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Steric effects in triorganosilanes: crystal and molecular structure of tribenzylsilane, a silane isomorphous with the corresponding silanol

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Abstract

The structure of tribenzylsilane, $(PhCH_2)_3SiH$, has been determined from single-crystal X-ray diffraction data. The crystal consists of isolated molecules with approximate three-fold rotational symmetry. The compound is isomorphous, and effectively isostructural, with tribenzylsilanol $(PhCH_2)_3SiOH$; the crystal structures are discussed in terms of the preferred molecular conformations.

Keywords: Silicon; Silanol; Crystal Structure

Introduction

The μ-oxo compounds $[(PhCH_2)_3M]_2O$ (M = Si, Ge, Sn, Ti) all contain strictly linear M–O–M bridges [1–4]. By contrast with these poly-benzyl derivatives, the analogous phenyl compounds exhibit linearity at oxygen only for M = Si [5], while for M = Ge or Sn the M–O–M skeletons are bent [6,7]. Possible ratinalisations of these differences can be based upon both steric and electronic factors. Recent structural evidence which supports the idea that $(PhCH_2)_3M$ groups are much more sterically-demanding than Ph_3M groups includes the observation of a complete absence of hydrogen bonding in the solid-state structures of both $(PhCH_2)_3COH$ [8] and $(PhCH_2)_3SiOH$ [9], whereas both Ph_3COH [10] and Ph_3SiOH [11] crystallise as hydrogen-bonded tetramers, albeit with markedly different structures, tetrahedral for Ph_3COH and puckered ring for Ph_3SiOH. The tribenzyl alcohols $(PhCH_2)_3COH$ and $(PhCH_2)_3SiOH$ prove to be isostructural [8,9], in contrast to Ph_3COH and Ph_3SiOH, and this observation suggests that their crystal structures are in fact dominated by the packing of the $(PhCH_2)_3M$ groups, and that the preferred packing leads to a structure in which hydrogen bonding is precluded. We have explored this idea further by determining the structure of the parent tribenzylsilane $(PhCH_2)_3SiH$, which proves firstly to be isomorphous, and effectively isostructural, with the corresponding tribenzylsilanol, and secondly to have a molecular volume almost identical to that of the silanol.

2. Experimental section

A sample of tribenzylsilane was prepared from $SiHCl_3$ [12]; crystals suitable for the X-ray investigation were grown from a solution in light petroleum (b.p. 40–60°C).

2.1. Data collection

Data were collected on a Rigaku AFC7S diffractometer with graphite-monochromated Mo Kα radiation with a crystal of dimensions $0.20 \times 0.12 \times 0.28$ mm. Cell dimensions were determined from the setting angles of 12 reflections in the range $18° < 2\theta < 23°$. The intensities of 4968 reflections were measured with a maximum of 2θ of 60° using ω-2θ scans. The intensities of three reflections were measured after every 150 reflections, and remained constant within experimental error throughout the data collection. 1571 Unique re-

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flections having $I > 3\sigma(I)$ were labelled observed and used in the structure solution and refinement. Lorentz and polarisation corrections were made, but no correction for absorption was applied.

2.2. Crystal data

Tribenzylsilane, $C_{21}H_{22}Si$, $M_r = 302.49$. Orthorhombic, space group *Pbca* (No. 61), $a = 26.706(3)$, $b = 16.819(3)$, $c = 8.011(3)$ Å; $V = 3598(2)$ Å^3; $Z = 8$; $D_c = 1.117$ g cm^{-3}; $F(000) = 1296$; Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 1.26 cm^{-1}; T = 296 K.

2.3. Structure solution and refinement

These were carried out with the TeXsan suite of programs [13]. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically: hydrogen atoms attached to carbon were included in the refinement in calculated positions, but the coordinates of the hydrogen attached to silicon were refined. The final refinement cycles included 206 variable parameters, and gave final values of $R = 0.037$, $wR = 0.024$, goodness-of-fit 1.55. The maximum shift/e.s.d. was 0.01, and the density range in the final difference map was $+0.12$ to -0.12 e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography)* (3rd Edition, Vol. C). The refined coordinates for the non-hydrogen atoms are given in Table 1, and selected molecular dimensions in Table 2; Fig. 1 shows a perspective view of the molecule and the atom-labelling scheme, and Fig. 2 shows a stereoview of the molecular packing in the crystal. Complete lists of bond lengths and angles and tables of anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

Table 1
Fractional atomic coordinates of tribenzylsilane

Atom	x	y	z	B_{eq}
Si(1)	0.86624(3)	0.02351(5)	0.6064(1)	4.61(2)
C(1)	0.8413(1)	0.0695(2)	0.8011(3)	5.75(8)
C(2)	0.8805(1)	0.0986(2)	0.9210(3)	4.72(8)
C(3)	0.8916(1)	0.1787(2)	0.9345(4)	5.26(8)
C(4)	0.9275(1)	0.2057(2)	1.0432(4)	6.39(10)
C(5)	0.9535(1)	0.1536(2)	1.1405(4)	7.2(1)
C(6)	0.9433(1)	0.0737(2)	1.1297(4)	6.9(1)
C(7)	0.9072(1)	0.0466(2)	1.0209(4)	5.78(9)
C(8)	0.9017(1)	−0.0701(2)	0.6530)3)	5.49(8)
C(9)	0.9194(1)	−0.1125(2)	0.4988(3)	4.40(7)
C(10)	0.9673(1)	−0.1019(2)	0.4366(4)	5.28(8)
C(11)	0.9822(1)	−0.1377(2)	0.2904(4)	6.06(9)
C(12)	0.9502(1)	−0.1866(2)	0.2037(4)	6.12(9)
C(13)	0.9029(1)	−0.1988(2)	0.2663(4)	5.73(9)
C(14)	0.8878(1)	−0.1622(2)	0.4110(4)	5.09(9)
C(15)	0.8130(1)	0.0008(2)	0.4624(4)	6.12(9)
C(16)	0.7831(1)	0.0727(2)	0.4131(4)	4.94(8)
C(17)	0.7997(1)	0.1219(2)	0.2871(4)	6.26(9)
C(18	0.7734(1)	0.1884(2)	0.2381(4)	7.5(1)
C(19)	0.7296(1)	0.2065(2)	0.3164(5)	7.7(1)
C(20)	0.7120(1)	0.1597(2)	0.4416(5)	7.3(1)
C(21)	0.7387(1)	0.0933(2)	0.4912(4)	6.18(9)

Table 2
Selected molecular dimensions (distances in Å; angles in °)

Bond lengths			
Si(1)–C(1)	1.864(3)	C(1)–C(2)	1.502(3)
Si(1)–C(8)	1.876(3)	C(8)–C(9)	1.502(3)
Si(1)–C(15)	1.871(3)	C(15)–C(16)	1.501(4)
Bond angles			
C(1)–Si(1)–C(8)	111.2(1)	Si(1)–C(1)–C(2)	114.9(2)
C(1)–Si(1)–C(15)	109.2(1)	Si(1)–C(8)–C(9)	113.1(2)
C(8)–Si(1)–C(15)	109.6(1)	Si(1)–C(15)–C(16)	113.7(2)
Torsional angles			
Si(1)–C(1)–C(2)–C(3)	103.0(3)		
Si(1)–C(8)–C(9)–C(10)	96.0(3)		
Si(1)–C(15)–C(16)–C(17)	81.3(3)		
H(1)–Si(1)–C(1)–C(2)	55.5(9)		
H(1)–Si(1)–C(8)–C(9)	64.7(9)		
H(1)–Si(1)–C(15)–C(16)	58.2(9)		

2.4. Molecular-orbital calculations

All calculations were by the AMI method [14], as incorporated in the MOPAC system [15], version 6.0. Published atomic parameters were employed [14,16].

3. Results and discussion

Tribenzylsilane crystallises in the orthorhombic space group *Pbca* with one molecule in the asymmetric unit, there is thus no crystallographic symmetry imposed on the molecules, although the isolated

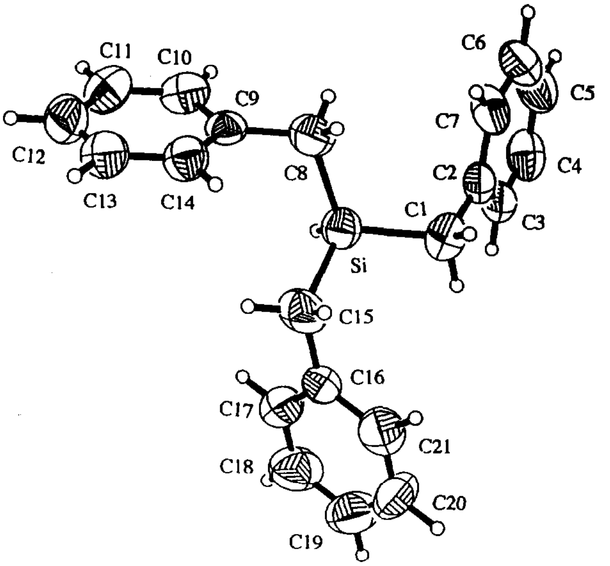

Fig. 1. Perspective view of the tribenzylsilane molecule, showing the atom-labelling scheme.

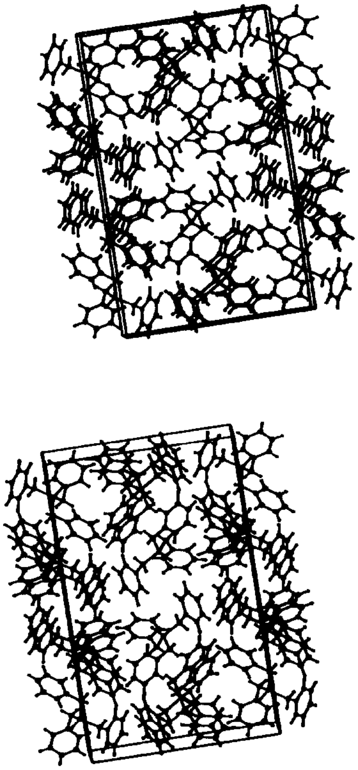

Fig. 2. A stereoview of the molecular packing in the crystal structure of tribenzylsilane, viewed along the c axis.

molecules are expected to exhibit three-fold rotational symmetry. This behaviour contrasts with that of, for example, $[(PhCH_2)_3Si]_2O$ [1]: in this μ-oxo compound the three-fold rotational symmetry of the molecule is utilised in the crystal as the molecules lie along the three-fold axis of a rhombohedral unit cell. Despite the absence of crystallographically imposed symmetry, the molecules exhibit approximate C_3 symmetry as evidenced by the Si–C and C–C bond lengths and the C–Si–C and Si–C–C bond angles of the central core of the molecule (Table 2). Furthermore, the torsional angles H–Si–C–C show nearly perfect staggering about the Si–C bond of each benzyl substituent, while the torsional angles Si–C–C–C show that for each substituent the phenyl ring is approximately normal to the Si–C–C plane. Overall the molecular symmetry is close to C_3 despite the lack of crystallographic symmetry. While the bond lengths found in tribenzylsilane are all unexceptional, the Si–C–C bond angles, which range from 113.1(2)° to 114.9(2)° with mean 113.9°, are significantly larger than the tetrahedral angle. Such large Si–C–C angles have also been found in $[(PhCH_2)_3Si]_2O$ [1]: similar large M–C–C angles are found in analogous $[(PhCH_2)_3M]_2O$ compounds for M = Ge, Sn and Ti [2–4], while in $(PhCH_2)_3COH$ the corresponding C–C–C angles range from 116.9(2)° to 116.9(2)°, with a mean of 116.5°.

The requirement for staggering about the Si–C bonds together with the preferred orientation of the phenyl rings perpendicular to the Si–C–C planes determines the observed C_3 conformation of the $(PhCH_2)_3Si$ group. Any alternative conformations fulfilling the above requirements, such as those without approximate three-fold rotational symmetry or that having all torsional angles H–Si–C–C of ca. 180°, are ruled out by the resulting close proximity of the phenyl groups. The conformation found here for tribenzylsilane is, in fact, entirely typical of $(PhCH_2)_3M$ groups when M is non-planar and effectively four-coordinate. This conformation is observed also in $[(PhCH_2)_3M]_2O$ (M = Si, Ge, Sn, Ti) [1–4]; $(PhCH_2)_3MOH$ (M = C, Si) [8,9]; $[(PhCH_2)_3M]_2S$ (M = Ge, Sn) [17,18]; $(PhCH_2)_3$-Al, in which the aluminium is rendered non-planar by interaction with a C–H bond from a neighbouring molecule [19]; $[(PhCH_2)_3Al]OEt_2$ [20]; and $(PhCH_2)_3$-$Zr(C_5H_5)$ [21]. A notable exception is provided by $(PhCH_2)_3Ti(C_5Me_5)$ [22], where there is some evidence for an agostic $CH_2 \cdots Ti$ interaction involving one only of the benzyl groups.

That the crystal structure of tribenzylsilane is in fact dominated by its preferred molecular structure, specifically by the preferred conformation of the benzyl groups, is confirmed by a comparison of the structures of tribenzylsilane and tribenzylsilanol [9]. These two compounds crystallise with identical space groups. *Pbca*, they have very similar unit-cell dimensions, and very similar atomic coordinates; they are, in fact, isomorphous, and but for the extra oxygen atom in $(PhCH_2)_3SiOH$, they are isostructural. In each case the crystal structure is determined by the packing of the $(PhCH_2)_3Si$ groups, with the remaining hydrogen atom or hydroxyl group simply fitting into the appropriate cavity adjacent to the silicon atom. This packing serves, in both $(PhCH_2)_3COH$ [8] and $(PhCH_2)_3SiOH$ [9], to prevent any close contacts between hydrogen atoms and hence to prevent any hydrogen bonding, even though hydrogen bonding is often regarded as one of the strongest intermolecular forces in organic molecular crystals [23]. The unimportance of the Si–H or Si–OH groups for the molecular arrangement within the crystal structure is further shown by the values of V/Z, the effective volume per molecule: 450 Å^3 for $(PhCH_2)_3SiH$ and 451 Å^3 for $(PhCH_2)_3SiOH$ [9]. By contrast, the effective molecular volume for $(PhCH_2)_3$-COH [8], which is isostructural with $(PhCH_2)_3SiOH$, is only 431 Å^3 reflecting the shorter bonds from the central atom to the benzylic methylene carbon atoms (mean bond lengths: 1.539 Å in $(PhCH_2)_3COH$ [8] and 1.92 Å in $(PhCH_2)_3SiOH$ [9]). For $(PhCH_2)_3Al$ [19], which coincidentally also crystallises in space group *Pbca* although with markedly different cell dimensions, V/Z is 428 Å^3, the rather low value possibly reflecting the intermolecular $C–H \cdots Al$ interactions.

Tribenzylsilane molecules of precise or approximate

C_3 symmetry are chiral; the adoption of a centrosymmetric space group requires the presence of both enantiomeric forms, in equal abundance. Calculation of the molecular structure for an isolated (gas-phase) molecule, using the AM1 method [14] gave a structure of precise C_3 molecular symmetry, with torsional angles C–C–Si–H and C–C–C–Si of 45.8° and 90.3° respectively, reasonably similar to those (Table 2) for the molecules in the crystal. Furthermore, the calculations show that there is a pathway for the isomerisation of the free molecule, from one C_3 enantiomorph to the other, involving concerted rotation about all three Si–C bonds, which has an activation barrier of only 5.7 kJ mol^{-1}. Thus although the molecular conformation is frozen in the crystalline state, in the gas phase or in solution, rapid equilibrium between the two conformational enantiomers is to be expected.

The dominant effects of the preferred $(PhCH_2)_3Si$ conformation on the crystal structures of tribenzylsilane and tribenzylsilanol suggest in turn that the observed linear M–O–M bridges in $[(PhCH_2)_3M]_2O$ (M = Si, Ge, Sn) [1–3] may result from steric, rather than electronic factors [24].

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