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Preliminary communication

Crystallographic evidence for intermolecular hydrogen bonding between aryl groups and OH groups in silanols

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Abstract

In crystals of the silanols $(Me_3Si)_3CSiPh(X)OH$ (X = I or OMe) there is intermolecular $\pi \cdots HO$ bonding between a phenyl group in one molecule and an OH group in another, and there are probably intramolecular $\pi \cdots HO$ interactions in two silanols previously reported to show no hydrogen bonding. It is suggested that similar interactions should exist for OH groups attached to other metals or metalloids.

Crystallographic evidence was presented previously for the presence of intramolecular $\pi \cdots HOSi$ bonding in crystals of the silanediol **1** (in this instance alongside intermolecular $O \cdots HO$ bonding) [1] and the silanol **2a** [2], with the O–HO bond in each case inclined to the plane of the ring (at angles of 75 and 42° in **1** and **2**, respectively) and the H atom lying virtually above the periphery of the ring close to one of the atoms of the ring, *i.e.* above the π-cloud. Similar hydrogen bonding was later observed in the silanol **2b** [3]. We have now observed, in crystals of silanols **3a** and **3b**, what we believe to be the first examples of *inter*molecular $\pi \cdots HOSi$ bonding, and also found indications of intramolecular $\pi \cdots HOSi$ interactions in crystals of two silanols previously thought to show no hydrogen bonding.

$OH(SiPh_2)_7OH$	$(PhMe_2Si)_3CMe(X)OH$	$(Me_3Si)_3CSiPh(X)OH$
1	**2**	**3**
	a, X = H **b**, X = Me	**a**, X = I **b**, X = OMe **c**, X = OH

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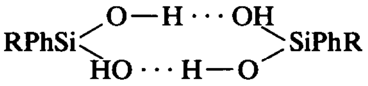
$\mathrm{RPh(MeO)SiOH \cdots O(H)SiPh(OMe)R}$

I



II

$\mathrm{R = (Me_3Si)_3C}$

This work began with the determination of the crystal structure of silanol **3a**, which was available to us from earlier studies [4]. We expected to observe O ··· HO bonding, since the related silanol **3b** was previously judged to form open-chain dimers of type **I**, and the related diol **3c** cyclic dimers of type **II** [5]. To our surprise we found that **3a** showed no O ··· HO bonding (and also no I ··· HO bonding, which is also possible in principle), and only discrete monomers appeared to be present. However when we reexamined the structure of **3a** in the light of the observations on silanols **1**, **2a** and **2b** we found that the molecules appeared to be held in pairs by intermolecular $\pi \cdots$ HO bonding in which the OH group in each molecule interacts with the phenyl group in the other. * As shown in Fig. 1, each

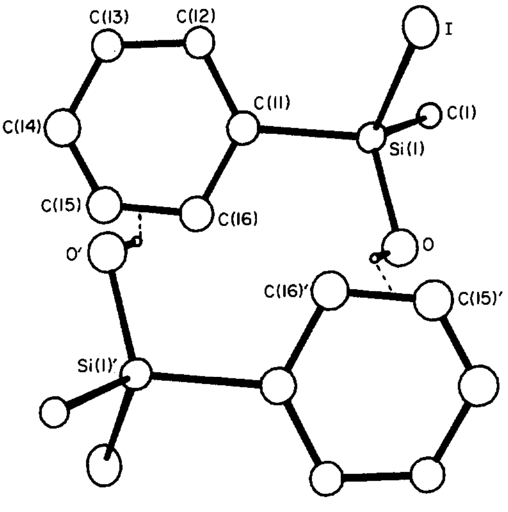


Fig. 1. The hydrogen-bonded pair of molecules of **3a** with the $\mathrm{Me_3Si}$ groups on C(1) and C(1)' omitted for clarity. The symmetry element is $1-x,\ -y,\ -z$. Relevant distances: H(0) ··· C(15)', 3.0 Å; H(0) ··· C(16)', 3.1 Å; H(0) and 0 from the plane of the C(11)–C(16) ring, 2.9 and 3.25 Å, respectively.

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* *Crystal data:* $\mathrm{C_{16}H_{33}OISi_4}$, $M = 480.7$, monoclinic, space group $P2_1/c$, $a = 9.472(1)$, $b = 13.128(2)$, $c = 18.654(4)$ Å, $\beta = 91.27(1)°$, $U = 2319.0$ Å^3, $Z = 4$, $D_c = 1.4$ g cm^{-3}, $F(000) = 984$. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 15.7$ cm^{-1}. Data were collected from a crystal of *ca.* $0.18 \times 0.10 \times 0.12$ mm on an Enraf-Nonius CAD4 diffractometer. Structure solution was by heavy atom methods and refinement was by full matrix least squares with only the I and Si atoms anisotropic because of the limited data. The H(O) hydrogen atom was found on a difference map and its position refined but with a fixed isotropic temperature factor. The other H atoms were fixed at calculated positions. The Si atom within the $\mathrm{(Me_3Si)_3C}$ system were disordered in a commonly observed way with an occupancy ratio of 87/13; the lower occupancy Si sites were refined isotropically. Refinement converged at $R = 0.067$, $R' = 0.069$ for 998 reflections with $|F^2| > 3\sigma(F^2)$ and $2 < \theta < 25°$. Lists of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

O–H bond is directed towards the region above one of the C–C bonds of the ring in an adjacent molecule. (The O–H bond makes an angle of *ca.* 36° with the plane of the ring.)

Initially there was an element of doubt about the reality of the interaction because the apparent distance of the H atom from the relevant bond, C(15′)–C(16′), *viz.* 2.95(20) Å, seemed somewhat long (although a distance of 3.0 Å between the hydrogen atoms and the plane of the ring was reported for the hydrogen-bonded benzene-water complex, $C_6H_6 \cdot H_2O$, in the gas phase [6]) and the H atom appeared to lie slightly outside the region above the ring rather than immediately above the C(15′)–C(16′) bond, but this could reasonably be attributed to the imprecision in the data, and it seemed very unlikely that it was only by chance that the molecules took up positions so close to those appropriate to $\pi \cdots$HO interaction. The probability that such interaction was present was strengthened by the observation that the IR spectrum of solid **3a** has its ν(OH) band (sharp) at 3585 cm^{-1}, close to the region associated with intermolecular $\pi \cdots$HOSi bonding [2,7], and that, presumably because of dissociation of the pairs, in the spectrum of a CCl_4 solution this band is replaced by one at 3656 cm^{-1}, in the region expected for a free SiOH group [7]. (In the case of the intramolecularly bonded silanols **1**, **2a** and **2b** the $\pi \cdots$HO bands in the 3600 cm^{-1} region are retained in the spectra of CCl_4 solutions. [2,3,7].)

Virtually all doubt was subsequently removed by the finding of clear evidence for the same type of bonding in the case of silanol **3b**, the published data [5] for which we reexamined in the light of the results for **3a**. This revealed the presence, alongside the previously observed O$\cdots$HO bonding, of the intermolecular $\pi \cdots$HO interaction depicted in Fig. 2. The (O)H atom lies almost directly above the C(13) atom at a distance of 2.5 Å from it, the O–H bond making an angle of 49° with the plane of the phenyl ring. The presence of this bonding accounts for the absence of the OH$\cdots$OMe bonding that had previously been expected [5].

We are aware of only three silanols, $(Me_3Si)_2CSiAr_2CHSiAr_2OH$ (Ar = mesityl), **4** [8], $[Ru(\eta^6\text{-}Ar)Cl_2(PPh_2CH_2SiMe_2OH)]$ (Ar = *p*-cymene) **5** [9], and $Ar_2SiSiH\text{-}{}^tBuSiAr_2Si{}^tBuOH$ (Ar = 2,6-diethylphenyl), **6** [10] (though there may be more) that were judged from crystallographic studies to show no hydrogen bonding. Since all three contain aryl groups that, because they bear electron-releasing substituents, should be even better hydrogen-bond acceptors than phenyl, we reexamined the published data for them, which unfortunately did not include coordinates of the (O)H atoms. For compound **4** this confirmed that there is no hydrogen bonding of any kind, possibly because of the steric effects of the mesityl groups, but for the other two the positions of the O atoms in each case are consistent with intramolecular $\pi \cdots$HO interaction. (Details will be published elsewhere.) It is very likely that there is intramolecular $\pi \cdots$OH interaction in both cases, and that this accounts for the absence of the expected O$\cdots$HO bonding.

There is crystallographic evidence [11] for $\pi \cdots$OH bonding, both intra- and inter-molecular, between aryl groups and the OH groups of phenols or alcohols; in some cases the O–H bonds are directed more or less towards the centroids of the rings and perpendicular to them, and in others the hydrogen atoms lie over the π-system above C–C bonds of the ring, as in the the case of the silanols **1**, **2a**, **2b**, **3a**, **3b**, and (probably) **5** and **6**. There are also examples of $\pi \cdots$HO interaction, of the first type, between water molecules and aryl groups [12]. It is to be expected

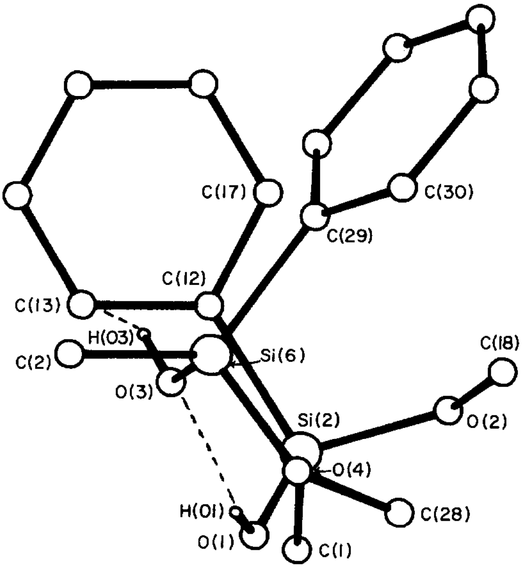

Fig. 2. The relevant portion of the hydrogen-bonded pair of molecules of **3b**. (For the atoms in the complete pair see ref. 7.) Relevant distances: H(03) · · · C(13), 2.5 Å; H(03) · · · C(12), 2.8 Å; H(03) and O(3) from plane of C(12)–C(17) ring, 2.5 and 3.2 Å, respectively.

that interactions will be found in which the (O)H atoms of silanols lie more or less over the centres of the rings rather than above the peripheral π-cloud.

It is likely that, once they are sought, $\pi \cdots$ HO interactions will be observed for hydroxides of other metals and metalloids.

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