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The crystal structure of the triclinic polymorph of hexameric (trimethylsilyl)methyl lithium, $C_{24}H_{66}Li_6Si_6$

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Abstract

$C_{24}H_{66}Li_6Si_6$, triclinic, $P\bar{1}$ (no. 2), $a = 12.2492(9)$ Å, $b = 12.4617(9)$ Å, $c = 14.3841(11)$ Å, $\alpha = 74.189(6)^\circ$, $\beta = 74.543(7)^\circ$, $\gamma = 85.970(6)^\circ$, $V = 2036.2(3)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0465$, $wR_{ref}(F^2) = 0.0802$, $T = 173(2)$ K.

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The molecular structure of the title compound is shown in the figure, with the labeling scheme indicating the asymmetric unit. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Needle, colorless
Size:	0.30 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.22 mm ⁻¹
Diffractometer, scan mode:	Xcalibur S, ω -scans
θ_{max} , completeness:	26°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	13964, 7965, 0.049
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3837
$N(param)_{refined}$:	457
Programs:	CrysAlis ^{PRO} [1], SHELX [2–5], Mercury [6], publCIF [7], WinGX and ORTEP [8]

Source of materials

Single crystals of the title compound, suitable for X-ray structural analysis, were obtained from a concentrated solution of (trimethylsilyl)methyl lithium in pentane at room temperature within one day.

Experimental details

Single-crystal X-ray diffraction analysis was performed on an Oxford Diffraction CCD Xcalibur S diffractometer [1] at

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Li1	0.3877(4)	0.4387(4)	0.4496(3)	0.0293(11)
Li2	0.5156(4)	0.5994(4)	0.3636(3)	0.0291(12)
Li3	0.4378(4)	0.6542(4)	0.5182(3)	0.0306(12)
Li4	0.1607(4)	1.0592(4)	0.9707(3)	0.0303(12)
Li5	0.0113(4)	0.8632(4)	0.9423(3)	0.0303(12)
Li6	0.0743(4)	0.8843(4)	1.0857(3)	0.0310(12)
Si1	0.25936(7)	0.74690(6)	0.43493(6)	0.0278(2)
Si2	0.70000(7)	0.77965(6)	0.46615(5)	0.0264(2)
Si3	0.44114(7)	0.50122(6)	0.80146(5)	0.0279(2)
Si4	0.34127(7)	0.91510(6)	0.90257(5)	0.0276(2)
Si5	−0.10647(7)	0.86207(7)	0.79800(6)	0.0317(2)
Si6	−0.00987(7)	0.66224(6)	1.16733(6)	0.0282(2)
C1	0.3178(2)	0.8434(2)	0.30893(19)	0.0419(8)
H1A	0.399250	0.853446	0.298308	0.063*
H1B	0.279702	0.915676	0.304944	0.063*
H1C	0.305140	0.811571	0.257394	0.063*
C2	0.1019(2)	0.7422(2)	0.4655(2)	0.0436(8)
H2A	0.078588	0.706959	0.420674	0.065*
H2B	0.071861	0.818304	0.456997	0.065*
H2C	0.072251	0.698988	0.534931	0.065*
C3	0.2931(4)	0.8091(3)	0.5291(3)	0.0439(10)
C4	0.3289(3)	0.6105(2)	0.4400(2)	0.0255(7)
C5	0.7681(3)	0.6788(3)	0.5565(3)	0.0376(9)
C6	0.8178(2)	0.8662(2)	0.37040(19)	0.0405(8)
H6A	0.872396	0.817726	0.337913	0.061*
H6B	0.855841	0.906206	0.402933	0.061*
H6C	0.787045	0.920024	0.320134	0.061*
C7	0.6111(2)	0.8756(2)	0.5350(2)	0.0434(9)
H7A	0.583389	0.936564	0.487731	0.065*
H7B	0.656651	0.906254	0.568349	0.065*
H7C	0.546563	0.834245	0.585073	0.065*
C8	0.6109(3)	0.7014(3)	0.4208(2)	0.0294(8)
C9	0.5722(2)	0.5286(3)	0.8330(2)	0.0506(9)
H9A	0.637379	0.497195	0.792729	0.076*
H9B	0.565612	0.493921	0.904139	0.076*
H9C	0.582649	0.609285	0.818803	0.076*
C10	0.4256(3)	0.3477(3)	0.8287(3)	0.0381(9)
C11	0.3172(2)	0.5470(2)	0.8893(2)	0.0493(9)
H11A	0.322983	0.627191	0.881290	0.074*
H11B	0.316209	0.506297	0.958212	0.074*
H11C	0.247123	0.531495	0.874586	0.074*
C12	0.4494(3)	0.5633(2)	0.6677(2)	0.0252(7)
C13	0.4215(2)	0.8994(3)	0.7771(2)	0.0504(9)
H13A	0.406374	0.825660	0.771332	0.076*
H13B	0.502816	0.907240	0.769110	0.076*
H13C	0.397585	0.957191	0.724931	0.076*
C14	0.3986(2)	0.8124(2)	0.9984(2)	0.0479(9)
H14A	0.367291	0.827412	1.063787	0.072*
H14B	0.481356	0.818753	0.980297	0.072*
H14C	0.377452	0.736785	1.001643	0.072*
C15	0.3748(3)	1.0572(3)	0.9052(4)	0.0507(10)
C16	0.1862(2)	0.9023(3)	0.9296(2)	0.0256(7)
C17	0.0098(4)	0.7582(3)	0.8129(4)	0.0511(11)
C18	−0.0888(3)	0.9110(2)	0.65977(19)	0.0503(9)
H18A	−0.152251	0.959645	0.645976	0.075*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H18B	−0.087396	0.846539	0.632850	0.075*
H18C	−0.017573	0.952593	0.628081	0.075*
C19	−0.2435(3)	0.7864(3)	0.8560(2)	0.0712(12)
H19A	−0.249493	0.751569	0.927031	0.107*
H19B	−0.247299	0.728735	0.822322	0.107*
H19C	−0.306025	0.839063	0.849288	0.107*
C20	−0.0962(3)	0.9714(3)	0.8602(2)	0.0292(8)
C21	0.0482(2)	0.5724(2)	1.08196(19)	0.0442(9)
H21A	−0.013782	0.546051	1.062491	0.066*
H21B	0.086771	0.508278	1.116130	0.066*
H21C	0.102189	0.615383	1.022134	0.066*
C22	−0.1004(2)	0.5710(2)	1.28393(19)	0.0462(9)
H22A	−0.128958	0.614211	1.333060	0.069*
H22B	−0.055402	0.508184	1.311474	0.069*
H22C	−0.164314	0.542780	1.268507	0.069*
C23	0.1118(3)	0.7057(3)	1.2036(3)	0.0411(9)
C24	−0.0763(3)	0.7899(3)	1.1020(2)	0.0323(8)
H3A	0.267(2)	0.763(2)	0.5910(18)	0.028(9)*
H3B	0.251(2)	0.877(2)	0.5289(18)	0.049(9)*
H3C	0.366(2)	0.829(2)	0.513(2)	0.053(12)*
H4A	0.3146(18)	0.5963(17)	0.3829(16)	0.019(7)*
H4B	0.288(2)	0.564(2)	0.4884(18)	0.035(9)*
H5A	0.807(2)	0.624(2)	0.530(2)	0.052(10)*
H5B	0.718(2)	0.647(2)	0.6176(18)	0.027(8)*
H5C	0.816(2)	0.719(2)	0.573(2)	0.052(10)*
H8A	0.5760(19)	0.7528(19)	0.3843(16)	0.020(8)*
H8B	0.652(2)	0.675(2)	0.3840(17)	0.023(9)*
H10A	0.490(2)	0.3135(19)	0.7992(17)	0.029(8)*
H10B	0.358(2)	0.331(2)	0.8088(19)	0.051(10)*
H10C	0.417(2)	0.314(2)	0.894(2)	0.051(10)*
H12A	0.3758(19)	0.5622(18)	0.6671(16)	0.018(7)*
H12B	0.4624(19)	0.6309(19)	0.6607(17)	0.019(7)*
H15A	0.350(2)	1.066(2)	0.969(2)	0.048(10)*
H15B	0.350(2)	1.113(2)	0.859(2)	0.052(11)*
H15C	0.454(2)	1.061(2)	0.8953(18)	0.039(9)*
H16A	0.1812(19)	0.829(2)	0.9320(16)	0.027(7)*
H16B	0.173(2)	0.9311(19)	0.8708(17)	0.028(8)*
H17A	0.081(3)	0.792(3)	0.786(2)	0.059(13)*
H17B	0.003(2)	0.704(2)	0.7794(19)	0.053(9)*
H17C	0.004(3)	0.720(2)	0.875(2)	0.058(12)*
H20A	−0.158(2)	1.0121(18)	0.8559(16)	0.023(7)*
H20B	−0.047(2)	1.011(2)	0.816(2)	0.044(11)*
H23A	0.140(2)	0.645(2)	1.2394(19)	0.044(9)*
H23B	0.171(2)	0.731(2)	1.1512(18)	0.033(9)*
H23C	0.092(2)	0.763(2)	1.242(2)	0.063(10)*
H24A	−0.1198(19)	0.8160(18)	1.1474(16)	0.025(8)*
H24B	−0.126(2)	0.7634(19)	1.0807(17)	0.021(8)*

173(2) K using graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å). The crystal structure was solved with direct methods (SHELXS-97 [2, 3]) and refined against *F*² with the full-matrix least-squares method (SHELXL-2018/3 [2, 4, 5]). A multi-scan absorption correction using the implemented CrysAlis RED program was employed [1]. The non-hydrogen

atoms were refined using anisotropic displacement parameters. The methylene hydrogen atoms and the methyl hydrogen atoms bonded to C3, C5, C10, C15, C17, and C23 were located on the difference Fourier map and refined independently. All other hydrogen atoms were placed in idealized geometric positions and each was assigned a fixed isotropic displacement parameter based on a riding-model. The U_{iso} values for the methyl hydrogen atoms were set to $1.5U_{eq}$ of the parent carbon atoms with the methyl C—H distances constrained to 0.98 Å. The visualization of the molecular structure shown in the figure was performed using Mercury 4.1.0 [6].

Discussion

(Trimethylsilyl)methylolithium ($LiCH_2SiMe_3$) is a commonly used reagent for silyl transfer reactions [9, 10], for halogen-lithium exchange [11], and was recently used for the deprotonation of toluene to form pure crystalline benzylolithium [12]. The crystal structure of $LiCH_2SiMe_3$ was first reported by Tecle et al. as a hexameric aggregate in the monoclinic crystal system, space group $P2_1/n$ [13]. In addition to the donor base-free molecular structure of $[LiCH_2SiMe_3]_6$, only a few deaggregated structures of (trimethylsilyl)methylolithium have been reported to date [14–17]. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) and (–)-sparteine form the dimers $[(TMEDA) \cdot LiCH_2SiMe_3]_2$ and $[\{-sparteine\} \cdot LiCH_2SiMe_3]_2$, whereas *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) forms the monomeric $[(PMDETA) \cdot LiCH_2SiMe_3]$ adduct [14]. Diethyl ether and *tert*-butylmethyl ether deaggregate the hexameric parent compound $[LiCH_2SiMe_3]_6$ to the unsymmetrically coordinated tetramers $[(Et_2O)_2 \cdot (LiCH_2SiMe_3)_4]$ and $[(tBuOMe)_2 \cdot (LiCH_2SiMe_3)_4]$, while dimethoxyethane (DME) forms the dimer $[(DME) \cdot (LiCH_2SiMe_3)]_2$ [15]. In 2015, we reported on a dimeric (trimethylsilyl)methylolithium species using a chiral dimethoxysilane as chelating ligand [16]. A recently published article describes a monomeric complex consisting of (trimethylsilyl)methylolithium and the bidentate chiral ligand (1*R*,2*R*)-*N,N,N',N'*-tetramethylcyclohexane-1,2-diamine together with a symmetrically and an unsymmetrically coordinated dimeric quinuclidine adduct of $[LiCH_2SiMe_3]_6$ [17].

The molecular structure of the title compound presented herein is the second polymorph found for (trimethylsilyl)methylolithium. The hexamer $[LiCH_2SiMe_3]_6$ crystallized in the triclinic crystal system, space group $P\bar{1}$. The asymmetric unit contains two crystallographically independent half aggregates, each being arranged around a center of inversion (*cf.* the figure). The lithium atoms of each hexamer are three-fold coordinated and build a trigonal antiprismatic geometry with average $Li \cdots Li$ distances of 3.22 Å within the triangular base and 2.45 Å between neighboring lithium atoms when

following the lithium core in a zig-zag course. These distances are similar to those in monoclinic $[LiCH_2SiMe_3]_6$ (2.45 Å and 3.18 Å) [13]. The bond lengths between the silicon and methylene carbon atoms differ from 1.839(3) Å (C4–Si1) to 1.868(3) Å (C24–Si6). The carbanionic carbon atoms are coordinated to three lithium centers leading to a $[Li_6C_6]$ core that features two $[Li_3C_3]$ six-membered folded chairs arranged in parallel with alternating Li–C bond lengths ranging from 2.139(5) Å (C4–Li3) to 2.280(5) Å (C20–Li4#2 and Li4–C20#2; #2 = $-x, -y + 2, -z + 2$), which are similar to those found in monoclinic (trimethylsilyl)methylolithium (2.15 Å to 2.29 Å) [13].

Lithium-hydrogen interactions in organolithium compounds and their possible contribution to the aggregate formation have been the subject of discussion for a long time [13, 18, 19]. Similar to the monoclinic hexamer $[LiCH_2SiMe_3]_6$, the here described triclinic polymorph shows short $Li \cdots H$ distances ranging from 2.014 Å (Li1–H4B) to 2.218 Å (Li2–H8A) for the carbanionic methylene groups and from 2.264 Å (Li5–H17C) to 2.553 Å (Li5–H17A) for the C3, C5, C10, C15, C17, and C23 methyl groups that are oriented towards a lithium atom. The shortest $Li \cdots H$ distance found in the monoclinic polymorph amounts to 2.03(6) Å [13].

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