Hydrogen-bonding Interaction between a Hydroxy Group and the π-Electrons of an Aryl Group. Crystal Structure of [Tris(dimethylphenylsilyl)methyl]methylsilanol

Salih S. Al-Juaid, Ahmad K. A. Al-Nasr, Colin Eaborn* and Peter B. Hitchcock

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

In the crystal of the silanol $(Me_2PhSi)_3CSi(Me)(H)OH$ there is intramolecular hydrogen bonding between the OH group and the π-electron cloud of a phenyl group.

Organosilanols show a strong tendency to undergo association in the solid state through O–H···O bonding, and a wide range of hydrogen-bonded structures are known for them.[1] We have determined the crystal structures of several silanols in which a bulky group, including the very bulky group $(Me_3Si)_3C$, is attached to a silicon atom bearing one or more OH groups, and in all cases have observed intermolecularly hydrogen-bonded structures (for some of the various types see refs. 1–5); the simplest example is provided by the compound $(Me_3Si)_3C(Ph)(MeO)SiOH$, which forms a linear dimer $(Me_3Si)_3C(Ph)(MeO)SiOH\cdots O(H)Si(Ph)(OMe)C(SiMe_3)_3$.[2] We were thus surprised to find that crystals of the silanol **1**, containing the related bulky group $(Me_2PhSi)_3C$, are made up of discrete molecules, with the oxygen atoms well separated,

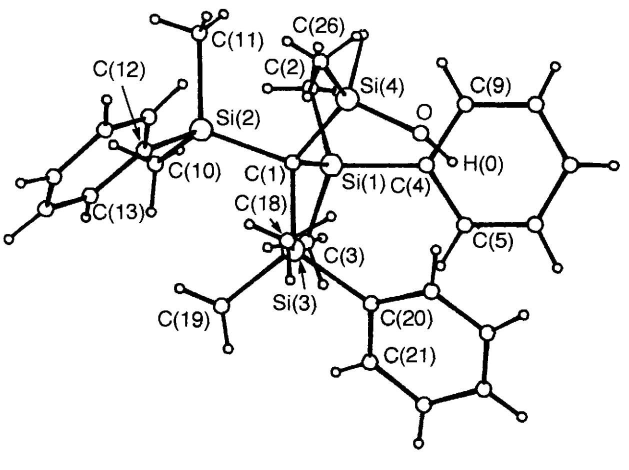

Fig. 1 View of the molecule of **1** perpendicular to the plane of the C(4)–C(9) phenyl group. Some relevant bond lengths and angles are: Si(4)–O 1.646(2), O–H 1.12(6) Å; Si(4)–O–H 123(3)°.

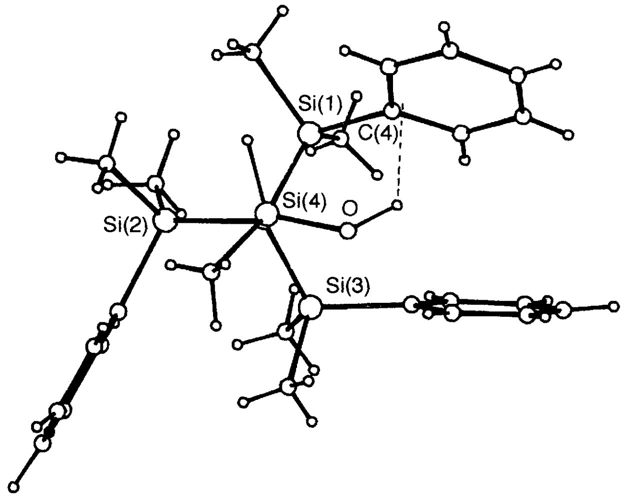

Fig. 2 View along the Si(4)–C(1) direction, showing normal[7] orientations for the $Si(2)Me_2Ph$ and $Si(3)Me_2Ph$ groups and a different orientation for the $Si(1)Me_2Ph$ group

but further analysis showed that this is because the OH group is engaged in intramolecular hydrogen bonding involving the π-electron cloud of a phenyl group. Such bonding was observed previously (in 1987) for one of the OH groups in the diol **2**, alongside intermolecular hydrogen bonding between the OH groups.† [6]

$(Me_2PhSi)_3CSi(Me)(H)OH$ **1** $HO(SiPh_2)_7OH$ **2**

Na_4[calix[4]arenesulphonate]·$13.5H_2O$ **3**

(9-anthryl)$C(CF_3)(H)OH$ **4**

Views of the molecule of **1** are shown in Figs. 1 and 2.‡ The H atom of the OH group lies almost directly above a carbon atom, C(4), of a phenyl group, at a distance of only 2.37(6) Å from that carbon; the distances to the adjacent C(5) and C(9) atoms are 2.65(6) and 2.61(6) Å, respectively, and that perpendicular to the mean plane of the ring is 2.33 Å. (In the silanol **2** the distance of the H atom of the OH group from the nearest carbon atom of the relevant phenyl group is 2.90 Å, and that from the mean plane of the ring 2.52 Å.) As expected in view of the diffuse nature of the π-cloud with which it interacts, the OH group shows a high thermal motion. It is significant that in order to facilitate the hydrogen bonding the face of the C(4)–C(9) ring is presented to the OH group, and so twisted away from the propeller position normally found in $(Me_2Ph)_3C$ groups,[7] whereas the other two rings have the usual orientation. {The planes of the rings are normally oriented at an angle of *ca.* 80–85° to the Si_3 plane;[7] the angles for the C(20)–C(25) and C(12)–C(17) rings are 88 and 85°, respectively, but that for the C(4)–C(9) ring is 56°. This is caused by a rotation about the C(1)–Si(1) bond, as can be seen from the torsion angles Si(4)–C(1)–Si(1)–C(4), 42°, Si(4)–C(1)–Si(2)–C(12), −87°, and Si(4)–C(1)–Si(3)–C(20), −77°.}

Two groups of workers, Atwood *et al.* and Rzepa *et al.*, have recently reported crystallographic demonstrations of hydrogen-bonding interaction between OH groups and the π-electrons of aromatic rings. (Neither report mentioned any previous example.) Atwood *et al.* observed such bonding between the two O–H bonds of a water molecule and the π-electrons of two aromatic rings in the calixerene derivative **3**;[8] they described each O–H bond of the water molecule as directed towards the centroid of an aromatic ring. Rzepa *et al.* observed such bonding in both the (*S*)- and (*R,S*)-forms of the anthracene derivative **4**, complementing π–π facial interactions between parallel anthracene ring systems; in the (*S*)-form there are dimers in which both OH groups point inwards to interact with a π-face of an opposing benzo ring, whereas in the (*R,S*)-form dimers resulting from the π–π facial interaction are linked to other such dimers by outward-pointing OH groups each directed towards the π-face of a benzo ring of another dimer.[9] In both forms the O–H bonds are not far from perpendicular to the plane of the aromatic system; they are directed towards the outside of one of the outer rings, at a distance of *ca.* 2.2 Å from the plane, in the (*S*)-enantiomer but rather more over towards the bond between an outer ring and the central ring, at a distance of *ca.* 2.3 Å from the plane, in the (*R,S*)-species. In contrast, in **1** the hydrogen atom lies in the π-cloud on the periphery of the ring, near the C(4) atom, with the OH bond making an angle of 42° with the phenyl plane. Recent calculations by Monte Carlo methods suggest that in the hydrogen-bonded complex $C_6H_6{\cdot}H_2O$ one OH bond is directed towards the centre of the ring.[10] However, the results of an IR spectroscopic study of such a complex in an argon matrix,[11] *ab initio* calculations,[12] and two-colour time-of-flight mass spectroscopy[13] have been interpreted in terms of a structure in which the water molecule lies almost parallel to the plane of the ring, with the O and (the two) H atoms *ca.* 3.2 and 3.0 Å, respectively, above the ring, so that the H atoms are directed towards the π-cloud above the

---

† The possibility that an unexpected band at 3600 cm^{-1} in the IR spectrum of solid $HO(SiPh_2)_xOH$ ($x = 4$) might arise from OH–π bonding was considered some time ago but disfavoured (A. W. P. Jarvie, A. Holt and J. Thompson, *J. Organomet. Chem.*, 1968, **11**, 625). That such a band does, indeed, arise from such bonding in this and the related diols with $x = 3$, 5, or 7 was recently confirmed [L. A. Leites, T. S. Yadritseva, V. V. Dement'ev, B. A. Antipova, T. M. Frunze and A. A. Zhdanov, *Organomet. Chem. USSR* (*Engl. Transl.*), 1989, **2**, 537].

‡ *Crystal data*: $C_{26}H_{38}OSi_4$, $M = 478.9$, monoclinic, space group $P2_1/c$, $a = 16.224(4)$, $b = 17.616(4)$, $c = 9.646(3)$ Å, $\beta = 100.27(2)°$, $U = 2712.9$ Å^3, $Z = 4$, $D_c = 1.17$ g cm^{-3}, $F(000) = 1032$. Monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 2.3$ cm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer in the θ–2θ scan mode. The structure was solved by direct methods and refined with non-hydrogen atoms isotropic. All hydrogen atoms were located on a difference map and refined freely with isotropic thermal parameters except for H(1) on Si(4) for which B_{iso} was fixed at 1.0 Å^2. Final residuals were $R = 0.043$, $R_w = 0.053$ for 3916 observed reflections with $|F^2| > 3\sigma(F^2)$ and $2 < \theta < 28°$. 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.

periphery of the ring. Probably both hydrogen bonding directed essentially towards the centre of the ring and that directed essentially towards a specific part of the π-cloud will be commonly observed.

It is noteworthy that in **2** the interaction of the OH group with the π-cloud occurs alongside OH$\cdots$O(H) bonding, in **4** it supplements π–π facial interaction, and in **3** it is partly the consequence of the fact that the relevant water molecule is held in place by ordinary hydrogen bonding to other water molecules, whereas in **1** the H–π interaction stands alone and is strong enough to preclude the usual OH$\cdots$O(H) bonding. Our observations provide strong support for the view expressed by Atwood *et al.*, on the basis of their observation of interactions involving water, that hydrogen bonding involving π-electrons will be found in a wide range of crystal structures. (The π-electrons of acetylenic and olefinic bonds should also be able to enter into such bonding; the energy of formation of the $H_2C{=}CH_2{\cdot}H_2O$ complex in an argon matrix[14] appears to be very similar to that for the $C_6H_6{\cdot}H_2O$ complex under similar conditions.[12]) Since silanols are more acidic than alcohols they can be expected to enter into such bonding more readily than the latter.

We thank Dr P. D. Lickiss, Professor J. N. Murrell and Dr A. J. Stace for helpful discussions, the SERC for support, and the Ministry of Higher Education of the Kingdom of Saudi Arabia for the award of postgraduate scholarships to (S. S. Al-J. and A. K. A. Al-N.).

Received, 25th June 1991; Com. 1/03169D

References

1 E. Lukevics, O. Pudova and R. Sturkovich, *Molecular Structures of Organosilicon Compounds*, Ellis Horwood, Chichester, 1989, pp. 175–179.

2 Z. H. Aiube, N. H. Buttrus, C. Eaborn, P. B. Hitchcock and J. A. Zora, *J. Organomet. Chem.*, 1985, **292**, 177.

3 N. H. Buttrus, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Organomet. Chem.*, 1986, **302**, 159; N. H. Buttrus, C. Eaborn, P. B. Hitchcock and A. K. Saxena, *J. Organomet. Chem.*, 1985, **284**, 291.

4 N. H. Buttrus, C. Eaborn, P. B. Hitchcock and A. K. Saxena, *J. Organomet. Chem.*, 1985, **287**, 157.

5 N. H. Buttrus, R. I. Damja, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Chem. Soc., Chem. Commun.*, 1985, 1385.

6 Yu. E. Ovichinnikov, V. E. Shklover, Yu. T. Struchkov, V. V. Dement'ev, T. M. Frunze and B. A. Antipova, *J. Organomet. Chem.*, 1987, **335**, 157.

7 J. L. Atwood, S. G. Bott, C. Eaborn, M. N. A. El-Kheli and J. D. Smith, *J. Organomet. Chem.*, 1985, **294**, 23.

8 J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr and R. L. Vincent, *Nature*, 1991, **349**, 683.

9 H. S. Rzepa, M. L. Webb, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 765.

10 W. L. Jorgensen and D. L. Severance, *J. Am. Chem. Soc.*, 1990, **112**, 4768.

11 A. Engdahl and B. Nelander, *J. Phys. Chem.*, 1985, **89**, 2860.

12 G. Kahlström, P. Linse, A. Wallqvist and B. Jönsson, *J. Am. Chem. Soc.*, 1983, **105**, 3777.

13 J. Wanna, J. A. Menapeace and E. R. Bernstein, *J. Chem. Phys.*, 1986, **85**, 1795.

14 A. Engdahl and B. Nelander, *Chem. Phys. Lett.*, 1985, **113**, 49.