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The crystal structure of adamantylmethoxydiphenylsilane, $C_{23}H_{28}OSi$

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Abstract

$C_{23}H_{28}OSi$, monoclinic, $P2_1/c$ (no. 14), $a = 14.2882(11)$ Å, $b = 17.8169(10)$ Å, $c = 7.6201(6)$ Å, $\beta = 103.780(8)^\circ$, $V = 1884.0(2)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0538$, $wR_{ref}(F^2) = 0.1241$, $T = 173(2)$ K.

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The molecular structure (left part) and the two-dimensional (2D) fingerprint plot (right part; showing all contributions of intermolecular contacts) of the title compound are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was obtained as a by-product in the reaction of adamantyltrimethoxysilane with phenyllithium

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.30 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.13 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
θ_{max} , completeness:	29.9°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	15475, 4795, 0.054
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3241
$N(param)_{refined}$:	338
Programs:	CrysAlis ^{PRO} [1], SHELX [2–5], Olex2 [6], WinGX/ORTEP [7], CrystalExplorer17 [8–10]

in diethyl ether/dibutyl ether. Crystals suitable for single-crystal X-ray diffraction analysis were obtained after filtration from a concentrated solution of the crude mixture in diethyl ether/dibutyl ether at room temperature within one day.

Experimental details

Single-crystal X-ray diffraction analysis of adamantylmethoxydiphenylsilane was performed on an Oxford Diffraction CCD Xcalibur S Diffractometer equipped with a Sapphire3 CCD detector at 173(2) K using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). Data

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.39183 (18)	0.55609 (15)	0.1620 (3)	0.0302 (5)
H1A	0.344 (2)	0.5666 (15)	0.056 (4)	0.059 (8)*
H1B	0.4165 (19)	0.6019 (17)	0.218 (4)	0.066 (9)*
H1C	0.439 (2)	0.5273 (15)	0.124 (4)	0.068 (9)*
C2	0.24224 (12)	0.46467 (10)	0.5219 (3)	0.0161 (4)
C3	0.32901 (14)	0.42936 (11)	0.6591 (3)	0.0207 (4)
H3A	0.3568 (13)	0.4667 (11)	0.747 (3)	0.016 (5)*
H3B	0.3788 (14)	0.4143 (11)	0.596 (3)	0.022 (5)*
C4	0.29661 (15)	0.36154 (11)	0.7538 (3)	0.0241 (5)
H4	0.3512 (15)	0.3431 (11)	0.838 (3)	0.028 (6)*
C5	0.25269 (16)	0.30202 (11)	0.6134 (3)	0.0245 (5)
H5A	0.2360 (15)	0.2583 (13)	0.678 (3)	0.032 (6)*
H5B	0.3009 (14)	0.2857 (11)	0.547 (3)	0.024 (5)*
C6	0.16531 (14)	0.33542 (11)	0.4792 (3)	0.0210 (4)
H6	0.1391 (14)	0.2974 (11)	0.388 (3)	0.022 (5)*
C7	0.19733 (15)	0.40326 (11)	0.3839 (3)	0.0200 (4)
H7A	0.1404 (15)	0.4241 (11)	0.297 (3)	0.025 (6)*
H7B	0.2417 (14)	0.3882 (10)	0.319 (3)	0.016 (5)*
C8	0.16617 (14)	0.48869 (10)	0.6261 (3)	0.0206 (4)
H8A	0.1951 (13)	0.5292 (11)	0.718 (3)	0.020 (5)*
H8B	0.1072 (13)	0.5105 (10)	0.536 (3)	0.016 (5)*
C9	0.13449 (15)	0.42015 (11)	0.7222 (3)	0.0243 (5)
H9	0.0889 (14)	0.4350 (10)	0.786 (3)	0.019 (5)*
C10	0.22228 (17)	0.38702 (12)	0.8555 (3)	0.0276 (5)
H10A	0.2037 (15)	0.3459 (12)	0.919 (3)	0.033 (6)*
H10B	0.2484 (14)	0.4237 (12)	0.948 (3)	0.028 (6)*
C11	0.09054 (15)	0.36089 (12)	0.5811 (3)	0.0256 (5)
H11A	0.0668 (13)	0.3167 (11)	0.641 (3)	0.021 (5)*
H11B	0.0357 (15)	0.3794 (11)	0.502 (3)	0.027 (6)*
C12	0.35666 (14)	0.61289 (10)	0.5871 (3)	0.0187 (4)
C13	0.31701 (16)	0.66250 (11)	0.6927 (3)	0.0258 (5)
H13	0.2460 (14)	0.6654 (10)	0.679 (3)	0.016 (5)*
C14	0.37521 (17)	0.70776 (12)	0.8234 (3)	0.0332 (5)
H14	0.3469 (17)	0.7396 (14)	0.899 (3)	0.045 (7)*
C15	0.47464 (17)	0.70377 (13)	0.8538 (3)	0.0353 (6)
H15	0.5165 (15)	0.7379 (13)	0.940 (3)	0.037 (6)*
C16	0.51568 (16)	0.65382 (12)	0.7546 (3)	0.0329 (5)
H16	0.5877 (16)	0.6495 (12)	0.777 (3)	0.033 (6)*
C17	0.45751 (14)	0.60918 (11)	0.6237 (3)	0.0236 (5)
H17	0.4885 (14)	0.5762 (11)	0.562 (3)	0.022 (5)*
C18	0.18264 (13)	0.59858 (10)	0.2527 (3)	0.0187 (4)
C19	0.13572 (15)	0.56110 (12)	0.0933 (3)	0.0260 (5)
H19	0.1561 (15)	0.5114 (13)	0.071 (3)	0.035 (6)*
C20	0.06044 (16)	0.59322 (12)	−0.0340 (3)	0.0302 (5)
H20	0.0275 (17)	0.5634 (13)	−0.146 (3)	0.045 (7)*
C21	0.02969 (15)	0.66508 (12)	−0.0058 (3)	0.0294 (5)
H21	−0.0262 (15)	0.6865 (12)	−0.094 (3)	0.034 (6)*
C22	0.07570 (15)	0.70426 (12)	0.1470 (3)	0.0292 (5)
H22	0.0544 (15)	0.7541 (14)	0.163 (3)	0.037 (6)*
C23	0.15084 (15)	0.67164 (11)	0.2746 (3)	0.0248 (5)
H23	0.1797 (15)	0.7006 (12)	0.380 (3)	0.030 (6)*
O	0.35523 (9)	0.51318 (7)	0.28997 (18)	0.0217 (3)
Si	0.28431 (4)	0.54843 (3)	0.41056 (7)	0.01617 (14)

collection and reduction were performed using the CrysAlisPro software system, version 1.171.36.24 [1]. The crystal structure was solved with SHELXT 2018/2 using Olex2 [2, 3, 6]. The crystal structure was refined based on F^2 (SHELXL-2018/3) [3–5] using Olex2 [6] and the SHELX program package as implemented in WinGX [7]. A multi-scan absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK was employed [1]. The hydrogen atoms were located on the difference Fourier map and refined independently. The Hirshfeld surface [8] was mapped over d_{norm} ranging from 0.0222 to 1.3228 a.u. d_i and d_e in the 2D fingerprint diagram [9] are the distances from the surface to the nearest atom *interior* and *exterior* to the surface, respectively, and are each given in the range of 0.4–3.0 Å. The molecular structure and the 2D fingerprint plot of the title compound, shown in the figure, were created using CrystalExplorer 17.5 [10].

Comment

Methoxysilanes are common building blocks with many applications in preparative chemistry, e.g. they are used to form polymers [11] and silica-based materials [12], and for the silylation of surfaces [13, 14]. They are also widely used as valuable coupling reagents [15, 16] for the controlled design of polysiloxanes [17, 18], as synthesis intermediates [19–21], and for the construction of specially functionalized methoxysilanes [22–28] and siloxanes [22, 23, 26, 29, 30]. We recently reported an in-depth structural study on the involvement of the *tert*-butyldiphenylsilyl (TBDPS) moiety in intermolecular interaction pattern in the crystalline state [31]. Bulky and rigid silyl moieties play an important role in protecting group chemistry [32] and the TBDPS group has therefore become an indispensable component for protecting functional groups in organic total synthesis [33, 34].

Herein, the crystal structure of adamantylmethoxydiphenylsilane is presented, i.e. a bulkier analog of *tert*-butylmethoxydiphenylsilane described previously [31]. There is one title molecule in the asymmetric unit (see the left part of the Figure). The comparison with the recently described *tert*-butyl derivative [31] shows that the replacement of a *tert*-butyl group by an adamantyl group has no significant influence on the intramolecular structural parameters. Both compounds deviate only slightly from an ideal tetrahedral coordination around the silicon atom. The Si–C2 bond length from the silicon atom to the

adamantyl group is 1.8844(18) Å, which is similar to the corresponding bond length of 1.8889(16) Å in the *tert*-butyl compound [31].

The intermolecular interaction pattern of the title compound shows some differences compared to that reported for the *tert*-butyl derivative [31]. In general, due to the higher steric demand of the adamantyl group, the title compound is less densely packed than the *tert*-butyl compound, which can be seen at the dotted region in the 2D fingerprint plot indicating large distances for a number of H...H and H...C contacts (see the figure) [9]. The shortest H...H contact (2.377 Å) can be found between the adamantyl (H10B) and a phenyl group (H19). C–H...C(π) contacts are important structure-determining interactions [31, 35, 36]. The small wings that can be attributed to edge-shifted C(aryl)–H...C(π) contacts are also somewhat more pronounced here than for the *tert*-butyl compound [31], with the closest H...C contact being found for C14–H14...C13 (2.948 Å). In addition, the adamantyl group is involved in the shortest C–H...C(π) contact that can be found in the crystal structure (2.909 Å), with the C–H group pointing more towards a single carbon atom (C11–H11A...C22). Although weak C–H...O contacts only contribute 2.2% to the intermolecular interactions in the title compound, they might play an important directional role for the crystal packing [31, 37–39]. The shortest intermolecular H...O contact that can be found is 2.756 Å (C17–H17...O), which is slightly longer than the H...O contact in the *tert*-butyl compound [31].

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