Hydrogen-bonded adducts of triphenylsilanol with diamines: a finite ten-molecule aggregate, and chain, sheet and framework structures built from O—H···O, O—H···N and C—H···π(arene) hydrogen bonds

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The structures of five hydrogen-bonded adducts of triphenylsilanol, Ph_3SiOH, with diamines have been determined. In the 4:1 adduct formed with 1,4-diazabicyclo[2.2.2]octane, $(Ph_3SiOH)_4 \cdot C_6H_{12}N_2$ (I) (triclinic, $P\bar{1}$, $Z' = 2$), there are two independent five-component aggregates built from O—H···N and O—H···O hydrogen bonds, in one of which the diamine exhibits orientational disorder: these two aggregates are linked into a cyclic ten-molecule unit by means of two independent C—H···π(arene) hydrogen bonds. The 4:1 adduct formed with 1,2-bis(4-pyridyl)ethene, $(Ph_3SiOH)_4 \cdot C_{12}H_{10}N_2$ (II) (triclinic, $P\bar{1}$, $Z' = 0.5$), forms a similar five-component aggregate which lies across a centre of inversion: a single C—H···π(arene) hydrogen bond links these aggregates into a molecular ladder. With N,N'-dimethylpiperazine, triphenylsilanol forms a 2:1 adduct, $(Ph_3SiOH)_2 \cdot C_6H_{14}N_2$ (III) (monoclinic, $P2_1/c$, $Z' = 0.5$), in which a three-component aggregate built from O—H···N hydrogen bonds lies across a centre of inversion: two independent C—H···π(arene) hydrogen bonds link these aggregates into sheets. In the hydrated 2:1 adduct formed with 1,2-bis(4'-bipyridyl)ethane, $(Ph_3SiOH)_2 \cdot C_{12}H_{12}N_2 \cdot H_2O$ (IV) (triclinic, $P\bar{1}$, $Z' = 1$), a combination of two independent O—H···O and two independent N—H···O hydrogen bonds links the five molecular components into a centrosymmetric eight-molecule aggregate, and six independent C—H···π(arene) hydrogen bonds link these chains into a continuous three-dimensional framework structure. In the dihydrated 2:1 adduct formed with 4,4'-bipyridyl, $(Ph_3SiOH)_2 \cdot C_{10}H_8N_2 \cdot (H_2O)_2$ (V) (triclinic, $P\bar{1}$, $Z' = 1$), a combination of four independent O—H···O and two independent N—H···O hydrogen bonds links the five molecular components into a chain of rings, and four independent C—H···π(arene) hydrogen bonds link these chains into a continuous three-dimensional framework structure.

1. Introduction

We have recently observed that co-crystallization, from methanol solutions, of mixtures of triphenylsilanol, Ph_3SiOH [A, see Scheme (I)], and 4,4'-bipyridyl, $NC_5H_4–C_5H_4N$ (B), gave a 1:1 adduct $Ph_3SiOH \cdot C_{10}H_8N_2$, in which the two molecular components are linked by an O—H···N hydrogen bond, and a 4:1 adduct $(Ph_3SiOH)_4 \cdot C_{10}H_8N_2$ (Bowes et al., 2003). In the 4:1 adduct, two triphenylsilanol molecules are linked to the 4,4'-bipyridyl via O—H···N hydrogen bonds and two further triphenylsilanol molecules are linked to the first pair via O—

H···O hydrogen bonds. However, it did not prove possible to isolate or identify the expected 2:1 adduct, $(Ph_3SiOH)_2 \cdot C_{10}H_8N_2$, containing O—H···N but not O—H···O hydrogen bonds. Moreover, three different polymorphs of the 4:1 adduct were characterized, all in the triclinic space group $P\bar{1}$ and having Z' values of 0.5, 1 and 4, respectively. These polymorphs, which are at least pairwise concomitant, all exhibit considerable disorder, even at 150 K, particularly involving the orientation of the phenyl rings. By contrast, the 1:1 adduct has a fully ordered structure in which the bimolecular aggregates generated by the O—H···N hydrogen bond are linked into a continuous three-dimensional framework structure by no fewer than four different C—H···π(arene) hydrogen bonds involving both phenyl and pyridyl rings as acceptors.

Intrigued by the crystallization behaviour of this system, giving 1:1 and 4:1 adducts but no 2:1 adduct, as well as by the polymorphism of the 4:1 adduct, we have now investigated the co-crystallization of a range of mixtures containing triphenylsilanol and other diamines, including 1,2-bis(4-pyridyl)-ethene (C), 1,2-bis(4-pyridyl)ethane (D), 1,4-diazabicyclo[2.2.2]octane (DABCO, E), N,N′-dimethylpiperazine (F), piperazine (G) and hexamethylenetetramine (H).

(A)

(B)

(C)

(D)

(E)

(F)

(G)

(H)

(I)
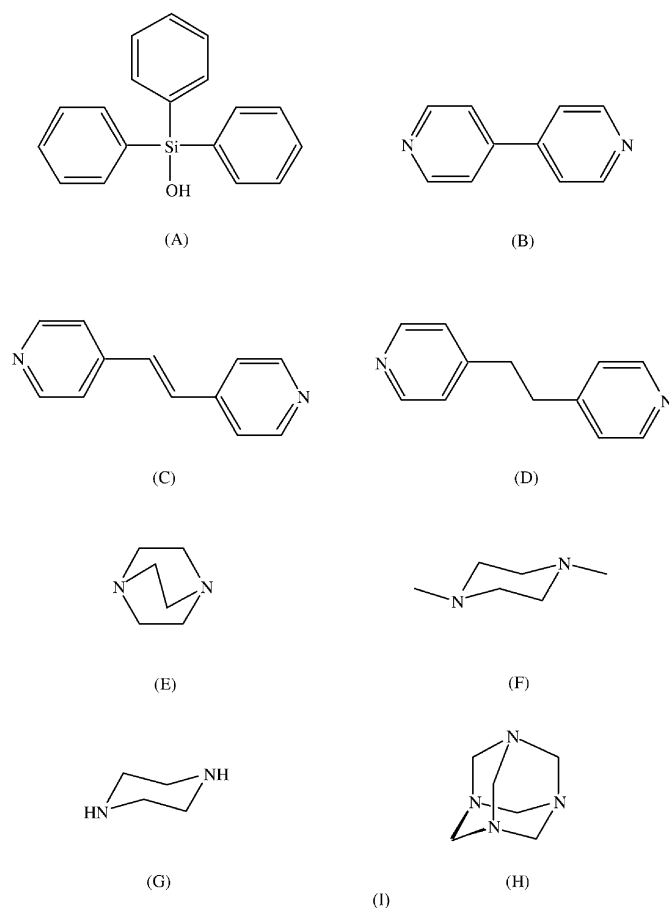
In the cases of diamines (C) and (E), methanol solutions containing triphenylsilanol and the diamine in molar ratios of 1:1, 2:1 or 4:1 (triphenylsilanol:diamine in all cases) uniformly

yielded the 4:1 adducts (I) and (II) only as the sole crystalline products. In contrast, diamine (F) produced only the 2:1 adduct (III), whereas diamine (D) produces the mono-hydrated 2:1 adduct (IV). Use of the amines (G) and (H) consistently failed to produce any crystalline adducts and triphenylsilanol was the only solid product isolated from crystallizations involving these amines. In addition, we have now isolated and characterized a further product in the triphenylsilanol–4,4′-bipyridyl system, namely the hydrated 2:1 adduct $(Ph_3SiOH)_2 \cdot C_{10}H_8N_2 \cdot (H_2O)_2$ (V).

2. Experimental

2.1. Synthesis

For each of compounds (I)–(IV), stoichiometric quantities of triphenylsilanol and the diamines (E), (C), (F) or (D), respectively, equivalent to 1:1, 2:1 and 4:1 molar ratios in each case, were separately dissolved in dry methanol. The corresponding solutions were mixed and set aside to crystallize, consistently providing samples of (I)–(IV). Analyses: found for (I), C 76.9, H 6.5, N 2.2%; $C_{78}H_{76}N_2O_4Si_4$ requires C 76.9, H 6.3, N 2.3%; found for (II), C 78.6, H 5.4, N 2.1%; $C_{84}H_{74}N_2O_4Si_4$ requires C 78.3, H 5.8, N 2.2%; found for (III), C 76.2, H 6.9, N 3.9%; $C_{42}H_{46}N_2O_2Si_2$ requires C 75.6, H 7.0, N 4.2%; found for (IV) C 75.8, H 6.0, N 3.3%; $C_{48}H_{46}N_2O_3Si_2$ requires C 76.3, H 6.1, N 3.7%. For (V) equimolar quantities of triphenylsilanol and 4,4′-bipyridyl were employed in a similar co-crystallization. Analysis for (V): found C 75.3, H 5.7, N 3.7%; $C_{46}H_{44}N_2O_4Si_2$ requires C 74.2, H 6.0, N 3.8%. When piperazine (G) or hexamethylenetetramine (H) were employed in similar co-crystallization experiments, the crystallized products were consistently found to be pure triphenylsilanol. Crystals of (I)–(V) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples.

2.2. Data collection, structure solution and refinement

Diffraction data for (I)–(V) were collected at 150 (1) K using a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed. Compounds (I), (II), (IV) and (V) are all triclinic, and for each of them the space group $P\bar{1}$ was selected and confirmed by the successful structure analyses: for (III) the space group $P2_1/c$ was uniquely assigned from the systematic absences. The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). All H atoms were located from difference maps and all were fully ordered. Those bonded to water O atoms were placed at positions located from the difference maps and treated as riding atoms with an O—H distance of 0.99 Å, as deduced from the difference maps; all other H atoms were treated as riding atoms with distances C—H 0.95 Å and hydroxy O—H 0.84 Å. In (I) one of the DABCO components, that containing N21 and N22, is disordered over

Table 1
Experimental details.

	(I)	(II)	(III)	(IV)	(V)
Crystal data					
Chemical formula	$C_6H_{12}N_2\cdot4C_{18}H_{16}OSi$	$2C_{18}H_{16}OSi\cdot0.5C_{12}H_{10}N_2$	$C_{18}H_{16}OSi\cdot0.5C_6H_{14}N_2$	$2C_{18}H_{16}OSi\cdotC_{12}H_{12}N_2\cdot H_2O$	$2C_{18}H_{16}OSi\cdot C_{10}H_8N_2\cdot2H_2O$
M_r	1217.77	643.91	333.49	755.05	745.01
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a, b, c (Å)	15.2124 (5), 18.9580 (4), 23.3561 (7)	8.6418 (2), 14.1263 (3), 16.3149 (4)	14.6528 (10), 8.1361 (4), 16.7852 (10)	8.7793 (4), 14.3503 (7), 16.8948 (6)	8.9058 (4), 13.9098 (8), 16.9083 (8)
α, β, γ (°)	86.713 (2), 85.727 (2), 81.563 (2)	64.5048 (10), 84.1339 (10), 79.7744 (13)	90.00, 117.868 (4), 90.00	76.612 (2), 88.287 (2), 83.816 (2)	75.053 (3), 88.509 (3), 86.951 (3)
V (Å^3)	6637.0 (3)	1768.42 (7)	1769.00 (18)	2058.58 (16)	2020.67 (18)
Z	4	2	4	2	2
D_x (Mg m^{-3})	1.219	1.209	1.252	1.218	1.224
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	30 027	8105	3291	9333	7517
θ range (°)	2.6–27.5	2.6–27.5	2.8–25.5	2.6–27.5	2.6–25.5
μ (mm^{-1})	0.14	0.14	0.14	0.13	0.13
Temperature (K)	150 (1)	150 (1)	150 (1)	150 (1)	150 (1)
Crystal form, colour	Block, colourless	Needle, colourless	Plate, colourless	Needle, colourless	Block, colourless
Crystal size (mm)	$0.34 \times 0.32 \times 0.12$	$0.30 \times 0.28 \times 0.25$	$0.44 \times 0.30 \times 0.04$	$0.20 \times 0.12 \times 0.04$	$0.24 \times 0.17 \times 0.10$
Data collection					
Diffractometer	Kappa-CCD	Kappa-CCD	Kappa-CCD	Kappa-CCD	Kappa-CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	None	None	None
T_{min}	0.972	0.914	–	–	–
T_{max}	0.986	0.967	–	–	–
No. of measured, independent and observed reflections	58 413, 30 027, 13 026	23 113, 8105, 6126	15 411, 3291, 2276	21 083, 9333, 5498	21 774, 7517, 4671
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.093	0.051	0.099	0.074	0.078
θ_{max} (°)	27.5	27.5	25.5	27.5	25.5
Range of h, k, l	$-19 \Rightarrow h \Rightarrow 19$ $-24 \Rightarrow k \Rightarrow 24$ $-29 \Rightarrow l \Rightarrow 30$	$-11 \Rightarrow h \Rightarrow 11$ $-18 \Rightarrow k \Rightarrow 18$ $-20 \Rightarrow l \Rightarrow 21$	$-17 \Rightarrow h \Rightarrow 17$ $-9 \Rightarrow k \Rightarrow 9$ $-20 \Rightarrow l \Rightarrow 20$	$-11 \Rightarrow h \Rightarrow 11$ $-17 \Rightarrow k \Rightarrow 18$ $-20 \Rightarrow l \Rightarrow 21$	$-10 \Rightarrow h \Rightarrow 10$ $-16 \Rightarrow k \Rightarrow 16$ $-20 \Rightarrow l \Rightarrow 20$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.073, 0.225, 0.96	0.041, 0.109, 1.02	0.047, 0.133, 1.03	0.059, 0.155, 1.02	0.052, 0.131, 1.01
No. of reflections	30 027	8105	3291	9333	7517
No. of parameters	1331	427	237	499	490
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1027P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.511P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 0.2885P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.384P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.001	0.004	0.001	0.001
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.56, −0.47	0.23, −0.31	0.24, −0.40	0.62, −0.33	0.60, −0.46
Extinction method	None	SHELXL	SHELXL	SHELXL	SHELXL
Extinction coefficient	–	0.0085 (14)	0.011 (3)	0.0072 (12)	0.0037 (7)

Computer programs: *Kappa-CCD server software* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997), *SHELXL*97 (Sheldrick, 1997), *PLATON* (Spek, 2003), *PRPKAPPA* (Ferguson, 1999), *WINGX* (Farrugia, 1999).

two sets of sites, with refined occupancies of 0.798 (3) and 0.202 (3), where the two set of sites have essentially identical N positions but the —CH$_2$—CH$_2$— bridges in the two orientations are effectively rotated by *ca* 60° about the N···N vector: the C and N atoms of the minor component were refined isotropically.

Table 2
Selected geometric parameters (Å, °).

(a) Si—O distances
(I)

Si1—O1	1.637 (2)	Si2—O2	1.631 (2)
Si3—O3	1.634 (2)	Si4—O4	1.633 (2)

(II)

Si1—O1	1.636 (2)	Si2—O2	1.627 (2)

(III)

Si1—O1	1.624 (2)

(IV)

Si1—O1	1.633 (2)	Si2—O2	1.630 (2)

(V)

Si1—O1	1.640 (2)	Si2—O2	1.634 (2)

(b) Torsional and dihedral angles
(I)

O1—Si1—C111—C112	−83.6 (2)	O2—Si2—C211—C212	−63.4 (2)
O1—Si1—C121—C122	18.6 (2)	O2—Si2—C221—C222	−18.4 (2)
O1—Si1—C131—C132	0.6 (2)	O2—Si2—C231—C232	−7.4 (2)
O3—Si3—C311—C312	59.5 (2)	O4—Si4—C411—C412	56.0 (2)
O3—Si3—C321—C322	7.7 (2)	O4—Si4—C421—C422	57.9 (2)
O3—Si3—C331—C332	61.1 (2)	O4—Si4—C431—C432	10.6 (2)
N11—C11—C12—N12	−9.1 (4)		
N11—C13—C14—N12	−8.9 (4)		
N11—C15—C16—N12	−9.4 (4)		
N21—C21—C22—N22	3.7 (7)	N31—C31—C32—N32	−5 (2)
N21—C23—C24—N22	2.9 (6)	N31—C33—C34—N32	−2 (2)
N21—C25—C26—N22	2.2 (6)	N31—C35—C36—N32	−2 (2)

(II)

O1—Si1—C11—C12	−43.5 (2)	O2—Si2—C41—C42	−5.8 (2)
O1—Si1—C21—C22	−39.6 (2)	O2—Si2—C51—C52	−75.6 (2)
O1—Si1—C31—C32	−33.6 (2)	O2—Si2—C61—C62	17.2 (2)
(N1—C6)^(C4—C7—C7^{i}—C4^{i})	10.0 (2)		

(III)

O1—Si1—C11—C12	−46.8 (2)
O1—Si1—C21—C22	−42.9 (2)
O1—Si1—C31—C32	−24.1 (2)

(IV)

O1—Si1—C111—C112	7.9 (2)	O2—Si2—C211—C212	−47.2 (2)
O1—Si1—C121—C122	−0.8 (2)	O2—Si2—C221—C222	−66.2 (2)
O1—Si1—C131—C132	56.6 (2)	O2—Si2—C231—C232	−43.2 (2)
C13—C14—C17—C27	−154.8 (3)	C14—C17—C27—C24	169.3 (3)
C23—C24—C27—C17	−119.6 (3)		

(V)

O1—Si1—C111—C112	−60.9 (2)	O2—Si2—C211—C212	−4.7 (2)
O1—Si1—C121—C122	−61.5 (2)	O2—Si2—C221—C222	10.9 (2)
O1—Si1—C131—C132	−40.6 (2)	O2—Si2—C231—C232	−59.6 (2)
(N1—C16)^(N2—C26)	35.3 (2)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Supramolecular analyses were made and the diagrams were prepared with the aid of *PLATON* (Spek, 2003). Details of selected molecular dimensions and hydrogen-bond dimensions are given in Tables 2 and 3.[1] Figs. 1–14 show the mole-cular components, with the atom-labelling schemes, and aspects of the supramolecular structures.

3. Results and discussion

3.1. Crystallization characteristics

For each of the amines (*C*) and (*E*) [see Scheme (I)], co-crystallization with triphenylsilanol from solution in dry methanol containing molar ratios of triphenylsilanol-to-amine of 1:1, 2:1 or 4:1 consistently provided pure samples of the 4:1 adducts (II) and(I), respectively. Similar mixtures of triphenylsilanol with the amines (*B*) and (*F*) consistently yielded the mono-hydrated 2:1 adduct (IV) and the solvent-free 2:1 adduct (III), respectively. This behaviour may be contrasted with that of mixtures of triphenylsilanol with (*B*), again in dry methanol, where a 1:1 molar ratio yielded a 1:1 adduct, but where both 2:1 and 4:1 molar ratios gave concomitant polymorphs of the 4:1 adduct (Bowes *et al.*, 2003): presumably in the formation of (IV), the water has an atmospheric origin. However, when deliberately damp methanol was employed as the solvent for an equimolar mixture of triphenylsilanol with (*B*), the product was not the expected 1:1 adduct, but instead the hydrated 2:1 adduct (V). All attempts to obtain adducts of triphenylsilanol with the amines (*G*) and (*H*) have so far been unsuccessful.

It is notable that in (I) and (II), the 4:1 aggregates formed by the hard hydrogen bonds have all of their triphenylsilanol components fully ordered. This is in marked contrast to the various polymorphs of the 4:1 adduct formed between triphenylsilanol and 4,4′-bipyridyl, where there is very extensive orientational disorder of the phenyl groups, even at 150 K (Bowes *et al.*, 2003). In triphenylsilanol itself, the phenyl disorder is modest at low temperatures, but intractable at ambient temperatures (Bowes *et al.*, 2002).

By contrast with the reactions involving triphenylsilanol and the amines (*B*)–(*F*), these amines with triphenylmethanol, Ph₃COH, in methanol solutions consistently gave pure triphenylmethanol as the sole crystalline product, regardless of whether the input molar ratio of triphenylmethanol to amine was 1:1, 2:1 or 4:1.

3.2. Dimensions and conformations

The independent Si—O distances in (I)–(V) (Table 2) span the rather narrow range 1.624 (2)–1.640 (2) Å and no individual value is markedly different from the values (Bowes *et al.*, 2002, 2003) in tetrameric triphenylsilanol itself or in its 4:1 adduct with 1,4-dioxan, mean values 1.645 (6) and 1.639 (2) Å, respectively; in the $Z' = 0.5$ and $Z' = 1$ polymorphs of the 4:1 adduct of triphenylsilanol with 4,4′-bipyridyl, mean values

1.633 (4) and 1.634 (7) Å, respectively; or in the 1:1 adduct formed with 4,4′-bipyridyl, 1.629 (2), and in the 2:1 adduct formed with dimethylsulfoxide, 1.636 (2) Å.

The highest possible symmetry for the non-H atoms in a triphenylsilanol molecule is C_{3v} ($3m$) and there are two conformations, defined by O—Si—C—C torsional angles of zero or 90°, respectively, which have this symmetry. In the event, the inner triphenylsilanol molecule in (II), containing Si1, the unique triphenylsilanol molecule in (III) and one of the triphenylsilanol molecules in each of (IV) and (V), those containing Si2 and Si1, respectively, all have conformations fairly close to C_3 (3) symmetry for the non-H atoms: the numerical values of the O—Si—C—C torsional angles in these components lie in the range 24.1 (2) to 66.2 (2)° with a mean of ca 46°, just midway between the two C_{3v} conformations. However, only one of the triphenylsilanol molecules, that in (III) containing Si2, has a conformation close to Cs (m) symmetry for the non-H atoms. In this molecule the O—Si—C—C torsional angle for one phenyl ring is close to 90° and those for the other two rings are close to zero, but with opposite signs (Table 2). The remaining independent triphenylsilanol molecules have conformations in which the non-H atoms do not even approximate to any symmetry above C_1.

The fully ordered DABCO unit in (I) exhibits the usual twist away from D_{3h} ($\bar{6}m2$) symmetry towards D_3 (32) symmetry, with a mean N—C—C—N torsional angle of 9.1 (4)°. The major component of the disordered DABCO shows a much smaller distortion, with a mean N—C—C—N torsional angle of 2.9 (6)°, while for the minor component the mean N—C—C—N torsional angle is not significantly different from zero.

In each of compounds (I) and (II) the O—H···N hydrogen bonds are shorter than the O—H···O hydrogen bonds, although the difference is less marked in (II) than in (I). In (IV) and (V) the O—H···O hydrogen bonds involving triphenylsilanol as a donor and water as an acceptor are markedly shorter than those involving water as a donor and triphenylsilanol as an acceptor. In (V) both of the hydrogen bonds, to N as well as to O as an acceptor, are markedly shorter with O21 as a donor as compared with O11 as a donor.

3.3. Supramolecular structures

3.3.1. Hydrogen bonds generate a finite, zero-dimensional aggregate. The hard (Braga et al., 1995; Desiraju & Steiner, 1999) hydrogen bonds generate two independent five-component aggregates in the 4:1 adduct (I), both of which lie in general positions in the space group $P\bar{1}$; in each aggregate an inner pair of triphenylsilanol molecules is linked to a DABCO unit via O—H···N hydrogen bonds, with an outer pair of triphenylsilanol molecules again linked to the first pair via O—H···O hydrogen bonds (Fig. 1). While all 24 of the independent phenyl rings in (I) are fully ordered, only one of the DABCO units is so ordered. In aggregate 1, containing N11 and N12, the DABCO is fully ordered, but in aggregate 2, containing N21 and N22, there are two orientations of the DABCO unit, related by a rotation of approximately 60°

about the N21···N22 vector and having occupancies of 0.798 (3) and 0.202 (3), respectively.

There are two significant C—H···π(arene) hydrogen bonds in (I) which serve to link the two independent five-component aggregates into a single ten-component unit. Atoms C134 and C724 act as hydrogen-bond donors, respectively, to rings C621–C626 and C411–C416, thus producing an aggregate in which two DABCO and six triphenylsilanol molecules are linked into a large rectangular ring, with the two remaining triphenylsilanol molecules pendent from it (Fig. 2).

Each of the two independent five-component aggregates has a pseudo-inversion centre at the centre of the DABCO moiety. One DABCO molecule (N11–C16) is centred at approximately ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{4}$) and the other (N21–C26) is centred at approximately ($\frac{1}{2}$, 0, $\frac{1}{4}$). This overall 10-molecule aggregate is approximately centrosymmetric about the point ($\frac{1}{2}$, $\frac{3}{4}$, $\frac{1}{4}$), but the disorder of the type 2 DABCO molecule and the detailed conformations of the triphenylsilanol components (see above, §3.2) both preclude the possibility of any additional symmetry.
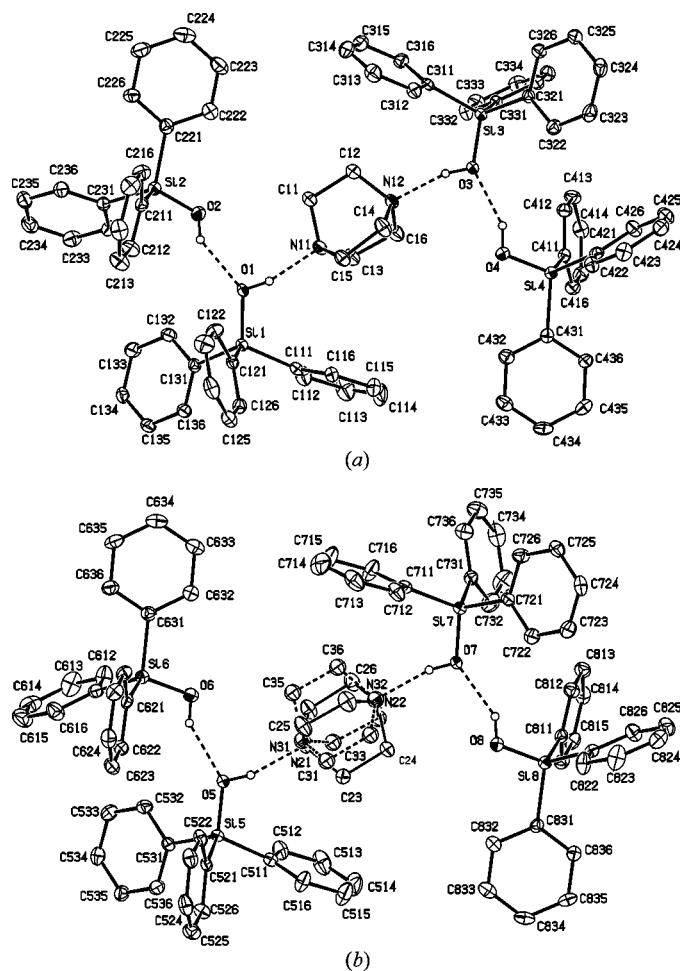

(a)

(b)

Figure 1
The two independent five-component aggregates in (I), showing the atom-labelling scheme: (a) aggregate 1 containing a fully ordered DABCO unit; (b) aggregate 2 containing a disordered DABCO unit (see text). Displacement ellipsoids are drawn at the 30% probability level and the H atoms bonded to C atoms are omitted for the sake of clarity.

Table 3
Hydrogen-bond parameters (Å, °).

D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
(I)			
O1—H1$\cdots$N11	1.82	2.642 (3)	165
O2—H2$\cdots$O1	2.01	2.727 (3)	143
O3—H3$\cdots$N12	1.82	2.642 (3)	164
O4—H4$\cdots$O3	1.95	2.729 (3)	153
O5—H5$\cdots$N21	1.80	2.620 (6)	164
O6—H6$\cdots$O5	2.00	2.736 (3)	146
O7—H7$\cdots$N22	1.81	2.633 (7)	164
O8—H8$\cdots$O7	1.96	2.701 (3)	146
C134—H134$\cdots$Cg1$^{a,\text{i}}$	2.79	3.576 (3)	141
C724—H724$\cdots$Cg2$^{b,\text{ii}}$	2.68	3.536 (3)	150
(II)			
O1—H1$\cdots$N1	1.85	2.653 (2)	159
O2—H2$\cdots$O1	1.98	2.691 (2)	142
C33—H33$\cdots$Cg3$^{c,\text{ii}}$	2.69	3.635 (2)	173
(III)			
O1—H1$\cdots$N1	1.92	2.721 (2)	159
C13—H13$\cdots$Cg3$^{c,\text{iii}}$	2.94	3.821 (3)	154
C23—H23$\cdots$Cg3$^{c,\text{iv}}$	2.93	3.746 (3)	145
(IV)			
O1—H1$\cdots$O3$^{\text{v}}$	1.85	2.641 (3)	161
O2—H2$\cdots$N2	1.96	2.753 (3)	163
O3—H31$\cdots$O1	1.90	2.801 (2)	167
O3—H32$\cdots$N1	1.88	2.791 (3)	170
C16—H16$\cdots$Cg4$^{d,\text{vi}}$	2.91	3.782 (3)	153
C23—H23$\cdots$Cg5$^{e,\text{vii}}$	2.75	3.440 (3)	130
C115—H115$\cdots$Cg6$^{f,\text{viii}}$	2.94	3.757 (3)	145
C214—H214$\cdots$Cg7$^{g,\text{ix}}$	2.75	3.621 (3)	152
C224—H224$\cdots$Cg8$^{h,\text{x}}$	2.81	3.622 (3)	144
C235—H235$\cdots$Cg5$^{e,\text{xi}}$	2.77	3.603 (3)	147
(V)			
O1—H1$\cdots$O11	1.84	2.660 (3)	164
O2—H2$\cdots$O21	1.85	2.640 (3)	156
O11—H11$A\cdots$N1	1.83	2.817 (3)	175
O11—H11$B\cdots$O1$^{\text{xii}}$	1.86	2.817 (3)	162
O21—H21$A\cdots$N2	1.75	2.730 (4)	170
O21—H21$B\cdots$O2$^{\text{xiii}}$	1.81	2.678 (3)	144
C114—H114$\cdots$Cg4$^{d,\text{xiv}}$	2.87	3.717 (3)	148
C124—H124$\cdots$Cg5$^{e,\text{xv}}$	2.82	3.635 (3)	145
C135—H135$\cdots$Cg8$^{h,\text{xvi}}$	2.82	3.660 (3)	148
C215—H215$\cdots$Cg9$^{j,\text{xvii}}$	2.83	3.659 (3)	147

Footnotes: (*a*) Cg1 is the centroid of the ring C621–C626; (*b*) Cg2 is the centroid of the ring C411–C416; (*c*) Cg3 is the centroid of the ring C21–C26; (*d*) Cg4 is the centroid of the ring C221–C226; (*e*) Cg5 is the centroid of the ring C211–C216; (*f*) Cg6 is the centroid of the ring C131–C136; (*g*) Cg7 is the centroid of the ring C121–C126; (*h*) Cg8 is the centroid of the ring C111–C116; (*j*) Cg9 is the centroid of the ring C231–C236;   Symmetry codes: (i) $x, 1+y, z$;   (ii) $-1+x, y, z$;   (iii) $x, -1+y, z$;   (iv) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$;   (v) $1-x, 1-y, 1-z$;   (vi) $3-x, 1-y, 2-z$;   (vii) $-1+x, y, z$;   (viii) $1-x, -y, 1-z$;   (ix) $2+x, y, z$;   (x) $2+x, y, 1+z$;   (xi) $4-x, -y, 2-z$;   (xii) $3-x, -y, 1-z$;   (xiii) $-x, -y, -z$;   (xiv) $2-x, -y, -z$;   (xv) $2-x, -y, 1-z$;   (xvi) $3-x, -1-y, 1-z$;   (xvii) $-x, 1-y, -z$.

3.3.2. Hydrogen bonds generate a one-dimensional structure.

In the 4:1 adduct (II), the 1,2-bis(4-pyridyl)ethene unit lies across a centre of inversion in the space group $P\bar{1}$, selected for the sake of convenience as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Two triphenylsilanol molecules are linked to the diamine *via* short O—H$\cdots$N hydrogen bonds and a further pair of triphenylsilanol molecules are linked to the first pair *via* short O—H$\cdots$O hydrogen bonds. The five-component molecular aggregate (Fig. 3) generated in (I) by the hard hydrogen bonds is thus

very similar to that found in each of the polymorphs of the 4:1 adduct formed with 4,4′-bipyridyl.

However, a striking difference between the adducts formed by 4,4′-bipyridyl and 1,2-bis(4-pyridyl)ethene lies in the degree of disorder: whereas all three polymorphs of the 4,4′-bipyridyl adduct exhibit extensive disorder, all components of the 1,2-bis(4-pyridyl)ethene (I) are fully ordered. It is therefore possible to analyse in a straightforward way the effect of the soft (Braga *et al.*, 1995; Desiraju & Steiner, 1999) C—H$\cdots\pi$(arene) hydrogen bonding in (II), where there is a single such interaction of structural significance. The aromatic atom C33 in the type 1 silanol molecule (containing Si1) at (x, y, z) lies in the five-component aggregate centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and it acts as a hydrogen-bond donor to the aromatic ring C21–C26 in the type 1 silanol at $(-1+x, y, z)$, which is part of the
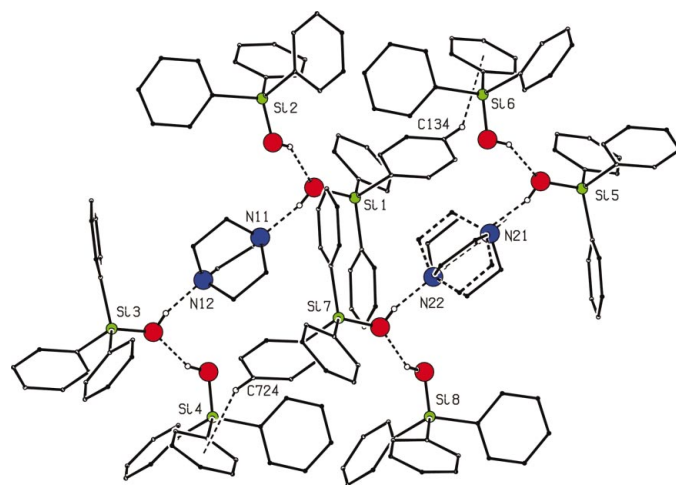

Figure 2
Part of the crystal structure of (I) showing the formation of a ten-molecule aggregate. For the sake of clarity, the H atoms bonded to C atoms and the unit-cell box are omitted.
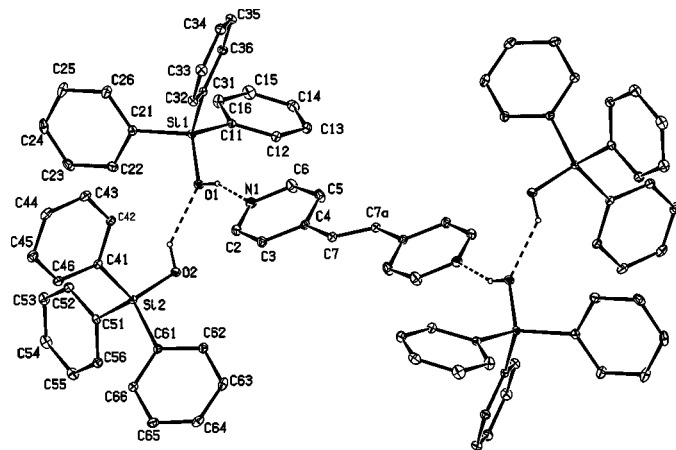

Figure 3
The five-component aggregate in (II), showing the atom-labelling scheme: the atom marked 'a' is at the symmetry position $(1-x, 1-y, 1-z)$. Displacement ellipsoids are drawn at the 10% probability level and the H atoms bonded to the C atoms are omitted for the sake of clarity.

aggregate centred at $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Propagation of this interaction by translation and inversion thus generates a chain of edge-fused rings, alternatively regarded as a molecular ladder, running parallel to the [100] direction (Fig. 4).

3.3.3. Hydrogen bonds generate a two-dimensional structure. Compound (III) (Fig. 5) is a solvent-free 2:1 adduct in which the N,N'-dimethylpiperazine component lies across a centre of inversion, selected as that at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with the
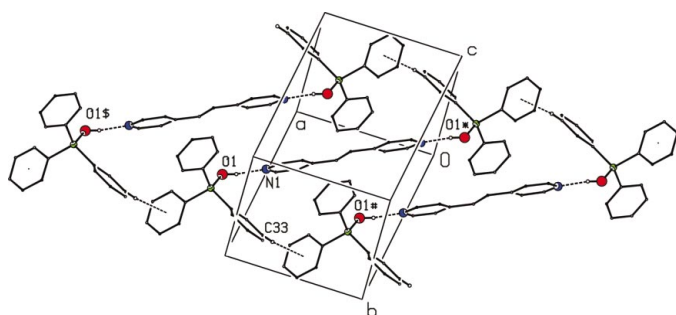
Figure 4
Part of the crystal structure of (II) showing the formation of a molecular ladder along [100]. For the sake of clarity, the outer triphenylsilanol molecules (containing Si2) and the H atoms bonded to C atoms are omitted. The atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(-1+x, y, z)$ and $(1+x, y, z)$, respectively.
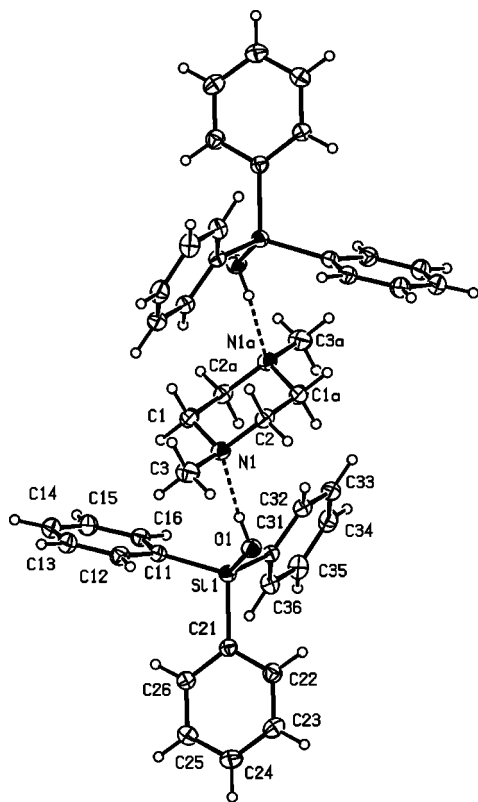
Figure 5
The three-component aggregate in (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and the atoms marked 'a' are at the symmetry position $(1-x, 1-y, 1-z)$.

triphenylsilanol molecules linked to it *via* a unique $O-H\cdots N$ hydrogen bond (Table 3) to form a centrosymmetric three-component aggregate. There are no aromatic $\pi\cdots\pi$ stacking interactions in the structure of (III), but two independent $C-H\cdots\pi$(arene) hydrogen bonds link the molecules into sheets: it is convenient to consider each of these interactions in turn as the substructures which they generate are entirely different.

In the first of these soft hydrogen bonds, the phenyl C13 atom in the molecule at (x, y, z), which lies in the three-molecule aggregate centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as a hydrogen-bond donor to the phenyl ring C21–C26 in the molecule at $(x, -1+y, z)$, a part of the three-molecule aggregate centred at $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$. Propagation of this hydrogen bond by translation and inversion generates a chain of edge-fused rings, or a molecular ladder, running parallel to the [010] direction (Fig. 6).

By contrast with this one-dimensional substructure the second $C-H\cdots\pi$(arene) hydrogen bond generates a two-dimensional substructure. The phenyl atom C23 in the molecule at (x, y, z) acts as a donor to the ring C21–C26 in the molecule at $(2-x, \frac{1}{2}+y, \frac{3}{2}-z)$, which is part of the three-molecule aggregate centred at $(\frac{3}{2}, 1, 1)$; the ring C21–C26 in the molecule at (x, y, z) itself accepts a similar hydrogen bond from the C23 atom in the molecule at $(2-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, which is part of the three-component aggregate centred at $(\frac{3}{2}, 0, 1)$. The action of the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ also links the reference aggregate centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ directly to those centred at $(-\frac{1}{2}, 0, 0)$ and $(-\frac{1}{2}, 1, 0)$. Hence, this single soft hydrogen bond links each three-molecule aggregate to four others, thus generating a sheet parallel to $(10\bar{2})$ (Fig. 7). If the three-component aggregates are regarded as the nodes of the
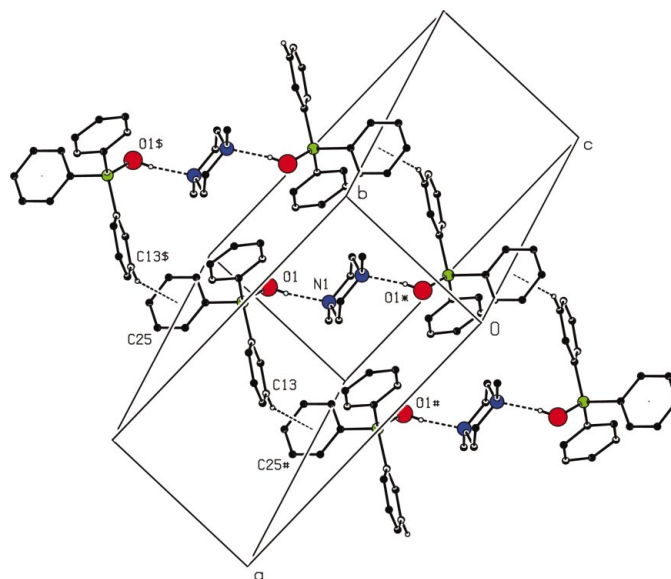

Figure 6
Part of the crystal structure of (III) showing the formation of a molecular ladder along [010]. For the sake of clarity the H atoms bonded to C atoms, but not involved in the hydrogen-bond motif shown, are omitted. The atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(1-x, 1-y, 1-z)$, $(x, -1+y, z)$ and $(x, 1+y, z)$, respectively.

corresponding net, this is of the (4,4) type (Batten & Robson, 1998).

3.3.4. Hydrogen bonds generate a three-dimensional structure.

Hard hydrogen bonds generate a finite aggregate: The hard hydrogen bonds in (IV) link the four independent molecular components into a finite, centrosymmetric aggregate of eight molecules (Fig. 8), where all of the individual components lie in general positions. The diamine unit acts as a double acceptor of O—H···N hydrogen bonds, one from the water molecule *via* H32 and one from the triphenylsilanol molecule containing Si2 (Table 3). The water molecule also acts as a hydrogen-bond donor, *via* H31, to triphenylsilanol O1 within the asymmetric unit, while O1 at (x, y, z) in turn acts as a donor to the water atom O3 at $(1 - x, 1 - y, 1 - z)$. Hence, a centrosymmetric $R_4^4(8)$ ring is generated, lying at the centre of

the eight-molecule aggregate centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. There is just one such aggregate per unit cell, but as the overall length of the aggregate exceeds 30 Å, portions of each aggregate occupy parts of several cells.

An extensive series of C—H···π(arene) hydrogen bonds (Table 3) links the eight-component aggregates into a continuous three-dimensional framework and the formation of this framework can most readily be analysed in terms of a number of individual one-dimensional substructures. In the simplest of these, the C115 atom in the internal triphenylsilanol molecule at (x, y, z), which lies in the eight-component aggregate centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as a hydrogen-bond donor to the aryl ring C131–C136 of the corresponding silanol molecule at $(1 - x, -y, 1 - z)$, which itself lies in the aggregate centred at $(\cdots, -\frac{1}{2}, \frac{1}{2})$. Propagation of this interaction by translation and inversion then generates a chain containing two types of ring running parallel to the [010] direction, which is built from just the internal silanol molecules and the water molecules (Fig. 9). In a somewhat similar motif, the C235 atom at (x, y, z) acts as a hydrogen-bond donor to the ring C211–C216 at $(4 - x, -y, 2 - z)$, which lies in the aggregate centred at $(\frac{7}{2}, -\frac{1}{2}, \frac{3}{2})$, thereby generating a second chain of rings, thus time running parallel to the [3$\bar{1}$1] direction.

There are two one-dimensional substructures which each involve two C—H···π(arene) hydrogen bonds. In the first of these two, the C16 and C224 atoms at (x, y, z) act as hydrogen-bond donors, respectively, to rings C221–C226 at $(3 - x, 1 - y, 2 - z)$ and C111–C116 at $(2 + x, y, 1 + z)$, which both lie in the aggregate centred at $(\frac{5}{2}, \frac{1}{2}, \frac{3}{2})$; propagation of these hydrogen bonds then leads to a complex chain of rings running parallel to the [201] direction (Fig. 10). In the second

Figure 7
Stereoview of part of the crystal structure of (III) showing the formation of a (10$\bar{2}$) sheet. For the sake of clarity the H atoms bonded to C atoms, but not involved in the hydrogen-bond motif shown, are omitted.
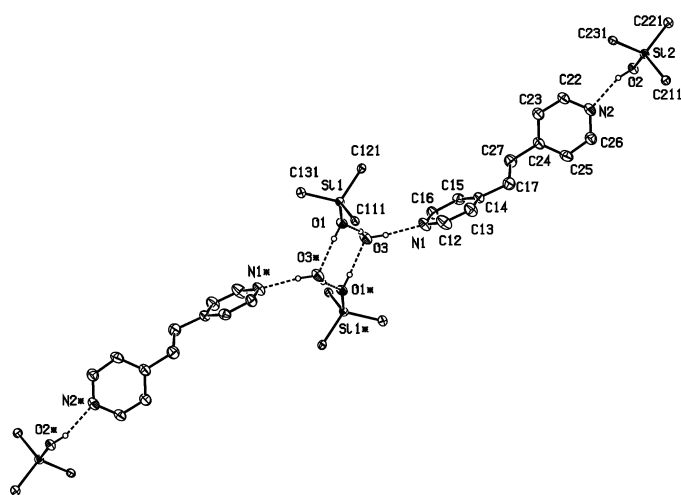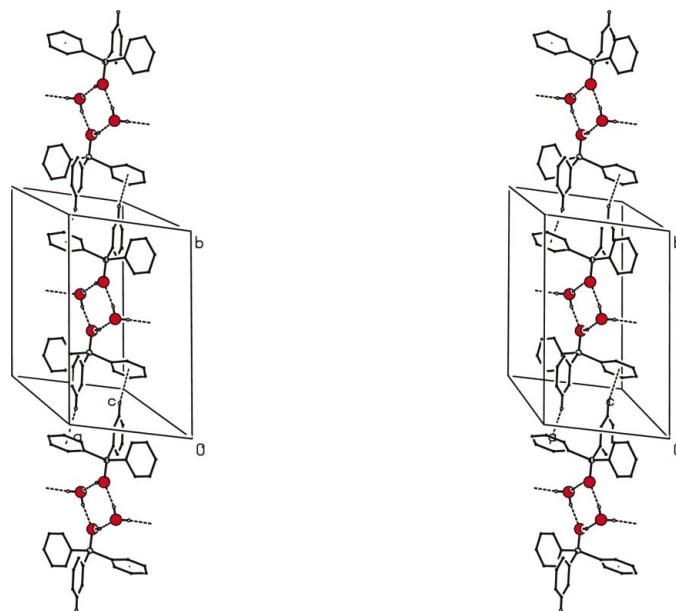

Figure 8
The eight-component aggregate in (IV) showing the atom-labelling scheme; phenyl C atoms are omitted except for those bonded to Si. Displacement ellipsoids are drawn at the 30% probability level and the atoms marked with an asterisk (*) are at the equivalent position $(1 - x, 1 - y, 1 - z)$. Only the H atoms involved in hydrogen bonding are shown.

Figure 9
Stereoview of part of the crystal structure of (IV) showing the formation of a chain of rings along [010]. For the sake of clarity the H atoms bonded to C atoms, but not involved in the hydrogen-bond motif shown, are omitted.

of these two substructures, the C23 and C214 atoms at (x, y, z) act as donors, respectively, to the rings C211–C216 at $(-1 + x, y, z)$ and to C121–C126 at $(2 + x, y, z)$, which lie respectively in the aggregates centred at $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$. Propagation of these interactions generates a ladder-type substructure of some complexity running parallel to the [100] direction (Fig. 11).

The combination of chains running parallel to [100], [010], [201] and [3$\bar{1}$1] is more than sufficient to link all of the eight-molecule aggregates into a single framework.

Hard hydrogen bonds generate a chain of rings: In our previous studies on adduct formation involving triphenylsilanol and 4,4′-bipyridyl, no 2:1 adduct was found: however, we have now isolated from methanol solution a dihydrated 2:1 adduct $(Ph_3SiOH)_2 \cdot C_{10}H_8N_2 \cdot (H_2O)_2$ (V). All five independent molecular components in (V) lie in general positions in the space group $P\bar{1}$ (Fig. 12). There are thus six independent O—H bonds available for hydrogen-bond formation, so that there are six independent hard hydrogen bonds within the structure, four of the O—H···O type and two of the O—H···N type; together these hard hydrogen bonds generate a one-dimensional substructure which combines simplicity and elegance.

Within the selected asymmetric unit, the two triphenylsilanol atoms O1 and O2 act as hydrogen-bond donors to water atoms O11 and O21, respectively, and these water atoms in turn act as donors, respectively, to the N1 and N2 atoms in the bipyridyl unit. There are thus two O—H bonds available to further link these five-molecule aggregates. The water atom O11 at (x, y, z) acts as a hydrogen-bond donor, *via* H11B, to the silanol atom O1 at $(3 - x, -y, 1 - z)$, thus forming a centrosymmetric $R_4^4(8)$ ring centred at $(\frac{3}{2}, 0, \frac{1}{2})$; in an entirely
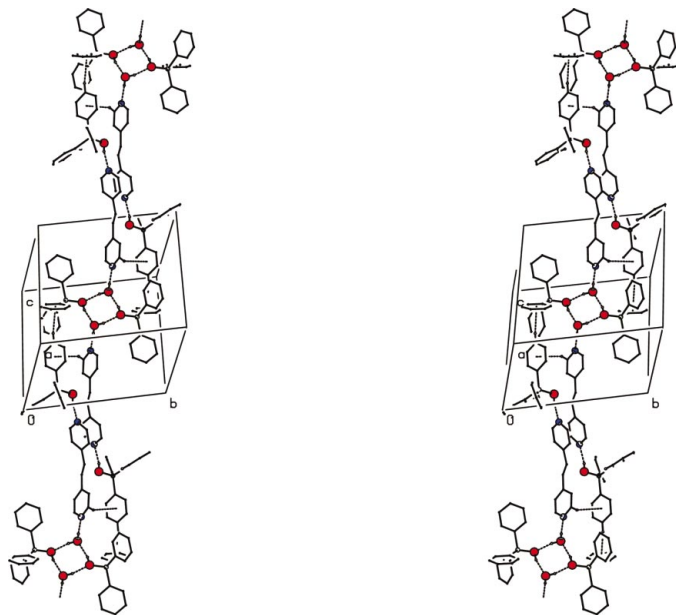
similar manner, the water O21 at (x, y, z) acts as a donor, *via* H21B, to the silanol atom O2 at $(-x, -y, -z)$, producing a second $R_4^4(8)$ ring, this time centred at (0, 0, 0). Propagation of these motifs by inversion thus generates a $C_8^8(30)[R_4^4(8)][R_4^4(8)]$ chain of rings running parallel to the [301] direction (Fig. 13).

There are four significant C—H···π(arene) hydrogen bonds in the structure of (V) (Table 3), all of which involve the phenyl groups only with no participation of the 4,4′-bipyridyl unit, and these link the [301] chains into a continuous three-dimensional framework. It is convenient to consider the effects of these interactions in pairs.

The phenyl atom C114 in the aggregate at (x, y, z) acts as a hydrogen-bond donor to the ring C221–C226 in the aggregate at $(2 - x, -y, -z)$, thus forming a centrosymmetric ring motif centred at (1, 0, 0); in combination with the $R_4^4(8)$ ring centred at (0, 0, 0) this interaction generates a chain of rings running parallel to the [100] direction. In addition, the phenyl C124 atom at (x, y, z) acts as a donor to the ring C211–C216 at $(2 - x, -y, 1 - z)$, forming another centrosymmetric ring motif, this time centred at $(1, 0, \cdots)$; in combination with the $R_4^4(8)$ ring centred at $(\frac{3}{2}, 0, \frac{1}{2})$, the second soft hydrogen bond generates another chain of rings running parallel to [100].

Similarly, the phenyl C135 and C215 atoms at (x, y, z) act as hydrogen-bond donors, respectively, to the rings C111–C116 at $(3 - x, -1 - y, 1 - z)$ and C231–C236 at $(-x, 1 - y, -z)$, thus forming two further centrosymmetric ring motifs, centred at $(\frac{3}{2}, -\frac{1}{2}, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$. In combination with the $R_4^4(8)$ rings centred at $(\frac{3}{2}, 0, \frac{1}{2})$ and (0, 0, 0), respectively, the two motifs generate two further chains of rings, both running parallel to the [010] direction (Fig. 14). Each of the independent [010] chains in (V) thus has an overall architecture very similar to that of the unique [010] chain in (IV) (Fig. 9).

The combination of the [301] chains generated by hard hydrogen bonds with the [100] and [010] chains involving both
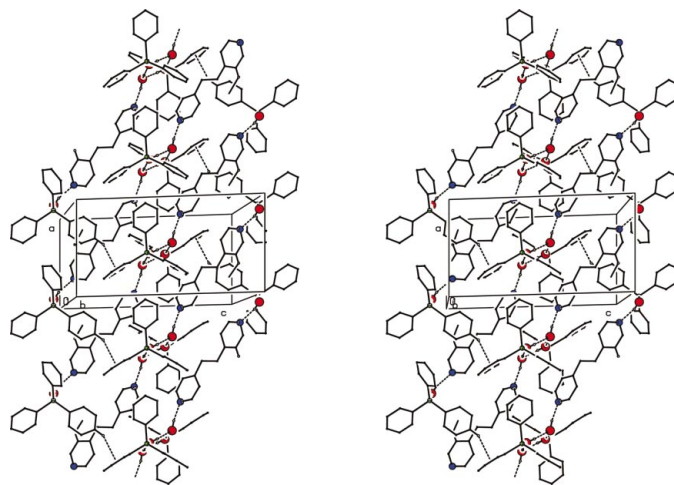
Figure 10
Part of the crystal structure of (IV), showing the formation of a chain of rings along [201]. For the sake of clarity the H atoms bonded to C atoms, but not involved in the hydrogen-bond motif shown, are omitted.

Figure 11
Part of the crystal structure of (IV) showing the formation of a molecular ladder along [100]. For the sake of clarity the H atoms bonded to C atoms, but not involved in the hydrogen-bond motif shown, are omitted.
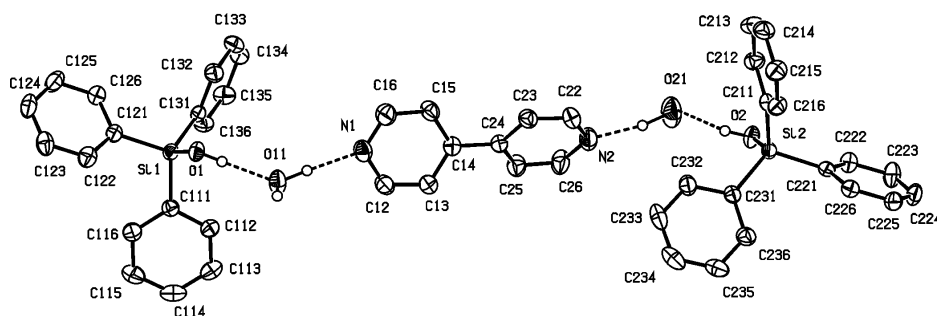
Figure 12
The independent molecular components in (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

hard and soft hydrogen bonds is sufficient to generate a continuous three-dimensional framework.

4. Concluding discussion

In (I) and (II) the hard hydrogen bonds generate five-component aggregates in which an inner pair of triphenylsi-
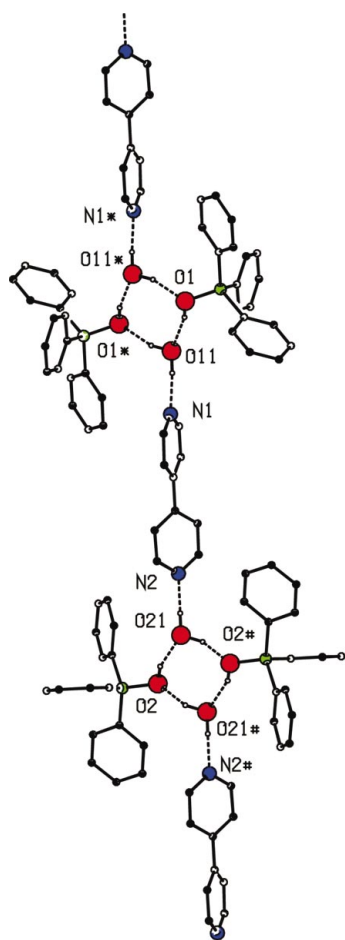

Figure 13
Part of the crystal structure of (V) showing the formation of a [301] chain generated by the hard hydrogen bonds. For the sake of clarity the unit-cell box is omitted. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(3 - x, -y, 1 - z)$ and $(-x, -y, -z)$, respectively.

lanol molecules are hydrogen bonded to the central double acceptor, with an outer pair of triphenylsilanol molecules linked to the inner pair by means of O—H···O hydrogen bonds. Entirely similar aggregates are found in the 4:1 adduct $(Ph_3SiOH)_4 \cdot C_4H_8O_2$ formed with 1,4-dioxan (Bourne *et al.*, 1991; Bowes *et al.*, 2002) and in all three polymorphs of the 4:1 adduct $(Ph_3SiOH)_4 \cdot C_{10}H_8N_2$ formed with 4,4′-bipyridyl (Bowes *et al.*, 2003). Moreover, (II) crystallizes in the space group $P\bar{1}$ with $Z' = 0.5$, as do the 1,4-dioxan adduct and the simplest of the 4,4′-bipyridyl adducts. Compound (I), on the other hand, crystallizes in the space group $P\bar{1}$ with $Z' = 2$, while the other two polymorphs of the 4,4′-bipyridyl adduct, both of which crystallize in the space group $P\bar{1}$, have Z' values of $2 \times 0.5 = 1$ and $(4 \times 0.5) + 2 = 4$, respectively. No example has yet been observed of a 4:1 adduct in which a single five-component aggregate, of the general type exemplified by (I) and (II), lies in a general position.

At the start of this work, we had expected that 2:1 adducts of triphenylsilanol with diamines would represent the dominant stoichiometry, with hard hydrogen bonds giving rise to three-component aggregates: in the event, this has proved not to be so. Such an adduct is found with *N,N′*-dimethylpiperazine (III), but the only 2:1 adduct so far observed with 4,4′-bipyridyl is the hydrated compound (V), where the $R_4^4(8)$ rings are reminiscent of those in tetrameric triphenylsilanol itself. Similarly, with 1,2-bis(4-pyridyl)ethane, while the adduct (IV) does indeed contain a 2:1 ratio of triphenylsilanol to diamine molecules, this is also a hydrate and again, as in (V), there is a $R_4^4(8)$ ring present, analogous to those in $(Ph_3SiOH)_4$. In addition, we may note here the formation of a 2:1 adduct $(Ph_3SiOH)_2 \cdot C_2H_6OS$ formed with dimethylsulfoxide, in which a three-component aggregate lies across a twofold rotation axis, with the sulfoxide O atom acting as a double acceptor of O—H···O hydrogen bonds (Bowes *et al.*, 2002). However, the failure of triphenylsilanol to form crystalline adducts with piperazine and hexamethylenetetramine is unexpected.

Likewise, having characterized a number of adducts of triphenylsilanol and various diamines, we had initially expected that an analogous series of adducts would readily be formed with triphenylmethanol, Ph_3COH. Our reasoning here was based on the fact that whereas in the cyclic tetramer of triphenylsilanol there is one fully ordered O—H···O hydrogen bond per O···O edge in the $R_4^4(8)$ ring (Bowes *et al.*, 2002), in the tetrahedral tetramer of triphenylmethanol (Ferguson *et al.*, 1992), there are only four hydroxyl H atoms distributed over the six O···O edges of the tetrahedron. These H atoms are, in fact, mobile over a number of sites at ambient temperature (Aliev *et al.*, 1998), and neutron diffraction at 100 K was required to locate these H sites unambiguously (Serrano-González *et al.*, 1999). Accordingly, we had expected that disruption of the triphenylmethanol tetramer would be
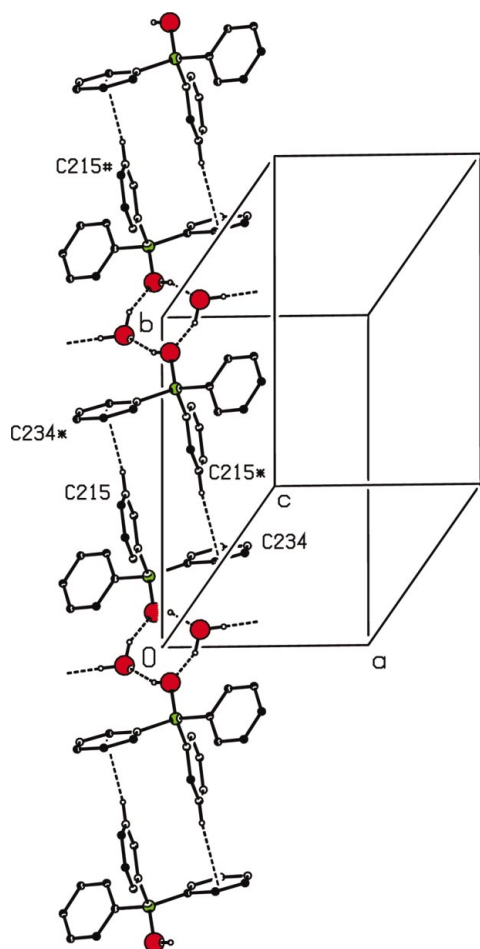
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Figure 14
Part of the crystal structure of (V) showing a representative example of a chain of rings generated by O—H$\cdots$O and C—H$\cdots\pi$(arene) hydrogen bonds, in this case running parallel to [010]. The atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-x, 1-y, -z)$ and $(x, 1+y, z)$, respectively.

achieved more readily than the disruption of the triphenylsi-lanol tetramer. Liberal application of hindsight suggests that an equally important consideration may be the intrinsic acidity of the hydroxyl groups in the two compounds Ph$_3$MOH (M = C or Si), where it is generally the case that silanols are more acidic than the corresponding carbinols (Eaborn, 1960; Sommer, 1965)

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