Crystal structure of 1r,2c,3c,4t,5t,6t-1,2,3,4,5,6-hexakis-trimethylsilanyloxy-cyclohexane, $C_{24}H_{60}O_6Si_6$

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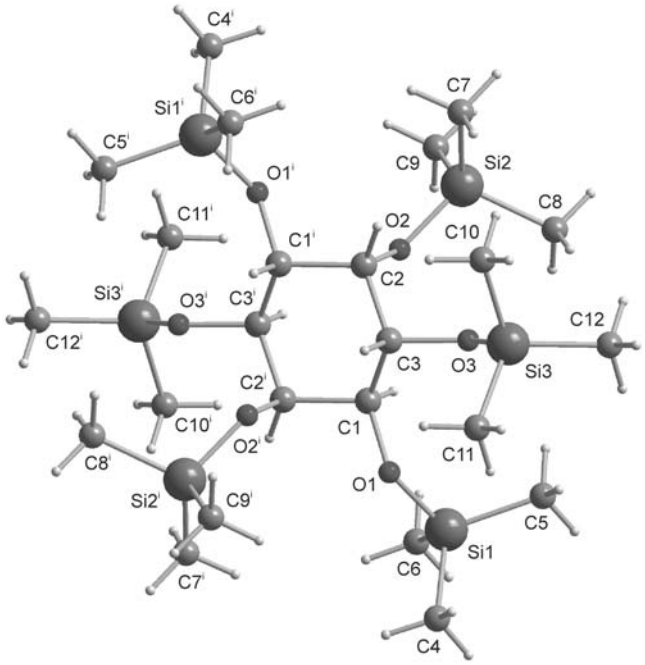
Received December 30, 2010, accepted and available on-line February 26, 2011; CCDC no. 1267/3353



Abstract

$C_{24}H_{60}O_6Si_6$, triclinic, $P\bar{1}$ (no. 2), a = 11.307(2) Å, b = 12.159(2) Å, c = 16.576(2) Å, α = 109.47(1)°, β = 94.64(1)°, γ = 111.65(1)°, V = 1942.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.118, T = 210 K.

Source of material

The title compound was synthesized by treating *neo*-inositol with trimethylsilyl chloride in triethylamine. Colorless crystals where obtained by slow volatilizing $CDCl_3$ from an NMR sample.

Experimental details

The hydrogen atoms were calculated in their expected positions and included in the refinement as riding atoms. The U_{iso}(H) values were constrained to be 1.2 U_{eq}(CH) and 1.5 U_{eq}(CH_3), respectively. In one of both molecules two methyl groups of one silanyloxy substituent are disordered over two sides with an occupation ratio of 0.5/0.5. The terminal methyl groups display enhanced librational motions, which is caused by rotation around the silicon-oxygen bond.

Discussion

In connection with our investigations concerning new molecular rods with ketal moeties as key structural element [1-3] we were interested in six-membered saturated rings bearing four hydroxyl groups with the stereochemical pattern 1r,2c,4t,5t and two additional substituents in 3- and 6-position. Two of the eight naturally occurring stereoisomeric inositols (1,2,3,4,5,6-hexahydroxy-cyclohexanes) meet these demands, namely *allo*-(1,2,3,4/5,6) and *neo*-(1,2,3/4,5,6) inositol. If the mentioned two substituents in 3- and 6-position should not break the symmetry of the building block, only the *neo*-isomer comes into consideration. Whereas *myo*-(1,2,3,5/4,6) inositol, which differs from *neo*-inositol only by the configuration of one stereocentre, is cheaply available, the required *neo*-inositol cannot be purchased in larger amounts. Some methods for the preparation of *neo*-inositol or its derivatives were reported but none of them were feasible [4]. We therefore developed a new efficient method for the preparation of *neo*- from *myo*-inositol [5].

The crystal structure of the title compound unequivocally proves the correct stereochemistry of the product. The asymmetric unit contains two halfs of two symmetry independent molecules. The other two halfs were generated by inversion centres in both molecules, giving the (1,2,3/4,5,6) arrangement in an ideal chair conformation. The puckering parameters are Q = 0.611(2) Å, θ = 3.27(1)°, φ = 0°. The conformation is closely related to the structure of *neo*-inositol [6]. However, the compactness of the structure reported here is very small, characterized by a low density (1.049 g·cm^{-3}), in contrast to that in *neo*-inositol with an unusually high density (1.69 g·cm^{-3}). Beside above-mentioned disordered methyl groups at one position of one molecule, there are only marginal differences in the conformations of the two molecules. Hence only one molecule is presented in the figure. Since the compound is centrosymmetric, the atoms C1 to C6 of the carbon skeletons are designated as C1, C2^i, C3^i, C1^i, C2 and C3 (symmetry code i: 2–x,2–y,2–z).

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.5 × 0.8 × 1.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.44 cm^{-1}
Diffractometer, scan mode:	STOE IPDS-2, $\Delta\omega$ = 1.0°
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12649, 6443
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4610
$N(param)_{refined}$:	344
Programs:	SHELXS-97, SHELXL-97 [7], DIAMOND [8]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	2*i*		1.0244	0.9356	1.0872	0.044
H(2)	2*i*		0.8954	0.8378	0.8589	0.044
H(3)	2*i*		1.1155	0.9513	0.9351	0.044
H(41)	2*i*		1.4663	1.0132	1.1671	0.215
H(42)	2*i*		1.4545	1.0185	1.2618	0.215
H(43)	2*i*		1.4544	1.1313	1.2360	0.215
H(51)	2*i*		1.0974	0.7435	1.1163	0.199
H(52)	2*i*		1.2149	0.7605	1.1838	0.199
H(53)	2*i*		1.2299	0.7548	1.0894	0.199
H(61)	2*i*		1.1990	0.9886	1.3145	0.203
H(62)	2*i*		1.0813	0.9720	1.2475	0.203
H(63)	2*i*		1.2053	1.1037	1.2895	0.203
H(71)	2*i*		0.6450	0.6815	0.7777	0.213
H(72)	2*i*		0.5980	0.5379	0.7671	0.213
H(73)	2*i*		0.7451	0.6195	0.7725	0.213
H(81)	2*i*		0.6783	0.4808	0.9270	0.160
H(82)	2*i*		0.7739	0.5973	1.0121	0.160
H(83)	2*i*		0.8244	0.5563	0.9265	0.160
H(91)	2*i*		0.5863	0.7172	1.0203	0.210
H(92)	2*i*		0.4917	0.6009	0.9347	0.210
H(93)	2*i*		0.5375	0.7418	0.9395	0.210
H(101)	2*i*		0.9769	0.6480	0.7469	0.148
H(102)	2*i*		1.1128	0.6623	0.7250	0.148
H(103)	2*i*		1.0840	0.7841	0.7625	0.148
H(111)	2*i*		1.3432	0.8488	0.9723	0.175
H(112)	2*i*		1.3185	0.9181	0.9125	0.175
H(113)	2*i*		1.3557	0.8019	0.8744	0.175
H(121)	2*i*		1.1501	0.5283	0.8439	0.171
H(122)	2*i*		1.0150	0.5144	0.8670	0.171
H(123)	2*i*		1.1421	0.5816	0.9424	0.171
H(1A)	2*i*		0.8514	0.8951	0.5268	0.044
H(2A)	2*i*		0.9571	1.1219	0.4265	0.044
H(3A)	2*i*		0.9480	0.9126	0.3759	0.043

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(41A)	2*i*		0.6104	0.4122	0.3848	0.147
H(42A)	2*i*		0.7532	0.4570	0.3706	0.147
H(43A)	2*i*		0.6475	0.4781	0.3181	0.147
H(51A)	2*i*		0.5161	0.6185	0.4782	0.144
H(52A)	2*i*		0.5595	0.6858	0.4130	0.144
H(53A)	2*i*		0.6144	0.7639	0.5147	0.144
H(61A)	2*i*		0.8581	0.6153	0.5682	0.143
H(62A)	2*i*		0.7146	0.5701	0.5811	0.143
H(63A)	2*i*		0.8062	0.7173	0.6153	0.143
H(71A)	2*i*		0.7822	1.1646	0.3884	0.336
H(72A)	2*i*		0.7248	1.2627	0.4335	0.336
H(73A)	2*i*		0.6440	1.1155	0.4095	0.336
H(81A)	2*i*	0.50	0.8073	1.2368	0.6720	0.256
H(82A)	2*i*	0.50	0.6629	1.1677	0.6160	0.256
H(83A)	2*i*	0.50	0.7436	1.3154	0.6417	0.256
H(84A)	2*i*	0.50	0.9662	1.3589	0.4846	0.246
H(85A)	2*i*	0.50	1.0043	1.4110	0.5876	0.246
H(86A)	2*i*	0.50	0.8908	1.4290	0.5408	0.246
H(91A)	2*i*	0.50	0.9559	1.4020	0.6206	0.260
H(92A)	2*i*	0.50	0.8981	1.3238	0.6775	0.260
H(93A)	2*i*	0.50	0.8181	1.3845	0.6399	0.260
H(94A)	2*i*	0.50	0.5936	1.0174	0.5012	0.291
H(95A)	2*i*	0.50	0.5875	1.1407	0.5679	0.291
H(96A)	2*i*	0.50	0.6609	1.0713	0.6011	0.291
H(10A)	2*i*		0.7636	1.0116	0.2407	0.120
H(11A)	2*i*		0.7469	0.8992	0.1530	0.120
H(12A)	2*i*		0.8774	0.9683	0.2257	0.120
H(13A)	2*i*		0.8544	0.7181	0.2336	0.143
H(14A)	2*i*		0.7263	0.6448	0.1585	0.143
H(15A)	2*i*		0.7254	0.6263	0.2477	0.143
H(16A)	2*i*		0.5000	0.7277	0.1832	0.140
H(17A)	2*i*		0.5168	0.8400	0.2710	0.140
H(18A)	2*i*		0.5009	0.7065	0.2714	0.140

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*		1.0876(2)	0.9824(2)	1.0600(1)	0.037(1)	0.032(1)	0.045(1)	0.0167(9)	0.006(1)	0.0171(9)
C(2)	2*i*		0.9170(2)	0.8872(2)	0.9226(1)	0.044(1)	0.0274(9)	0.037(1)	0.0149(9)	0.004(1)	0.0111(8)
C(3)	2*i*		1.0514(2)	0.9051(2)	0.9621(1)	0.046(1)	0.0269(9)	0.045(1)	0.0204(9)	0.012(1)	0.0168(9)
C(4)	2*i*		1.4272(4)	1.0400(5)	1.2150(4)	0.071(2)	0.198(5)	0.178(5)	0.033(3)	–0.015(3)	0.131(4)
C(5)	2*i*		1.1909(5)	0.7835(3)	1.1369(3)	0.225(5)	0.069(2)	0.093(3)	0.053(3)	–0.021(3)	0.042(2)
C(6)	2*i*		1.1748(5)	1.0120(5)	1.2679(3)	0.202(5)	0.229(5)	0.077(3)	0.167(5)	0.065(3)	0.086(3)
C(7)	2*i*		0.6690(5)	0.6220(4)	0.7934(2)	0.163(4)	0.087(3)	0.062(2)	–0.051(3)	–0.041(3)	0.026(2)
C(8)	2*i*		0.7509(4)	0.5639(3)	0.9490(3)	0.134(3)	0.049(2)	0.121(3)	0.016(2)	0.004(3)	0.044(2)
C(9)	2*i*		0.5631(3)	0.6848(4)	0.9572(4)	0.056(2)	0.116(3)	0.205(5)	–0.001(2)	0.025(3)	0.054(3)
C(10)	2*i*		1.0691(5)	0.7021(3)	0.7644(2)	0.169(4)	0.088(2)	0.065(2)	0.080(3)	0.040(2)	0.029(2)
C(11)	2*i*		1.3088(4)	0.8369(4)	0.9136(3)	0.097(3)	0.150(4)	0.144(4)	0.084(3)	0.065(3)	0.062(3)
C(12)	2*i*		1.1071(5)	0.5686(3)	0.8836(3)	0.208(5)	0.084(2)	0.114(3)	0.112(3)	0.067(3)	0.048(2)
O(1)	2*i*		1.2149(1)	1.0035(1)	1.0984(1)	0.0379(8)	0.0505(8)	0.053(1)	0.0209(7)	0.0026(8)	0.0260(8)
O(2)	2*i*		0.8231(1)	0.8190(1)	0.9603(1)	0.0438(9)	0.0307(7)	0.0490(9)	0.0092(6)	0.0045(8)	0.0159(7)
O(3)	2*i*		1.0530(2)	0.7827(1)	0.9451(1)	0.062(1)	0.0331(7)	0.055(1)	0.0296(7)	0.0155(9)	0.0185(7)
Si(1)	2*i*		1.24894(7)	0.95806(7)	1.17712(5)	0.0537(4)	0.0590(4)	0.0535(4)	0.0292(3)	0.0034(4)	0.0277(3)
Si(2)	2*i*		0.70512(7)	0.67411(6)	0.91342(5)	0.0576(4)	0.0397(4)	0.0572(5)	–0.0012(3)	–0.0065(4)	0.0192(3)
Si(3)	2*i*		1.13419(9)	0.72501(8)	0.87849(5)	0.0998(6)	0.0632(4)	0.0665(5)	0.0606(5)	0.0339(5)	0.0270(4)
C(1A)	2*i*		0.9018(2)	0.8722(2)	0.4838(1)	0.040(1)	0.0272(9)	0.040(1)	0.0124(9)	0.007(1)	0.0113(9)
C(2A)	2*i*		0.9583(2)	1.0813(2)	0.4685(1)	0.045(1)	0.031(1)	0.038(1)	0.0185(9)	0.008(1)	0.0157(9)
C(3A)	2*i*		0.8973(2)	0.9353(2)	0.4187(1)	0.037(1)	0.032(1)	0.038(1)	0.0141(9)	0.005(1)	0.0127(9)
C(4A)	2*i*		0.6784(4)	0.4767(3)	0.3732(2)	0.107(3)	0.041(2)	0.102(3)	–0.004(2)	0.001(2)	0.022(2)
C(5A)	2*i*		0.5873(3)	0.6814(4)	0.4677(3)	0.064(2)	0.097(2)	0.133(3)	0.021(2)	0.034(2)	0.063(2)
C(6A)	2*i*		0.7830(4)	0.6344(3)	0.5696(2)	0.122(3)	0.083(2)	0.081(2)	0.028(2)	0.010(2)	0.052(2)
C(7A)	2*i*		0.7303(8)	1.1842(7)	0.4294(3)	0.39(1)	0.347(9)	0.104(4)	0.338(9)	0.048(5)	0.082(5)
C(81A)	2*i*	0.50	0.748(2)	1.234(2)	0.6256(7)	0.28(2)	0.32(2)	0.106(8)	0.28(2)	0.12(1)	0.12(1)
C(82A)	2*i*	0.50	0.9332(9)	1.3727(8)	0.537(1)	0.125(7)	0.069(5)	0.33(2)	0.069(5)	0.048(9)	0.086(8)
C(91A)	2*i*	0.50	0.877(2)	1.344(1)	0.6286(9)	0.23(1)	0.095(7)	0.16(1)	0.115(9)	–0.03(1)	–0.039(7)
C(92A)	2*i*	0.50	0.641(1)	1.094(1)	0.553(1)	0.128(9)	0.23(1)	0.38(2)	0.15(1)	0.16(1)	0.20(2)
C(10A)	2*i*		0.7841(3)	0.9394(3)	0.2152(2)	0.098(2)	0.074(2)	0.065(2)	0.023(2)	0.011(2)	0.039(2)
C(11A)	2*i*		0.7608(4)	0.6866(3)	0.2210(2)	0.159(4)	0.072(2)	0.054(2)	0.069(2)	0.008(2)	0.004(2)

Table 3. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(12A)	2*i*		0.5370(3)	0.7675(4)	0.2454(2)	0.063(2)	0.097(3)	0.087(3)	0.011(2)	–0.012(2)	0.031(2)
O(1A)	2*i*		0.8445(2)	0.7356(1)	0.4372(1)	0.0491(9)	0.0269(7)	0.0502(9)	0.0108(7)	0.0029(8)	0.0128(6)
O(2A)	2*i*		0.8847(1)	1.1152(1)	0.5298(1)	0.0460(9)	0.0399(8)	0.0464(9)	0.0249(7)	0.0096(8)	0.0148(7)
O(3A)	2*i*		0.7670(1)	0.8923(1)	0.3737(1)	0.0394(8)	0.0398(8)	0.0422(9)	0.0170(7)	–0.0002(7)	0.0112(7)
Si(1A)	2*i*		0.72503(7)	0.63551(6)	0.46210(5)	0.0613(5)	0.0383(3)	0.0649(5)	0.0058(3)	0.0025(4)	0.0267(3)
Si(2A)	2*i*		0.80282(9)	1.20197(8)	0.53253(5)	0.0863(6)	0.0738(5)	0.0615(5)	0.0620(5)	0.0106(5)	0.0151(4)
Si(3A)	2*i*		0.71574(7)	0.82211(6)	0.26578(4)	0.0564(4)	0.0383(3)	0.0434(4)	0.0155(3)	–0.0031(3)	0.0118(3)

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