The crystal and molecular structure of tribenzylsilanol by Rietveld refinement of powder X-ray diffraction data

Philip Lightfoot, Christopher Glidewell and Peter G. Bruce

School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST (UK)

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Abstract

The crystal and molecular structure of tribenzylsilanol ($(PhCH_2)_3SiOH$) has been refined by the Rietveld method from X-ray powder diffraction data collected with a conventional laboratory powder diffractometer. The compound is isostructural with tribenzylmethanol ($(PhCH_2)_3COH$). The crystal consists of isolated molecules with approximate threefold molecular symmetry: there is no hydrogen bonding between the molecules.

Key words: Tribenzylsilanol; Hydrogen bonding; X-ray powder diffraction; Rietveld refinement; Crystal structure

1. Introduction

Main group organometallic hydroxo compounds often exhibit extensive hydrogen bonding in the solid state. Thus both Ph_3SiOH [1] and Ph_3GeOH [2] form cyclic tetramers in which the hydrogen-bonding motif is $R_4^4(8)$ [3,4], while $Ph_2Si(OH)_2$ forms cyclic trimers that are themselves linked to form a three-dimensional network [5]. By contrast the germanium diols $[(Me_3\text{-}Si)_2\text{-}N]_2Ge(OH)_2$ [6] and $(Me_3C)_2Ge(OH)_2$ [7] form single- and double-stranded chains respectively. The tetrameric structure of triphenylsilanol [1] is markedly different from that of the carbon analogue triphenylmethanol (Ph_3COH) [8] which crystallizes as almost perfectly tetrahedral tetramers, with necessarily disordered hydroxyl hydrogen atoms. In view of the structural differences between Ph_3COH on the one hand and Ph_3SiOH and Ph_3GeOH on the other hand, we decided to investigate the structure of $(PhCH_2)_3SiOH$ in order to compare it with that recently reported for $(PhCH_2)_3COH$ [9].

2. Experimental details

Tribenzylsilanol was prepared as described by Dilthey [10]; all attempts to obtain crystals suitable for a single-crystal X-ray diffraction study gave twinned crystals. The polycrystalline sample employed for X-ray powder diffraction was obtained from a solution in diethyl ether. For collection of powder X-ray diffraction data a polycrystalline sample was ground and then mounted in a disc between two layers of transparent tape, and the diffraction data were collected in transmission mode on a Stoe STADI/P high resolution X-ray powder diffractometer, using Ge-monochromated Cu $K\alpha_1$ radiation and a linear position-sensitive detector covering 6° in 2θ. The data collection time was 15 h. The powder diffractogram was indexed on the basis of the first 20 observable peaks using the program TREOR [11] and the space group was determined unambiguously as *Pcab*.

2.1. Crystal data

$C_{21}H_{22}OSi$; $M_r = 318.48$; orthorhombic; $a = 7.8759(3)$ Å, $b = 16.8276(8)$ Å, and $c = 27.1977(12)$ Å; $V = 3604.6$ Å^3; space group, *Pcab* (no. 61); $Z = 8$; $D_c = 1.174$ g cm^{-3}; $\lambda = 1.54051$ Å; $F(000) = 1360$.

The unit-cell dimensions and the space group suggested that $(PhCH_2)_3SiOH$ is isostructural with $(PhCH_2)_3COH$ [9]. This was confirmed by the subsequent successful refinement. Rietveld [12] refinement was carried out using as starting model atomic coordinates taken from the structure of $(PhCH_2)_3COH$. A total of 1122 reflections, distributed over 3750 data points, in the range $5° < 2\theta < 80°$ were used in the

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Correspondence to: Dr. C. Glidewell.

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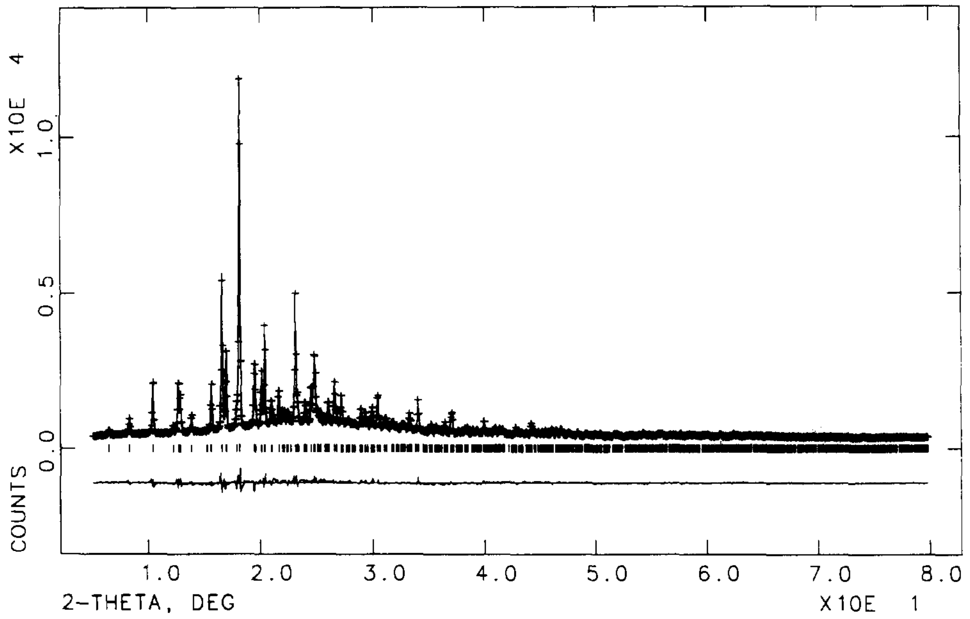

Fig. 1. Final observed (+), calculated (upper full curve) and difference (lower full curve) profiles for the Rietveld refinement of tribenzylsilanol. The reflection positions are marked.

refinement. Final convergence was achieved to give agreement factors $R_{wp} = 5.49\%$, $\chi^2 = 1.99$. Throughout the refinement, soft constraints were applied to the benzene rings such that the C–C distance was 1.40 ±

TABLE 1. Fractional atomic coordinates for tribenzylsilanol

	x	*y*	*z*
O(1)	0.486(2)	0.4112(7)	0.0969(5)
Si	0.3928(9)	0.4772(4)	0.1361(3)
C(1)	0.332(2)	0.5702(11)	0.0985(7)
C(11)	0.496(2)	0.6174(13)	0.0794(9)
C(12)	0.567(3)	0.5970(10)	0.0336(8)
C(13)	0.709(3)	0.6379(14)	0.0173(5)
C(14)	0.798(2)	0.6880(14)	0.0489(9)
C(15)	0.749(3)	0.6958(13)	0.0986(8)
C(16)	0.594(3)	0.6640(13)	0.1133(5)
C(2)	0.558(2)	0.5092(10)	0.1886(7)
C(21)	0.586(3)	0.4295(10)	0.2193(9)
C(22)	0.718(3)	0.3795(17)	0.2032(6)
C(23)	0.754(2)	0.3088(13)	0.2282(10)
C(24)	0.682(4)	0.2958(11)	0.2743(9)
C(25)	0.543(3)	0.3426(17)	0.2895(6)
C(26)	0.497(2)	0.4100(14)	0.2633(10)
C(3)	0.198(2)	0.4329(10)	0.1600(6)
C(31)	0.069(3)	0.3991(16)	0.1196(7)
C(32)	0.038(3)	0.3171(13)	0.1104(7)
C(33)	0.949(3)	0.2957(7)	0.0680(9)
C(34)	0.863(3)	0.3535(16)	0.0404(6)
C(35)	0.871(3)	0.4329(13)	0.0533(8)
C(36)	0.983(3)	0.4575(7)	0.0913(10)

Refined grouped isotropic temperature parameters are as follows: Si, 0.036(4) Å^2; O(1), C(1), C(2) and C(3), 0.028(4) Å^2; C(11)–C(16), 0.002(4) Å^2; C(21)–C(26), 0.036(4) Å^2; C(31)–C(36), 0.022(4) Å^2.

TABLE 2. Selected geometric parameters

(a) Distances			
Si–O(1)	1.70(1)	C(1)–C(11)	1.62(2)
Si–C(1)	1.93(2)	C(2)–C(21)	1.60(2)
Si–C(2)	2.00(2)	C(3)–C(31)	1.60(2)
Si–C(3)	1.83(2)		
(b) Angles			
O(1)–Si–C(1)	108(1)	Si–C(1)–C(11)	112(2)
O(1)–Si–C(2)	110(1)	Si–C(2)–C(21)	104(2)
O(1)–Si–C(3)	109(1)	Si–C(3)–C(31)	116(2)
C(1)–Si–C(2)	108(1)		
C(2)–Si–C(3)	114(1)		
C(3)–Si–C(1)	108(1)		

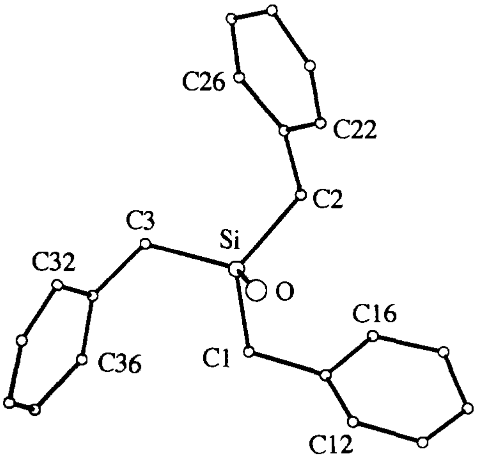

Fig. 2. Perspective view of the tribenzylsilanol molecule showing the atom-numbering scheme.

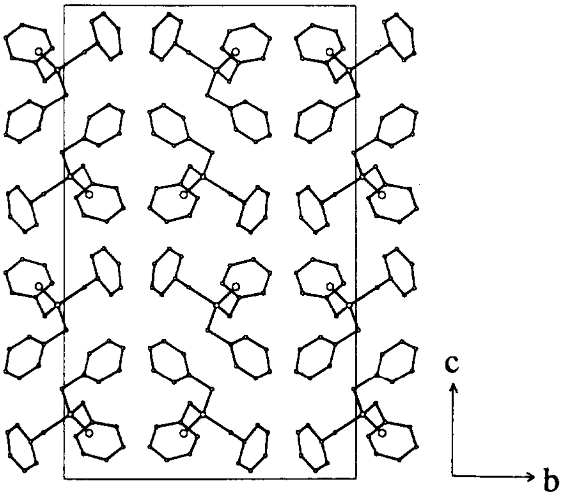

Fig. 3. The unit cell contents, viewed along the *a* axis.

0.01 Å and the C–C–C angle 120 ± 1°. All other structural parameters were allowed to vary freely, with isotropic temperature factors grouped according to atom type. The soft constraints effectively act as additional "observations" which are necessary to stabilize the refinement of such a complex structure from relatively few data.

The final atomic coordinates are given in Table 1 and selected molecular dimensions in Table 2. The final powder diffraction profile from the Rietveld refinement is given in Fig. 1. A perspective view of the molecule showing the atom-numbering scheme is shown in Fig. 2, and a view of the unit-cell contents is in Fig. 3.

3. Results and discussion

The crystals of tribenzylsilanol consist of isolated molecules having approximate threefold molecular symmetry, although no symmetry is imposed crystallographically. The compound is isomorphous and isostructural with tribenzylmethanol and the published atomic coordinates [9] for tribenzylmethanol were used as the initial model for Rietveld refinement.

The Si–O bond length, 1.70(1)Å, is closer to that found in Ph_3SiOH [1], which has two independent tetramers in the asymmetric unit, giving a Si–O distance range 1.633(5)–1.651(5) Å with a mean of 1.645 Å than to the values of 1.613(4) Å in $[(PhCH_2)_3Si]_2O$ [13] and 1.616(1) Å in $(Ph_3Si)_2O$ [14], in both of which the Si–O–Si fragment is strictly linear. The mean Si–C distance of 1.92 Å is again longer than the corresponding mean distance, 1.878 Å, in $[(PhCH_2)_3Si]_2O$.

The shortest intermolecular O · · · O distances in the *a*, *b* and *c* directions are 7.87 Å, 6.71 Å and 6.07 Å respectively, so that there is no intermolecular hydrogen bonding. The effective molecular volumes V/Z for $(PhCH_2)_3COH$ and $(PhCH_2)_3SiOH$ are 431 $Å^3$ and 451 $Å^3$ respectively; this difference on change of the central carbon for silicon is almost precisely the same as the difference between the V/Z of Ph_3COH, 360 $Å^3$, and Ph_3SiOH, 381 $Å^3$, and hence it appears that in this series of R_3MOH species the molecular volumes are not significantly influenced by the presence of hydrogen bonding, as opposed to its absence, or by its pattern.

The Rietveld method [12,15] using X-ray powder diffraction data has been widely used for the structure refinement of non-molecular solids where often only polycrystalline solids are available, particularly for those materials whose insolubility or refractory character prevents the production of samples suitable for single-crystal X-ray analysis. This refinement technique is also highly suitable for the structural study of polycrystalline molecular compounds, and structure refinement can be successful either when a plausible starting model is available [16], as here, or when a partial structure can be developed from the powder diffraction data by Patterson methods [17], direct methods [17,18] or by maximum-entropy techniques [19,20]. The study reported here is one of the few examples of the structure refinement of a molecular organometallic compound by the Rietveld method, the first being the *ab-initio* structure determination of (ferrocenylmethyl)trimethylammonium iodide [16]. Other examples of organometallic speciesdination compounds that have been studied by the Rietveld method are polymeric $[Ru(CO)_4]_n$ [21], a hydrated copper(II) 5-sulphonic-8-quinolinolato complex [22], and titanylphthalocyanine [23]. We feel that in view of the current state of the art in powder diffraction instrumentation and software there should be a wider appreciation of the possible applicability of this method to organometallic systems.

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