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[18] Crystal structure data for **2**: $C_{12}H_{18}Cl_2F_4Hg_2O_3S_3$, M_r = 854.52, monoclinic, space group $P2_1/c$, a = 8.149(1), b = 14.245(1), c = 19.214(1) Å, β = 96.90(1)°, V = 2214.3(3) Å^3, Z = 4, ρ_{calcd} = 2.563 g cm^{-3}, $F(000)$ = 1568, Enraf-Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation (λ = 0.71069 Å), T = − 82 °C. Data were corrected for Lorentz, polarization, and absorption effects (DIFABS). The structure was solved by direct methods and refined by full-matrix least-square methods against F^2 (SHELXTL-PLUS, SHELXL-93). Of 4794 measured reflections, 4512 were used for refinement. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized geometry and allowed to ride on their corresponding carbon atom with U_{iso} = 1.5 U_{eq} of the attached carbon atom. The structure converged for 235 refined parameters to $R1$ = 0.0347 and $wR2$ = 0.0887; max./min. residual electron density + 1.427/ − 2.291 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-124679. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+ 44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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[27] X-ray powder diffration (XRPD) data for **4**: d spacing [Å] (I/I_o): 10.85 (100), 6.26 (86.8), 4.57 (64.72), 4.20 (52.46), 3.91 (41.85), 3.36 (28.00), 3.27 (83.92), 3.22 (21.76), 3.16 (25.95), 2.97 (27.25), 2.93 (23.68), 2.63 (22.47), 2.57 (26.51), 2.39 (26.03). Simulated XRPD for **2** (intense peaks are given for comparison purposes): d spacing [Å] (I/I_o): 11.41 (57.48), 9.54 (92.87), 8.09 (100), 6.84 (71.73), 6.57 (15.97), 5.83 (53.45), 5.81 (44.38), 4.98 (33.54), 4.05 (22.68), 3.90 (16.25), 3.80 (17.24), 3.73 (20.69), 3.69 (33.31), 3.54 (31.58), 3.50 (19.89), 3.29 (28.99), 3.04 (20.70).

X-Ray Structure of a Heterochiral, Sulfoximine-Stabilized Dilithiomethane Derivative

Jürgen F. K. Müller,* Markus Neuburger, and Bernhard Spingler

Dilithiomethane and some of its heteroatom-stabilized analogues have been the subject of intensive research during recent years. On the one hand the elucidation of the nature and the structures of the compounds were pursued, whilst on the other hand several investigations addressed the synthetic utility of these reagents.[1] The structure of dilithiomethane, the simplest polylithiated compound, has been determined in the solid state by X-ray analysis and NMR spectroscopy, whereas in solution no experimental data are available.[2] Some experimental evidence for the existence of a dimeric species in the gas phase has been reported.[3] Computational studies suggest that dilithiomethane and its higher aggregates have tetrahedral and planar structures, respectively.[4] The structures of heteroatom-stabilized geminal dianions, including dilithiated phosphonates,[5] phosphinimines,[6] sulfones, and nitriles[7] have been determined in the solid state, in solution, and theoretically. The α,o-dilithiated intermediates known for structurally related sulfones and sulfoximines mimic the reactivity of an α,α-dianion in trapping reactions with electrophiles.[8] This is also the case for the so called

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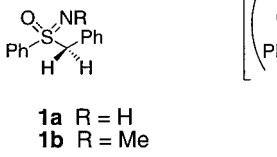
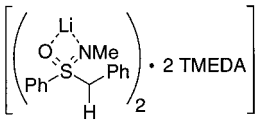
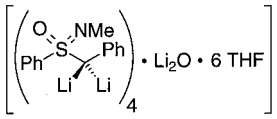
quasi-dianion complexes (QUADACs) such as the complex formed between monolithiated benzonitrile and lithium diisopropylamide (LDA).[9] Geminal dianions have been used successfully as supernucleophiles or bisnucleophiles in organic synthesis.[1] Surprisingly, chiral substituted dilithiomethane derivatives are still unknown and since both geminal lithium atoms are in a diastereotopic environment they promise to be exciting new reagents for asymmetric synthesis.[8, 10] Such reagents might induce two consecutive C–C bond formations in a stereoselective manner. Here we present the first experimental proof for such a chiral dilithiomethane derivative with the X-ray structure of an α,α-dilithiated sulfoximine.



1a R = H
1b R = Me



2



3

The monolithiated sulfoximine **2** was obtained by treating a solution of racemic **1b** in *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA) with one equivalent of *n*BuLi in hexane at -78°C. Yellow crystals suitable for X-ray analysis were grown from the resulting yellow-green solution. Figure 1 shows the molecular structure of the lithium complex **2**. For comparison the molecular structure of the starting material **1a** was also determined.[11]

In **2**, two lithiated benzylic sulfoximine units with opposite configuration at the S atom are linked by N-Li-O bridges to give an eight membered ring with the atom sequence $(Li(1)\text{-}N(1)\text{-}S(1)\text{-}O(1))_2$; such a coordination mode was previously known from lithiated allyl sulfoximines and from computational investigations.[12] Analogous arrangements have been observed in lithiosulfones.[13] The Li–C bond found in other lithiosulfoximines is absent.[14] The question as to whether the C(α) atom is pyramidal or not could not be answered with certainty because the benzylic proton was not located in the difference map. Lithiation of **1b** is accompanied by a shortening of the S-C(α) bond from 1.783(2) Å in **1a** to 1.66(1) Å in **2**.[12]

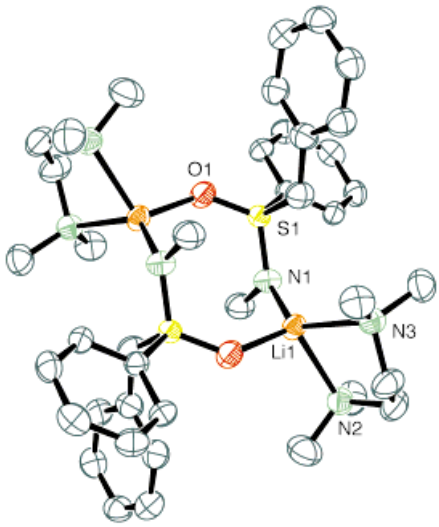


Figure 1. Molecular structure of **2** in the crystal. Hydrogen atoms are omitted for clarity.

Treatment of racemic **1b** with 2.5 equivalents of *n*BuLi in THF at -78°C in the presence of traces of H_2O yielded red crystals of **3**: a tetrameric heterochiral aggregate, consisting of four dilithiated sulfoximine units and a Li_6O core, which acts as a template for crystallization (Figure 2). No crystals could be obtained without small amounts of water. Compound **3** crystallizes in the space group $P\bar{1}$ and the unit cell contains one cluster together with two disordered THF molecules. Since the lattice is centrosymmetric the two portions of the cluster show a reversed configuration at the S atoms. The core of the aggregate is characterized by a distorted Li_6O octahedron and contains the crystallographic inversion centre. Such a structural motif has been found to be a characteristic feature in a α,o-dilithiated sulfoximine, a dilithiated sulfone, and a dilithiated phosphane.[7a, 8] A manifold of six-membered rings are connected to the central Li_6O core, which leads overall to a cyclic 16-membered $(Li(5)\text{-}C(1)\text{-}S(1)\text{-}O(1)\text{-}Li(4)\text{-}O(2)\text{-}S(2)\text{-}C(21))_2$ motif.

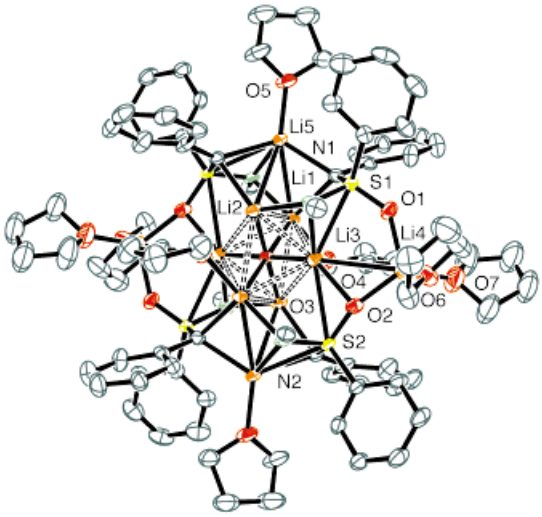


Figure 2. Molecular structure of **3** in the crystal. Hydrogen atoms and two disordered THF molecules are omitted for clarity.

Two different dilithiated C atoms are in the asymmetric unit, each connected to two Li^+ ions, and therefore distinctly pyramidalized. The two Li^+ ions coordinated at C(21) also coordinate to a neighboring sulfoximine nitrogen atom to form either Li(5)-C(21)-S(2)-N(2) four-membered ring motifs, as known from monolithiosulfoximines, or C(21)-Li(2)-N(3)-Li(3)-O(2)-S(2) six-membered rings. The two lithium ions also differ in their further coordination sphere: Li(2) shows heteroatom coordination (N(1), O(3)), whereas Li(5) has one additional C–Li bond, by bridging two different dimetalated C atoms, and a Li-N contact. The Li(5) ion is

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bound to C(1) as well as to C(21), leading to a Li(2)-C(21)-Li(5)-C(1)-S(1)-N(1) six-membered ring. An unusual three-coordination is found for Li(1), Li(2), and Li(3) of the Li_6O core.[15] The Li-C distances (2.19(2) – 2.21(2) Å) are similar to that in monolithiated sulfoximines. The Li-N bond length within the Li-C-S-N chelate (2.23(2) Å) is comparable to those from previous investigations.[12, 14] The Li-O bond length to the sulfoximine-O atoms are significantly longer than those within the Li_6O octahedron. The extremely short S–C(α) bonds (1.61(1) and 1.64(1) Å) compared to **1a** (1.783(2) Å) and **2** (ca. 1.66(1) Å) are characteristic and typical for related dilithiated sulfoximines, sulfones, phosphonates, and nitriles.[5–8] A comparison of **3** with **2** reveals that the atomic sequence of the eight-membered ring motif $(Li\text{-}N\text{-}S\text{-}O)_2$ in **2** is preserved in **3**. Insertion of the Li_6O core in this motif forms two Li(1)-N(2)-S(2)-O(2)-Li(3)-O(3) six-membered rings, which share the O(3) atom and thus lead to a spiro-type arrangement. Therefore, we conclude that the complex formed between the Li_6O core and the monolithiated sulfoximine units in **2** serves as a template for the formation of **3**. After dilithiation, the saturation of the second Li^+ ion with coordination partners from the sulfoximine group and the solvent leads to a higher aggregate than the monolithiated parent compound **2**. In addition, two C–Li bonds are formed for each sulfoximine unit, which represents a heterochiral dilithiomethane derivative with diastereotopic lithium atoms. Further studies in our group concentrate on the replacement of one of the diastereotopic lithium atoms by a transition metal, thus inducing a new stereogenic center at the C(α) atom.[16]

Experimental Section

2: A solution of **1b** (105 mg, 0.41 mmol) in TMEDA (2 mL) was treated with *n*BuLi in *n*-hexane (0.28 mL, 1.58 M, 0.45 mmol) at −78°C. After 24 h at room temperature yellow crystals of **2** were formed that were suitable for X-ray analysis (56 mg, 37%).

3: A solution of H_2O in THF (0.272 mL, 0.11 M, 0.03 mmol) was added to a solution of **1b** (54 mg, 0.22 mmol) in THF (2 mL). The resultant mixture was then treated with *n*BuLi in hexane (0.35 mL, 1.58 M, 0.55 mmol) at −78°C. After 24 h at −78°C red crystals of **3** that were suitable for X-ray analysis had grown (15 mg, 17%).

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[11] X-ray crystal data for **1**: $C_{13}H_{13}N_1O_1S_1$, $M_r = 231.31$, monoclinic, space group $P12_1/c1$, $a = 11.941(1)$, $b = 5.628(1)$, $c = 17.728(2)$ Å, $\alpha = 90$, $\beta = 104.703(9)$, $\gamma = 90$, $V = 1152.4(3)$ Å^3, $Z = 4$, $F(000) = 488$, $\rho_{calcd} = 1.33$ kg m^{-3}, $\mu = 0.25$ mm^{-1}, crystal dimensions = 0.1 × 0.45 × 0.5 mm, $T = 293$ K, radiation $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å), scan type $\omega/2\theta$, $\theta_{max} = 30.44$, 3017 measured reflections, 2809 independent reflections, 2020 reflections in refinement ($I > 3.00\sigma(I)$), 150 parameters, $R = 0.0381$. X-ray crystal data for **2**: $C_{20}H_{30}Li_1N_3O_1S_1$, $M_r = 367.48$, triclinic, space group $P\bar{1}$, $a = 9.623(1)$, $b = 10.194(3)$, $c = 11.501(4)$ Å, $\alpha = 104.60(2)$, $\beta = 96.38(2)$, $\gamma = 107.03(2)$, $V = 1022.8(5)$ Å^3, $Z = 2$, $F(000) = 396$, $\rho_{calcd} = 1.19$ kg m^{-3}, $\mu = 1.45$ mm^{-1}, crystal dimensions = 0.1 × 0.15 × 0.5 mm, $T = 193$ K, radiation $Cu_{K\alpha}$ ($\lambda = 1.54180$ Å), scan type $\omega/2\theta$, $\theta_{max} = 77.50$, 3253 measured reflections, 3101 independent reflections, 1458 reflections in refinement ($I > 3.00\sigma(I)$), 235 parameters, $R = 0.0875$, $R_w = 0.0640$. X-ray crystal data for **3**: $C_{48}H_{66}Li_5N_2O_{7.5}S_2$, $M_r = 889.89$, triclinic, space group $P\bar{1}$, $a = 12.675(2)$, $b = 13.348(2)$, $c = 15.152(2)$ Å, $\alpha = 81.26(1)$, $\beta = 87.95(1)$, $\gamma = 73.69(1)$, $V = 2431.8(7)$ Å^3, $Z = 4$, $F(000) = 950$, $\rho_{calcd} = 1.22$ kg m^{-3}, $\mu = 1.79$ mm^{-1}, crystal dimensions = 0.04 × 0.20 × 0.23 mm, $T = 193$ K, radiation $Cu_{K\alpha}$ ($\lambda = 1.54180$ Å), scan type $\omega/2\theta$, $\theta_{max} = 74.33$, 4240 measured reflections, 4078 independent reflections, 3102 reflections in refinement ($I > 3.00\sigma(I)$), 583 parameters, $R = 0.1492$, $R_w = 0.0694$, weighting scheme $\omega \times (1 - (\delta F/6\sigma F)^2)^2$, max./min. residual electron density 0.45/ − 1.10 e Å^{-3}, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = \{\Sigma((|F_o| - |F_c|)^2\omega)/\Sigma F_o^2\omega\}^{1/2}$. Crystals of **2** and **3** were stuck to a glass fibre with perfluoropolyether, mounted on the diffractometer, and cooled with an Oxford Cryostream apparatus to 193 K. The structure of **1a** was measured at room temperature in a glas capillary. Unit-cell parameters were determined by careful centering of 21 independent, strong reflections with $11 \le \theta \le 20$. Data collection was carried out using a Enraf-nonius CAD4 diffractometer equipped with a graphite monochromator. The usual corrections were applied. Absorption correction was carried out using φ scans. The structure was solved by direct

methods with the program SIR92.[17] Anisotropic least squares full matrix refinement was carried out on all non-hydrogen atoms using the program CRYSTALS.[18] The positions of the hydrogen atoms were determined geometrically. The disordered THF molecules in **3** were refined using appropriate restraints. Chebychev polynomial weights have been used to complete the refinement.[19] Scattering factors have been taken from *the International Tables*, *Vol. IV* (Ed.: T. Hahn), Kluwet Academic Publishers, London, **1995**, table 2.2B. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127623, 127624, and 127625. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Molecular Nanocapsules Based on Amphiphilic Hyperbranched Polyglycerols

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Dendrimers have been shown to exhibit unusual properties in recent years,[1] such as the topological encapsulation of various guests,[2] and dendrimers with amphiphilic core – shell structures have shown micelle-like properties that have led to the picture of a "unimolecular micelle".[3] However, most systems reported in this context show aggregation in solution as a result of their amphiphilic nature.[4] Amphiphilic polymers with core – shell structures that are aggregation-free in solution offer the attractive potential to act as phase-transfer agents in both polar [5, 6] and apolar environments.[7, 8] To date, this solubilization effect is believed to be uniquely related to the structurally perfect, yet tedious to prepare, dendrimers. The compact dendrimer topology is promising for controlled release[9] and confined chemical nanoreactors.[10]

Hyperbranched polymers (prepared in a one-step reaction from AB_m-type monomers and thus randomly branched in contrast to the perfectly branched dendrimers) are generally considered to be poorly defined because of their broad polydispersity,[11] which is a consequence of the commonly used step-growth-type of synthesis. Furthermore, hyperbranched polymers are characterized by a random distribution of functional groups throughout their globular structure. We reported recently the first controlled chain-growth-type of approach to hyperbranched polymers based on the anionic ring-opening multibranching polymerization (ROMBP) of glycidol.[12] The polyglycerols obtained can be tailored in terms of their core functionality and molecular weight by the monomer/initiator ratio employed. As a consequence of the quasi-living nature of the polymerization these highly flexible aliphatic polyetherpolyols exhibit unprecedentedly narrow polydispersities ($M_w/M_n < 1.5$, mostly < 1.3).

Very few examples of amphiphilic hyperbranched structures have been reported.[13, 14] Herein we describe the use of hyperbranched polyglycerols for the preparation of amphiphilic "molecular nanocapsules" for hydrophilic guests. In contrast to dendrimer scaffolds where functional groups are exclusively located at the surface, polyglycerol scaffolds also contain hydroxyl groups throughout the structure. If only a certain fraction of these hydroxyl groups is modified with hydrophobic alkyl chains (43 – 93 %), thereby leaving residual hydroxyl moieties, the inner sphere of the molecule remains highly hydrophilic (Figure 1). The considerable flexibility of the polyether structure should permit the hydroxyl groups to arrange in a manner that represents a solvating environment for polar guest molecules in apolar solvents.

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