Isolation of a Tetrahydroxydisiloxane formed during Hydrolysis of an Alkyltrichlorosilane: Crystal and Molecular Structure of $[Bu^t(OH)_2Si]_2O$

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Hydrolysis of Bu^tSiCl_3 affords the tetrahydroxydisiloxane $[Bu^t(OH)_2Si]_2O$ which has a linear Si–O–Si angle and which forms surprisingly stable hydrogen-bonded sheets in the solid state.

The hydrolysis of R_2SiCl_2 and $RSiCl_3$ compounds leads to the formation of a wide variety of polymers containing linear $-OSi(R_2)O-$ or branching $RSi(O)_3$ units which form the basis of the worldwide silicones industry.[1] Low molecular weight hydroxysiloxanes are rarely isolated during the hydrolysis of $RSiCl_3$ compounds because of the very ready condensation of silanols (SiOH containing species) to polymeric siloxanes. As part of a project to investigate the solid state structures of silanols we have now found that controlled hydrolysis of Bu^tSiCl_3 gives the partially condensed hydroxydisiloxane $[Bu^t(OH)_2Si]_2O$ **1** which has several unusual structural features. The hydrolysis of Bu^tSiCl_3 using 1.5 equivalents of water was reported 35 years ago to give a tricyclic tetrameric species $[Bu^tSiO_{1.5}]_4$.[2] Although $[C_6H_{11}(OH)_2Si]_2O$ has been reported[3] little information about it is known and **1** appears to be the first tetrahydroxydisiloxane to be isolated in a pure form and to be fully characterized.

The hydroxysiloxane **1** was prepared in 65% yield using a modification of Sommer and Tyler's method.[4] Thus addition of Bu^tSiCl_3 in diethyl ether during 20 min to an ice-cold mixture of KOH (3 equiv.), water and methanol gave a reaction mixture that became acidic as indicated by phenolphthalein. Addition of a further equivalent of KOH followed by stirring for a further 10 min gave an alkaline mixture. The organic layer was removed and the aqueous layer was extracted three times with ether. The combined organic solutions were evaporated under reduced pressure to leave a white solid which was crystallized from tetrahydrofuran to give **1** as colourless crystals which cleaved readily to form sheets.† The crystals soften at 160 °C and melt with decomposition over the range 177–212 °C, probably indicating further condensation and formation of polysiloxanes.

The crystal structure determination revealed (Fig. 1) that the molecules are hydrogen bonded together to form sheets in which Bu^t groups within each molecule are on opposite sides of the sheet so that they form hydrophobic layers which prevent hydrogen bonding between sheets. Only one set of hydrogen bonds is shown in Fig. 1; a second equivalent set can be generated in which the donor and acceptor sites in each –OH group are exchanged.

There are three distinct types of hydrogen bond present. One type O(1a)···O(2) (2.678 Å) links the molecules into chains while the others O(2)···O(2a) (2.686 Å) and O(1)···O(1a) (2.690 Å) link the chains, thus giving a sheet

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† *Selected spectroscopic data* for **1**: IR 3180 cm^{-1} (ν Si-OH, H-bonded); ^{1}H NMR ($CDCl_3$) δ 0.99 (OH) and 1.55 (Bu^t); mass spectrum (chemical ionisation NH_3) *m/z* 272 (100%, $[M + NH_4]^+$), 271 (70, $[M + NH_3]^+$) and 254 (2, $[M]^+$).

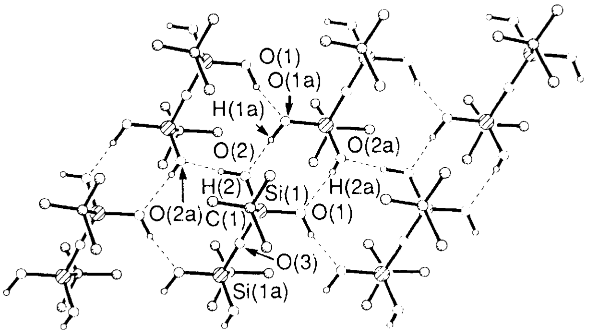

Fig. 1 Structure of **1**: hydrogen atoms in the Bu^t groups are omitted for clarity; dashed lines represent hydrogen bonds. Selected distances (Å) and angles (°): Si(1)–O(1) 1.626(2), Si(1)–O(2) 1.626(2), Si(1)–O(3) 1.600(1), Si(1)–C(1) 1.840(3), Si(1)–O(3)–Si(1a) 180.0(0), O(1)–Si(1)–O(2) 106.0(1).

formation. This type of structure is unusual as silanediols, *e.g.* $Bu^t_2Si(OH)_2$[5] and $(o\text{-tolyl})_2Si(OH)_2$[6] often form hydrogen bonded ladder-like chains, although in $Et_2Si(OH)_2$[7] the chains are linked so as to form layers. In dihydroxydisiloxanes $[R_2(OH)Si]_2O$ (R = Ph[8], Pr^i,[9] and 2-thienyl[10]) molecules are also hydrogen bonded to form chains. Hydrogen bonded sheets are found in $(cyclo\text{-}C_6H_{11})Si(OH)_3$[11] where, as in **1**, the hydrophobic R groups prevent hydrogen bonding between sheets. The only other structurally characterized compound containing two silanediol groups seems to be the adduct of 1,1,5,5-tetrahydroxy-3,3,7,7-tetraphenylcyclotetrasiloxane with two pyridine solvent molecules in which the siloxane molecules are hydrogen bonded to form chains.[12]

The structure was refined in $P\bar{1}$ as this resulted in narrower ranges of chemically equivalent bond lengths, *e.g.* within the Bu^t groups, and improved e.s.d.s. For example the C–C distances and their e.s.d.s range from 1.529(5) to 1.550(4) Å in $P\bar{1}$ whereas the range is 1.505(7) to 1.616(6) Å in $P1$.‡ [Similar reasoning was used in the assignment of the space group for $(Ph_3Si)_2O$[13].]

In $P\bar{1}$ the molecule has a crystallographically imposed centre of symmetry and thus a linear Si–O–Si linkage [171.6(6)° in $P1$]. Linear disiloxane linkages have previously unequivocally been found only in $(R_3Si)_2O$ (R = $CH{=}CH_2$, Ph and $PhCH_2$[14]) species in which all the groups on each silicon are the same. Numerous calculations have been carried out on small hydroxy-silanes and siloxanes to compare the structures of such species with the Si–O–Si networks found in silicates.[15] Although $[(HO)_3Si]_2O$ has been the subject of much discussion[16] no $[R(HO)_2Si]_2O$ species (R = H, alkyl or aryl) seem to have been the subject of calculations. At the 6-13G* level, calculations on $[(HO)_3Si]_2O$ give values of 165.4°, 1.610 Å, and 1.622 Å for the Si–O–Si angle, the bridging Si–O bond length, and the terminal Si–O bond length respectively.[17] These bond lengths compare well with the analogous bonds in **1** [1.600(1) and 1.626(2) Å respectively] but the Si–O–Si angle is somewhat lower than the 180° in **1**. It is, however, well known that the Si–O–Si angle is very flexible, the experimental barrier to linearization at oxygen in $(H_3Si)_2O$ being[18] only 1.3 kJ mol^{-1} and the Si–O–Si angle in $H_2C{=}SiH(OSiH_3)$ calculated as 178.1°.[19] It is possible that the rigid hydrogen bond network together with the *trans*-arrangement of the Bu^t groups are the reasons for the unusual, linear Si–O–Si angle. The compound is surprisingly thermally stable, only seeming to decompose at temperatures above about 160 °C.

In conclusion, it can be seen that careful hydrolysis of an alkyltrichlorosilane can allow isolation of a tetrahydroxydisiloxane which has unusual structural features and which can be seen as one of the simple units from which branched polysiloxanes may be made.

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‡ *Crystal data*: $C_8H_{22}O_5Si_2$, M = 254.4, colourless crystals, space group $P\bar{1}$, triclinic, a = 6.243(2), b = 6.232(2), c = 9.971(3) Å, α = 85.18(2), β = 80.77(2), γ = 70.58(2)°, U = 361.0(2) Å^3, Z = 1, D_c = 1.171 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, R = 0.038, R_w = 0.047 for 1127 observed reflections with $F_{obs} > 4.0\sigma(F)$. The hydrogen atoms were found from difference maps which also revealed a disorder associated with the hydroxy hydrogen atoms. This disorder was consistent with the presence in the structure of two sheets formed by the two possible sets of hydrogen bonds as described. All hydrogen atoms were incorporated in the refinement using a riding model and standard C–H and O–H distances. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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