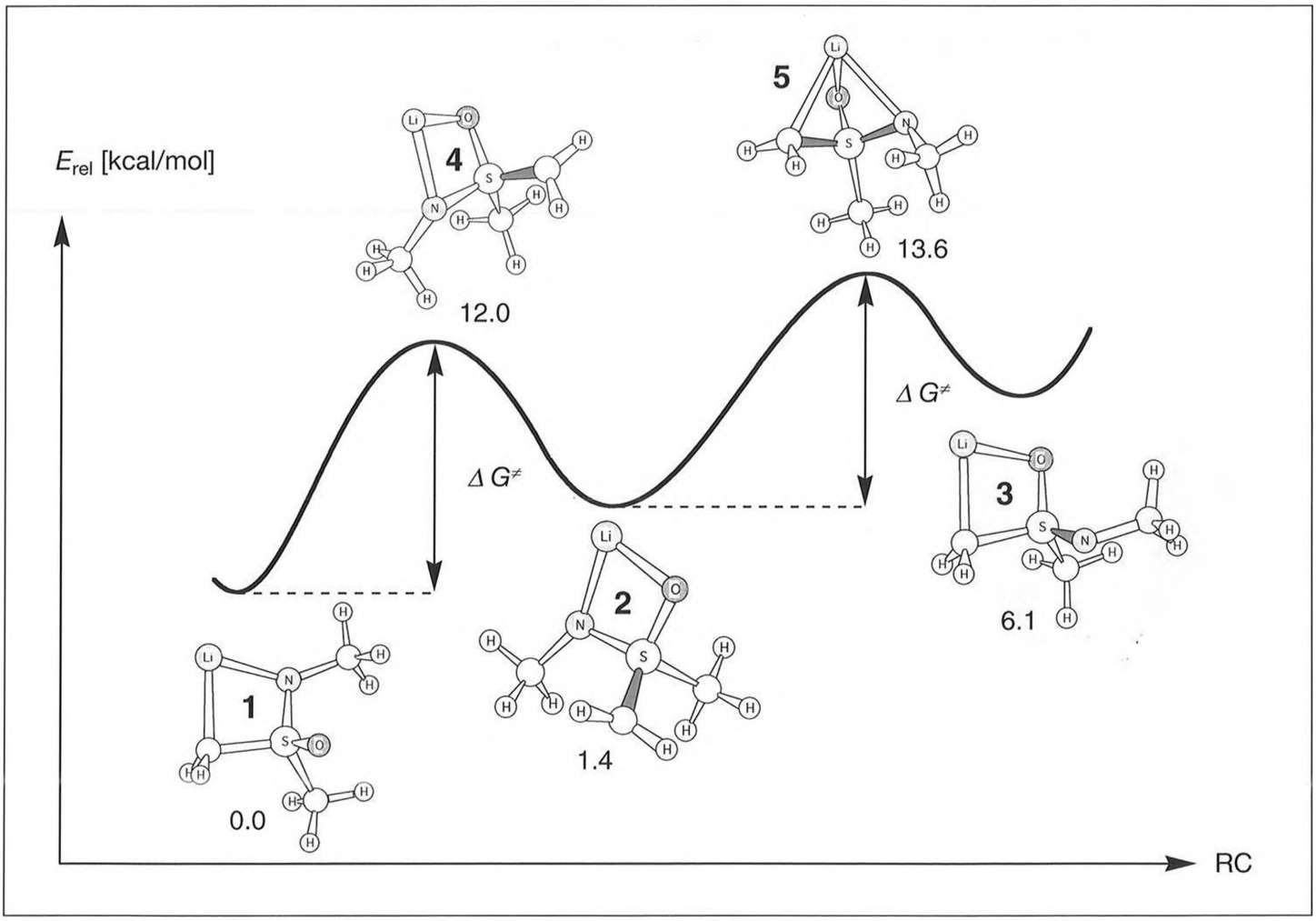

Fig. *Quantum-chemical calculations on monolithiosulfoximines*