

The 1:1 adduct of triphenylsilanol and 4,4'-bipyridyl, and three pairwise-concomitant triclinic polymorphs of the 4:1 adduct having $Z' = 0.5, 1$ and 4

Katharine F. Bowes,^a George Ferguson,^{a,b} Alan J. Lough^c and Christopher Glidewell^{a*}

^aSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, ^bDepartment of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and ^cLash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Correspondence e-mail: cg@st-andrews.ac.uk

Crystallization from methanol solution of mixtures of triphenylsilanol and 4,4'-bipyridyl has given a 1:1 adduct (I), $\text{Ph}_3\text{SiOH}\cdot\text{C}_{10}\text{H}_8\text{N}_2$, and three polymorphic 4:1 adducts (II)–(IV), $(\text{Ph}_3\text{SiOH})_4\cdot\text{C}_{10}\text{H}_8\text{N}_2$. In (I), the components are linked by a single $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond and by a number of $\text{C}-\text{H}\cdots\pi(\text{arene})$ hydrogen bonds to form a continuous three-dimensional structure. Compounds (II)–(IV) are all triclinic, space group $P\bar{1}$, with Z' values of 0.5, 1 and 4, respectively. The basic hydrogen-bonded aggregate is the same in each of (II)–(IV), having a pair of silanol molecules linked to the bipyridyl *via* $\text{O}-\text{N}\cdots\text{N}$ hydrogen bonds and a further pair of silanol molecules linked to the first pair *via* $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. In (II) there is just one such aggregate lying across a centre of inversion ($Z' = 0.5$) and in (III) there are two such aggregates, both lying across centres of inversion ($Z' = 2 \times 0.5 = 1$). In (IV) there are six independent aggregates of this type, four of which lie across centres of inversion and two of which lie in general positions, so that $Z' = (4 \times 0.5) + 2 = 4$. While the components in (I) are fully ordered, each of (II)–(IV) exhibits extensive disorder involving both the bipyridyl units and the phenyl rings of the silanol components.

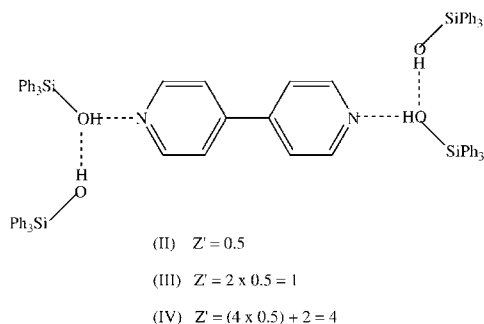
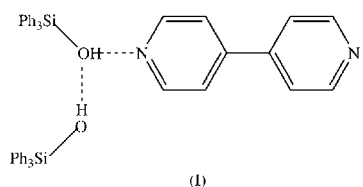
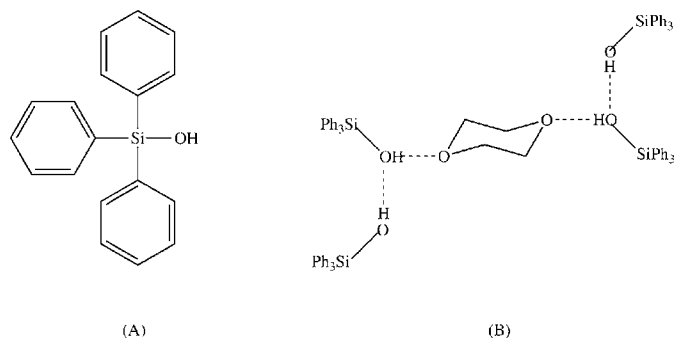
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1. Introduction

The structure of triphenylsilanol, Ph_3SiOH (*A*) [see Scheme (I)], was first established some years ago (Puff *et al.*, 1991) using diffraction data collected at 198 K. The compound was found to crystallize in space group $P\bar{1}$ with $Z = 16$, *i.e.* with $Z' = 8$, and the molecules are arranged to form two independent cyclic tetramers each having approximate $\bar{4}$ (S_4) symmetry, although H atoms bonded to O were not located.

A recent re-investigation of this compound (Bowes *et al.*, 2002) showed firstly that there is no change in structure between 120 and 298 K; secondly, that the hydroxyl H atoms are readily located using CCD data collected at 120 K and that these H atoms are fully ordered; thirdly, that the orientational disorder apparent at 198 K for one of the phenyl rings but not then modelled (Puff *et al.*, 1991) was easily handled with 120 K data, but that this type of disorder, possibly dynamic, was almost intractable at 298 K, with indications of disorder for at least eight of the 24 independent phenyl rings.



This tetrameric structure, despite the increasing mobility of the phenyl rings with increasing temperature, appears to be extremely robust and the same phase is obtained on crystallization of triphenylsilanol from a wide range of solvents including such potential acceptors of hydrogen bonds as acetone and ethyl acetate (Bowes *et al.*, 2002). Specific solvates are, however, obtained from dimethylsulfoxide (DMSO) solution, $(\text{Ph}_3\text{SiOH})_2 \cdot \text{DMSO}$ (Bowes *et al.*, 2002) and from 1,4-dioxan solution $(\text{Ph}_3\text{SiOH})_4 \cdot \text{C}_4\text{H}_8\text{O}_2$ (Bourne, Johnson *et al.*, 1991; Bowes *et al.*, 2002). The dioxan adduct consists of centrosymmetric five-molecule aggregates (B) (see Scheme (I)), in which two molecules of the silanol are linked to the dioxan *via* $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, with two further silanol molecules similarly linked to the first pair of silanol molecules. Likewise it has been reported (Bourne, Nassimbeni *et al.*, 1991) that crystallization of triphenylsilanol from mixtures of ethanol with methanol, propanol or water selectively yields a 4:1 ethanol solvate $(\text{Ph}_3\text{SiOH})_4 \cdot \text{C}_2\text{H}_6\text{O}$. Clearly the crystallization conditions which lead to the formation of phases other than the cyclic tetramer are highly specific: it is notable also that no other solvent-free polymorph of triphenylsilanol has yet been observed, suggesting that this phase may be particularly stable, despite the absence from the structure of both $\text{C}-\text{H} \cdots \pi(\text{arene})$ and $\pi \cdots \pi$ stacking interactions.

Continuing our investigations in this area, we have now turned to a rather more basic hydrogen-bond acceptor containing N rather than O as the acceptor site, namely 4,4'-bipyridyl, $\text{C}_{10}\text{H}_8\text{N}_2$. Here we report the structure of four distinct adducts formed between triphenylsilanol and 4,4'-bipyridyl, a 1:1 adduct $\text{Ph}_3\text{SiOH} \cdot \text{C}_{10}\text{H}_8\text{N}_2$ (I), and three polymorphic 4:1 adducts $(\text{Ph}_3\text{SiOH})_4 \cdot \text{C}_{10}\text{H}_8\text{N}_2$ (II)–(IV), all triclinic $P\bar{1}$, but having Z' values of 0.5 (II), 1 (III) and 4 (IV), respectively. Each of compounds (II)–(IV) proves to contain different numbers of the same basic supramolecular aggregate, but in unit cells of different shape and volume and hence these compounds provide examples not only of polymorphs with different Z' values but also, in fact, examples of concomitant polymorphism (Bernstein *et al.*, 1999), as co-crystallization experiments designed to yield 2:1 and 4:1 adducts each yield mixtures of at least two of (II)–(IV).

2. Experimental

2.1. Synthesis

Co-crystallization of a methanol solution containing equimolar quantities of triphenylsilanol and 4,4'-bipyridyl yielded analytically pure (I) as the sole product. Analysis for (I): found C 77.1, H 5.8, N 6.5%; $\text{C}_{28}\text{H}_{24}\text{N}_2\text{OSi}$ requires C 77.7, H 5.6, N 6.5%; a crystal of (I) suitable for single-crystal X-ray diffraction was selected directly from the analytical sample. Similar crystallization from solutions containing a 2:1 molar ratio of triphenylsilanol and 4,4'-bipyridyl gave solids whose elemental analyses were inconsistent, but which proved to contain both (II) and (III), along with 4,4'-bipyridyl. Crystallization of solutions containing a 4:1 ratio of triphenylsilanol and 4,4'-bipyridyl gave consistent and satisfactory analyses: found C 77.9, H 5.8, N 2.3%; $\text{C}_{82}\text{H}_{72}\text{N}_2\text{O}_4\text{Si}_4$ requires C 78.1, H 5.8, N 2.2%, although this material proved to contain both (III) and (IV).

2.2. Data collection, structure solution and refinement

Diffraction data for (I)–(IV) were collected at 150 (1) K using a Nonius Kappa CCD diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Other details of cell data, data collection and refinement are summarized in Table 1, together with details of the software employed. Compounds (I)–(IV) are all triclinic, and space group $P\bar{1}$ was selected for each of them. 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 included as riding atoms with distances $\text{C}-\text{H}$ 0.95 and $\text{O}-\text{H}$ 0.84 \AA .

In (I) the molecular components both lie in general positions and they are fully ordered, but in (II)–(IV) the majority of the individual 4,4'-bipyridyl units lie across centres of inversion, but there is extensive disorder in these compounds, involving both the phenyl and the pyridyl rings. In all disordered systems, initially tied free variables were refined for each pair of disordered rings. These occupancy values were

Table 1
Experimental table.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	C ₁₈ H ₁₆ OSi·C ₁₀ H ₈ N ₂	4C ₁₈ H ₁₆ OSi·C ₁₀ H ₈ N ₂	4C ₁₈ H ₁₆ OSi·C ₁₀ H ₈ N ₂	4C ₁₈ H ₁₆ OSi·C ₁₀ H ₈ N ₂
<i>M_r</i>	432.58	1261.78	1261.78	1261.78
Cell setting, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.9849 (3), 9.3118 (4), 15.2451 (7)	9.2128 (18), 10.244 (2), 19.036 (4)	10.1595 (19), 18.37 (4), 20.49 (4)	20.787 (4), 24.404 (5), 29.456 (6)
α , β , γ (°)	83.2841 (18), 89.1384 (17), 64.693 (10)	99.65 (3), 93.21 (3), 99.57 (3)	66.75 (3), 77.35 (3), 80.95 (3)	83.68 (3), 89.65 (3), 67.11 (3)
<i>V</i> (Å ³)	1144.3 (8)	1740.0 (7)	3417.5 (14)	13 671 (6)
<i>Z</i> , <i>Z'</i>	2, 1	1, 0.5	2, 2 × 0.5 = 1	8, 4 × 0.5 + 2 = 4
<i>D_x</i> (Mg m ⁻³)	1.255	1.204	1.226	1.226
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	5243	10 145	30 132	96 921
θ range (°)	2.7–27.6	2.5–27.5	2.5–27.5	2.5–27.5
μ (mm ⁻¹)	0.13	0.14	0.14	0.14
Temperature (K)	150 (1)	150 (1)	150 (1)	150 (1)
Crystal form, colour	Plate, colourless	Block, colourless	Block, colourless	Block, colourless
Crystal size (mm)	0.35 × 0.32 × 0.08	0.32 × 0.25 × 0.20	0.36 × 0.30 × 0.15	0.32 × 0.28 × 0.20
Data collection				
Diffractometer	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
Absorption correction	None	None	None	None
No. of measured, independent and observed parameters	16 245, 5243, 3778	22 073, 7927, 4784	48 587, 15 662, 8682	142 148, 62 054, 18 805
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
<i>R</i> _{int}	0.071	0.064	0.093	0.099
θ_{\max} (°)	27.6	27.5	27.5	27.5
Range of <i>h</i> , <i>k</i> , <i>l</i>	−11 ⇒ <i>h</i> ⇒ 11 −12 ⇒ <i>k</i> ⇒ 12 −19 ⇒ <i>l</i> ⇒ 19	−11 ⇒ <i>h</i> ⇒ 11 −13 ⇒ <i>k</i> ⇒ 13 −22 ⇒ <i>l</i> ⇒ 24	−13 ⇒ <i>h</i> ⇒ 13 −23 ⇒ <i>k</i> ⇒ 23 −26 ⇒ <i>l</i> ⇒ 26	−26 ⇒ <i>h</i> ⇒ 26 −31 ⇒ <i>k</i> ⇒ 31 −34 ⇒ <i>l</i> ⇒ 38
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.047, 0.129, 1.02	0.061, 0.183, 1.03	0.060, 0.185, 1.03	0.142, 0.511, 1.06
No. of relections	5243	7927	15 662	62 054
No. of parameters	291	419	856	1205
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.1806P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.4962P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2 + 1.2408P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1823P)^2 + 47.0084P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.002	0.001	0.001	0.005
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.36, −0.39	0.33, −0.26	0.41, −0.41	0.94, −1.19
Extinction method	SHELXL	SHELXL	None	None
Extinction coefficient	0.030 (5)	0.015 (4)	–	–

Computer programs: *Kappa-CCD Server Software* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 1997b), *SHELXL97* (Sheldrick, 1997a), *PLATON* (Spek, 2002), *PRPKAPPA* (Ferguson, 1999).

then examined and those which did not differ significantly from 0.5 were fixed at 0.5 in subsequent refinement cycles. Thus, in (II) the diamine lies across a centre of inversion, disordered over two sets of sites with equal occupancy, while in the silanol which contains Si2, two of the three phenyl rings are disordered, each over two sets of sites all with site occupancy 0.5. In (III) both the independent diamines lie across centres of inversion and both exhibit disorder. The diamine 1, containing N1, in (III) has the C atoms of the pyridyl rings disordered over two sites, with occupancies 0.548 (8) and 0.452 (8), while in diamine 2, containing N2, the two sets of C sites all have occupancy 0.5. The silanol molecules in (III) which contain Si12 has one of the phenyl rings disordered over

two sets of sites with occupancies 0.753 (3) and 0.247 (3). The silanol molecule in (III) which contains Si22 has two of its phenyl groups disordered in this way, one ring with occupancies 0.726 (4) and 0.274 (4), and the other ring having 0.5 occupancy for all the sites. In (IV) the four diamines containing N11, N21, N31 and N41 all lie across different centres of inversion, and for each there are two close but distinct orientations, with all sites having 0.5 occupancy. The other two diamine units, one containing N51 and N61, and the other containing N71 and N81, lie in general positions and they are fully ordered. In the silanol molecules in (IV) which contain Si11, Si12, Si22 and Si82, a single phenyl ring in each molecule is disordered over two sets of sites, all with occu-

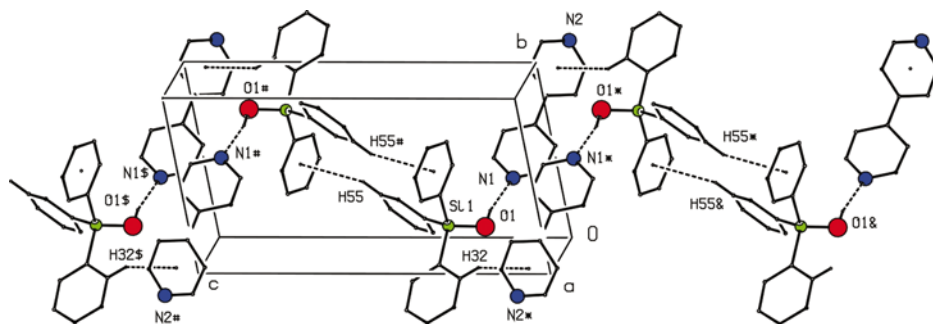


Figure 3

Part of the crystal structure of (I) showing the formation of a chain of rings along [001]. For the sake of clarity, H atoms bonded to C atoms, but which are not involved in the interactions depicted, are omitted. The atoms marked with an asterisk (*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions $(1-x, 1-y, -z)$, $(1-x, 1-y, 1-z)$, $(x, y, 1+z)$ and $(x, y, -1+z)$, respectively.

ADDSYM (Spek, 2002) showed no possible additional symmetry.

Supramolecular analyses were made and the diagrams were prepared with the aid of *PLATON* (Spek, 2002). Details of hydrogen-bond dimensions and selected molecular dimensions are given in Tables 2 and 3.¹ Figs. 1–10 show the molecular components, with the atom-labelling schemes, and aspects of the supramolecular structures.

3. Results and discussion

3.1. Crystallization characteristics and molecular constitutions

Crystallization of methanol solutions containing equimolar quantities of triphenylsilanol and 4,4'-bipyridyl yielded the 1:1 adduct $\text{Ph}_3\text{SiOH}\cdot\text{C}_{10}\text{H}_8\text{N}_2$ (I) as the sole identified solid product. In (I) the two components are linked by an $\text{O}\cdots\text{H}\cdots\text{N}$ hydrogen bond involving a hard (Desiraju & Steiner, 1999) hydrogen-bond donor and a hard hydrogen-bond acceptor (see §3.2). However, in such an equimolar mixture there is a threefold excess of hard hydrogen-bond acceptors (the pyridyl N and the silanol O atoms) over the hard hydrogen-bond donors (the hydroxyl groups). It was therefore expected that when the initial solution for crystallization contained a 2:1 molar ratio of triphenylsilanol and 4,4'-bipyridyl, a 2:1 adduct $(\text{Ph}_3\text{SiOH})_2\cdot\text{C}_{10}\text{H}_8\text{N}_2$ would result, expected in turn to contain a three-molecule aggregate, probably lying across a special position, in which each of the bipyridyl N atoms acted as an acceptor in an $\text{O}\cdots\text{H}\cdots\text{N}$ hydrogen bond.

However, no evidence whatsoever has been found for the formation of a solid 2:1 adduct. Instead crystallization of solutions containing a 2:1 molar ratio of the components yielded solid products containing 4:1 adducts $(\text{Ph}_3\text{SiOH})_4\cdot\text{C}_{10}\text{H}_8\text{N}_2$, together with some excess 4,4'-bipyridyl. This leads to elemental analyses which were not only

inconsistent between different samples, but which were not amenable to interpretation in terms of a single product having a simple rational ratio of triphenylsilanol to bipyridyl units. Moreover, the crystalline product of 4:1 stoichiometry thus obtained proved to contain at least two polymorphs, as both (II) and (III) were isolated from such a product.

By contrast, crystallization of a solution containing a 4:1 molar ratio of the components yielded an analytically pure material of 4:1 stoichiometry, as expected, but again this proved to be a mixture of polymorphs, since (III) and (IV) were isolated from it. Although an exhaustive examination of the solid products obtained from the 2:1 and three 4:1 solutions has not been carried out, it seems at least possible that each of the solid materials may in fact contain all three of the polymorphs (II)–(IV).

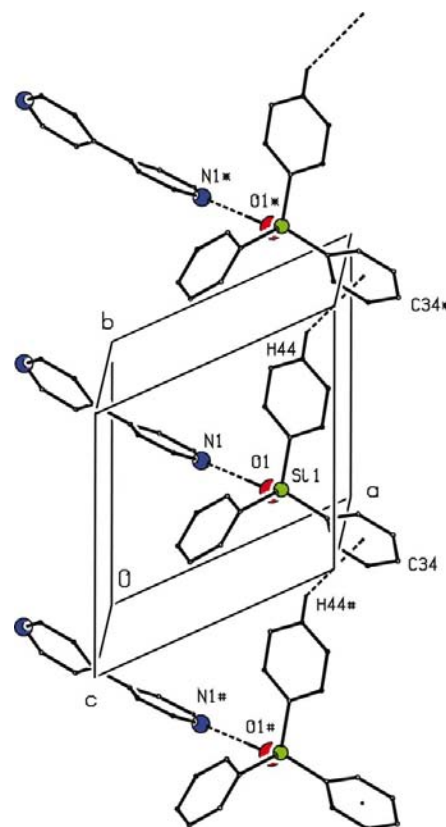


Figure 4

Part of the crystal structure of (I) showing the formation of a chain along [010]. For the sake of clarity, H atoms bonded to C atoms, but which are not involved in the interactions depicted, are omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, 1+y, z)$ and $(x, -1+y, z)$, respectively.

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0147). Services for accessing these data are described at the back of the journal.

Table 3
Selected geometric parameters (Å, °).

(I)			
Si1—O1	1.629 (2)	Si1—C41	1.873 (2)
Si1—C31	1.866 (2)	Si1—C51	1.871 (2)
O1—Si1—C31—C32	42.4 (2)		
O1—Si1—C41—C42	46.2 (2)		
Si1—C31	39.4 (2)		
(II)			
Si1—O1	1.637 (2)	Si2—O2	1.629 (2)
Si1—C11	1.891 (2)	Si2—C41†	1.862 (10)
Si1—C21	1.886 (2)	Si2—C51	1.860 (3)
Si1—C31	1.887 (2)	Si2—C61†	1.883 (3)
		Si2—C71†	1.888 (10)
		Si2—81†	1.902 (4)
O1—Si1—C11—C12	36.8 (2)	O2—Si2—C41—C42†	−86.8 (5)
O1—Si1—C21—C22	57.5 (2)	O2—Si2—C51—C52	3.2 (3)
O1—Si1—C31—C32	48.1 (2)	O2—Si2—C61—C62†	−4.0 (2)
		O2—Si2—C71—C72†	−62.6 (5)
		O2—Si2—C81—C82†	78.6 (5)
(III)			
Si11—O11	1.639 (2)	Si12—O12	1.632 (2)
Si11—C111	1.871 (2)	Si12—C141	1.860 (3)
Si11—C121	1.867 (2)	Si12—C151	1.873 (2)
Si11—C131	1.865 (2)	Si12—C161‡	1.893 (2)
		Si12—C171§	1.913 (4)
Si21—O21	1.640 (2)	Si22—O22	1.623 (2)
Si21—C211	1.870 (2)	Si22—C241†	1.865 (4)
Si21—C221	1.870 (2)	Si22—C251	1.868 (2)
Si21—C231	1.868 (2)	Si22—C261¶	1.911 (2)
		Si22—C271†	1.905 (4)
		Si22—C281††	1.880 (4)
O11—Si11—C111—C112	36.6 (2)	O12—Si12—C141—C142	98.1 (3)
O11—Si11—C121—C122	58.5 (2)	O12—Si12—C151—C152	4.5 (3)
O11—Si11—C131—C132	47.8 (2)	O12—Si12—C161—C162‡	−4.8 (2)
		O12—Si12—C171—C172§	110.5 (5)
O21—Si21—C211—C212	39.3 (2)	O22—Si22—C241—C242†	89.9 (3)
O21—Si21—C221—C222	58.3 (2)	O22—Si22—C251—C252	1.4 (3)
O21—Si21—C231—C232	51.1 (2)	O22—Si22—C261—C262¶	67.7 (2)
		O22—Si22—C271—C272†	124.7 (3)
		O22—Si22—C281—C282††	2.8 (4)
(IV)			
Si11—O11	1.645 (5)	Si12—O12	1.644 (5)
Si21—O21	1.643 (5)	Si22—O22	1.666 (5)
Si31—O31	1.638 (5)	Si32—O32	1.645 (5)
Si41—O41	1.649 (5)	Si42—O42	1.654 (5)
Si51—O51	1.646 (5)	Si52—O52	1.585 (5)
Si61—O61	1.642 (5)	Si62—O62	1.606 (5)
Si71—O71	1.638 (5)	Si72—O72	1.582 (5)
Si81—O81	1.646 (5)	Si82—O82	1.600 (5)
O11—Si11—C111—C112	36.3 (4)	O12—Si12—C141—C142	−64.7 (4)
O11—Si11—C121—C122	59.2 (4)	O12—Si12—C151—C152†	−67.3 (8)
O11—Si11—C131—C132†	42.6 (9)	O12—Si12—C161—C162	2.1 (4)
O11—Si11—C171—C172†	52.3 (9)	O12—Si12—C181—C182†	−10.6 (6)
O21—Si21—C211—C212	38.2 (3)	O22—Si22—C241—C242	−49.5 (3)
O21—Si21—C221—C222	59.7 (3)	O22—Si22—C251—C252†	−89.5 (7)
O21—Si21—C231—C232‡	55.2 (8)	O22—Si22—C261—C262	−2.1 (4)
O21—Si21—C271—C272§§	50.0 (12)	O22—Si22—C281—C282†	−120.6 (6)
O31—Si31—C311—C312	37.8 (3)	O32—Si32—C341—C342	−92.9 (4)
O31—Si31—C321—C322	58.4 (3)	O32—Si32—C351—C352¶¶	−1.3 (5)
O31—Si31—C331—C332	47.6 (4)	O32—Si32—C361—C362	7.0 (7)
		O32—Si32—C371—C372¶¶	55.4 (8)
		O32—Si32—C381—C382	15.1 (13)
O41—Si41—C411—C412	36.3 (3)	O42—Si42—C441—C442	85.0 (3)
O41—Si41—C421—C422	57.0 (3)	O42—Si42—C451—C452	−4.3 (4)
O41—Si41—C431—C432	51.2 (3)	O42—Si42—C461—C462	8.4 (4)
O51—Si51—C511—C512	37.0 (3)	O52—Si52—C541—C542†	−81.4 (8)
O51—Si51—C521—C522	59.9 (3)	O52—Si52—C551—C552†	2.3 (6)
O51—Si51—C531—C532	48.5 (4)	O52—Si52—C561—C562	0.9 (4)
		O52—Si52—C571—C572†	−65.7 (8)

3.2. Supramolecular structures

3.2.1. Compound (I). In (I) the components are linked by an O—H···N hydrogen bond (Table 2, Fig. 1), but the distal N atom in the bipyridyl unit, N2, does not act as a hydrogen-bond acceptor, even in a C—H···N hydrogen bond. Nor are there any aromatic π ··· π stacking interactions in the structure of (I); possibly the absence of these interactions is associated with the twisted conformation of the diamine unit, where the dihedral angle between the ring planes is 32.0 (2)°. In this respect, the structure of (I) is somewhat reminiscent of those of the 1:1 adducts formed by ferrocene-1,1'-diylbis(diphenylmethanol), [Fe(C₅H₄CPh₂OH)₂] with 1,2-bis(4-pyridyl)ethane (Zakaria *et al.*, 2001) and 1,2-bis(4-pyridyl)ethene (Zakaria *et al.*, 2002).

However, there are several C—H··· π (arene) hydrogen bonds in (I) (Table 2), whose combined effect is to link the bimolecular aggregates (Fig. 1) into a continuous three-dimensional framework. Thus, bipyridyl C23 at (*x*, *y*, *z*) acts as a hydrogen-bond donor to the pyridyl ring (N1, C12—C16) at (−*x*, 1 − *y*, −*z*), so generating a centrosymmetric ring, centred at (0, 0.5, 0). Similarly, phenyl C32 at (*x*, *y*, *z*) acts as a donor to the pyridyl ring (N2, C22—C26) at (1 − *x*, 1 − *y*, −*z*), so generating a second ring motif, this time centred at (0.5, 0.5, 0). Propagation of these two interactions by inversion thus generates a chain of rings running parallel to the [100] direction (Fig. 2).

Phenyl C55 at (*x*, *y*, *z*) acts as a hydrogen-bond donor to the phenyl ring (C41—C46) at (1 − *x*, 1 − *y*, 1 − *z*), producing a third centrosymmetric ring motif, centred in this case at (0.5, 0.5, 0.5). The combination of the two ring motifs having phenyl C as donors then generates a chain of rings running parallel to the [001] direction (Fig. 3). Finally, phenyl C44 at (*x*, *y*, *z*) acts as a donor to the phenyl ring (C31—C36) at (*x*, 1 + *y*, *z*), thus generating by translation a chain parallel to the [010] direction (Fig. 4). The combination of the [100], [010] and [001] chains suffices to generate a single three-dimensional framework.

Although C—H··· π (arene) interactions are absent from the structure of triphenylsilanol itself, they are an important feature of the supramolecular aggregation in both the DMSO adduct (Ph₃SiOH)₂·DMSO and the 1,4-dioxan adduct (Ph₃SiOH)₄·C₄H₈O₂

Table 3 (continued)

O61—Si61—C611—C612	−35.2 (3)	O52—Si52—C581—C582†	−69.1 (7)
O61—Si61—C621—C622	−56.6 (3)	O62—Si62—C641—C642	79.7 (4)
O61—Si61—C631—C632	−45.5 (4)	O62—Si62—C651—C652	4.2 (4)
		O62—Si62—C661—C662	−9.6 (3)
O71—Si71—C711—C712	40.4 (3)	O72—Si72—C741—C742†	−84.6 (8)
O71—Si71—C721—C722	57.3 (3)	O72—Si72—C751—C752†	2.2 (7)
O71—Si71—C731—C732	53.9 (3)	O72—Si72—C761—C762	−3.0 (4)
		O72—Si72—C771—C772†	−63.5 (8)
		O72—Si72—C781—C782†	82.2 (7)
O81—Si81—C811—C812	−37.9 (3)	O82—Si82—C841—C842†	84.7 (7)
O81—Si81—C821—C822	−56.2 (4)	O82—Si82—C851—C852	−61.4 (4)
O81—Si81—C831—C832	−49.6 (3)	O82—Si82—C861—C862	−6.9 (4)
		O82—Si82—C871—C872†	52.1 (7)
C53—C54—C64—C63	−153.7 (4)	C73—C74—C84—C83	−145.6 (4)

† Disordered phenyl ring, occupancy 0.5. ‡ Disordered phenyl ring, occupancy 0.753 (3). § Disordered phenyl ring, occupancy 0.247 (3). ¶ Disordered phenyl ring, occupancy 0.726 (4). †† Disordered phenyl ring, occupancy 0.274 (4). ††† Disordered phenyl ring, occupancy 0.64 (3). §§ Disordered phenyl ring, occupancy 0.36 (3). ¶¶ Disordered phenyl ring, occupancy 0.598 (5). Disordered phenyl ring, occupancy 0.67 (2). ¶¶¶ Disordered phenyl ring, occupancy 0.402 (5). Disordered phenyl ring, occupancy 0.33 (2).

(Bowes *et al.*, 2002). In the DMSO adduct, two distinct interactions of this type link the three-molecule aggregates formed by the O—H...O hydrogen bonds into a three-dimensional framework, while in the dioxan adduct the aggregates [B, see Scheme (I)] are linked into molecular ladders, again by means of two distinct C—H... π (arene) interactions.

3.2.2. Compounds (II)–(IV). Compounds (II)–(IV) all have 4:1 stoichiometry, $(\text{Ph}_3\text{SiOH})_4\cdot\text{C}_{10}\text{H}_8\text{N}_2$, and all contain the same five-molecule aggregate (Figs. 5–7), which is analogous to the aggregate found in the 4:1 adduct $(\text{Ph}_3\text{SiOH})_4\cdot\text{C}_4\text{H}_8\text{O}_2$, formed with 1,4-dioxan (Bourne, Johnson *et al.*, 1991; Bowes *et al.*, 2002). In such an aggregate, we can conveniently distinguish between an inner pair of triphenylsilanol molecules which provide the donors in the O—H...N hydrogen bonds and an outer pair of triphenylsilanol molecules which provide the donors in the O—H...O hydrogen bonds (Table 2).

In (II), having $Z' = 0.5$, there is a single aggregate lying across a centre of inversion in $P\bar{1}$, selected as that at (0.5, 0.5, 0.5) (Fig. 8). Two such aggregates occur in (III), again with both lying across centres of inversion. The aggregates containing N11 and N21 lie across the inversion centres at (0.5, 0.5, 0.5) and (0.5, 1.0, 0.5), respectively (Fig. 9), so that $Z' = 2 \times 0.5 = 1$. In each of (II) and (III) the phenyl rings of the inner triphenylsilanol molecules, containing Si1 in (II), and Si11 and Si21 in (III), are all fully ordered, while all the outer triphenylsilanol molecules exhibit some orientational disorder of the phenyl rings. Two of these rings are disordered in (II), while three of the six rings of the two independent outer triphenylsilanol molecules are disordered in (III) (Table 3).

There are six independent five-molecule aggregates in (IV). Four of these, containing the atoms N11, N21, N31 and N41, respectively (Figs. 7a–d), lie across the centres of inversion at (0, 0, 0), (0, 0, 0.5), (0.5, 0.5, 0) and (0.5, 0.5, 0.5), respectively, while the other two aggregates, containing atoms N51 and N61 (Fig. 7e) and N71 and N81 (Fig. 7f), lie in general positions. The aggregates in general positions exhibit approximate centrosymmetry, apart from the phenyl ring disorder, and their centroids lie close to (0.75, 0.25, 0.25) and (0.75, 0.25,

0.75), *i.e.* mid-way between pairs of genuine centres of inversion. Hence, $Z' = (4 \times 0.5 + 2) = 4$. There are thus aggregates in (IV) centred at the vertices of the cell and at its centre, as well as on two of the faces and four of the edges, in addition to the four aggregates in general positions within the cell (Fig. 10).

The disorder in (IV) is extensive (see §2.2). All four of the centrosymmetric amines are disordered over two sets of sites; two of the 24 phenyl rings in the inner triphenylsilanol molecules are disordered and nine of the 24 phenyl rings in the outer triphenylsilanol molecules are disordered. Overall in (II)–(IV), the inner triphenylsilanol molecules contain 33 independent rings, of which only two are disordered, but 14 of the 33 rings in the outer triphenylsilanol molecules are disordered. Of the nine independent bipyridyl units in (II)–(IV), seven are disordered.

3.3. Molecular conformations and dimensions

The Si—O distances (Table 3) show rather little variation apart from those in the heavily disordered outer triphenylsilanol components of (IV). Even here, although the overall range of the Si—O distances in (IV) runs from 1.582 (7) to 1.666 (5) Å, the mean value 1.63 (2) Å does not differ from the mean values in (II) and (III), 1.633 (4) and 1.634 (7) Å,

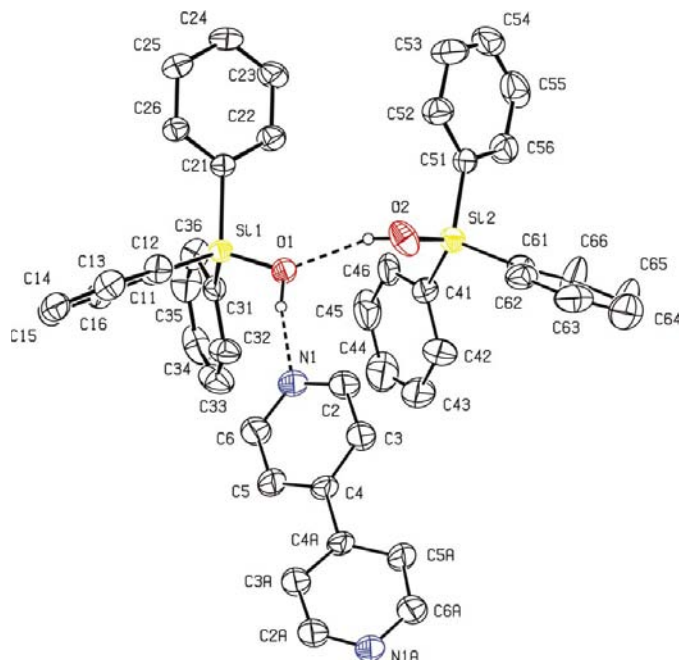


Figure 5

The independent molecular components of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity only one orientation is shown for each of the disordered components and H atoms bonded to C atoms are omitted. The atoms marked 'A' are at the symmetry position (1 - x, 1 - y, 1 - z).

nor from the unique value 1.629 (2) Å in (I). In tetrameric triphenylsilanol itself, the mean of the eight independent Si–O distances is 1.645 (6) Å, while in the 1,4-dioxan adduct, $(\text{Ph}_3\text{SiOH})_4 \cdot \text{C}_4\text{H}_8\text{O}_2$, whose centrosymmetric five-component

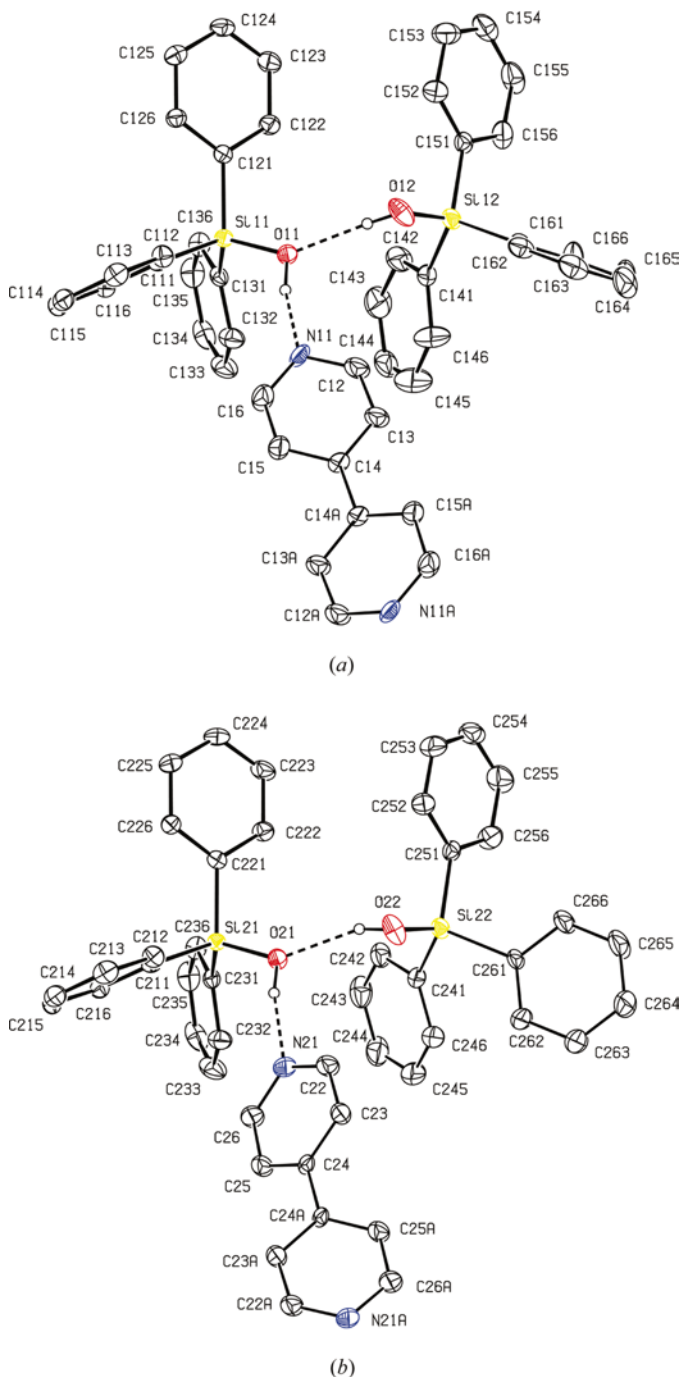


Figure 6
The independent molecular components of (III), showing the atom-labelling scheme: (a) for the aggregate centred at (0.5, 0.5, 0.5), where the atoms marked 'A' are at the symmetry position $(1-x, 1-y, 1-z)$; (b) for the aggregate centred at (0.5, 1.0, 0.5), where the atoms marked 'A' are at the symmetry position $(1-x, 2-y, 1-z)$. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity only one orientation is shown for each of the disordered components and H atoms bonded to C atoms are omitted.

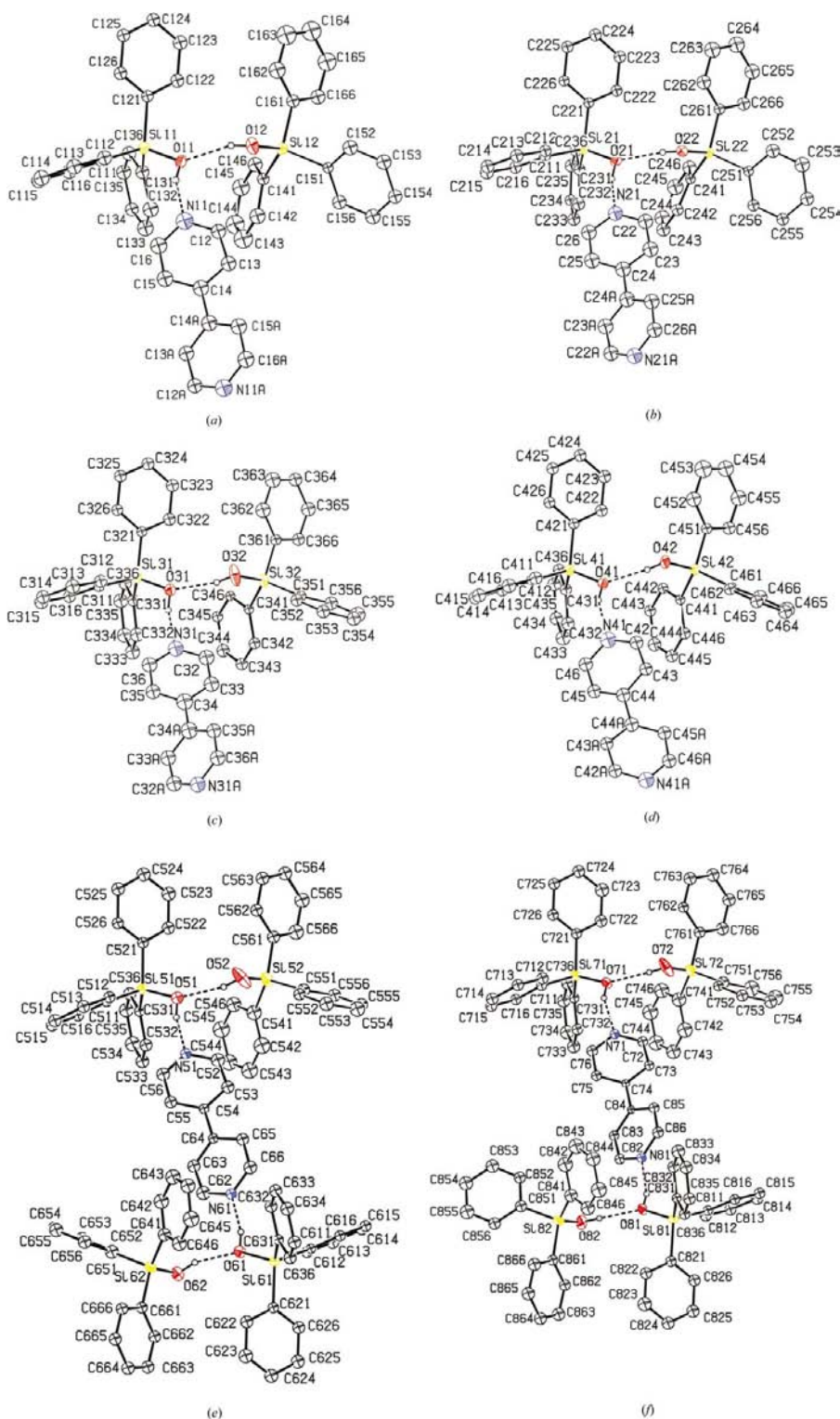
aggregate resembles those in (II)–(IV), the mean of the two independent Si–O distances is 1.639 (10) Å.

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 unique triphenylsilanol molecule in (I) and the fully ordered inner triphenylsilanol molecules in (II)–(IV) all have conformations 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 35.2 (3)– 59.9 (3) $^\circ$ with a mean of *ca* 46° , just mid-way between the two C_{3v} conformations. On the other hand, those few of the outer triphenylsilanol molecules which are fully ordered [those in (IV) containing O42 and O62 only] have conformations close to C_s (m) symmetry for the non-H atoms. In each of these molecules, 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 3). It is noticeable that for each of the aggregates lying in general positions (Figs. 7e and f), the conformations of the ordered inner triphenylsilanol molecules are related by an approximate inversion (Table 3), although the disorder in most of the outer triphenylsilanol molecules precludes any such comparison. We may note here that the very extensive disorder of the phenyl groups found here in (II)–(IV) has a close parallel in the structure of Ph_3SiOH itself (Puff *et al.*, 1991; Bowes *et al.*, 2002): this may well turn out to be a characteristic feature of systems containing a high proportion of Ph_3SiOH molecules.

4. Conclusions

There are no obvious relationships between the unit-cell dimensions for (II)–(IV) (Table 1, Figs. 8–10), and *ADDSYM* (Spek, 2002) did not detect any possible additional symmetry in any of these structures. Nonetheless, it is striking that the general orientation of the two independent five-component aggregates in (III) are the same and that the general orientation of all six such aggregates in (IV) are similar. Hence, it is likely that rather simple displacive phase transformations are possible between polymorphs (II), (III) and (IV). This hypothesis in turn is consistent with their concomitant crystallization, as the overall similarity in the arrangements of the aggregates means that differences between the overall supramolecular interaction energies in these polymorphs are likely to be quite small.

As noted earlier (§3.2.2), the structure of the hydrogen-bonded aggregates in (II)–(IV) closely resembles that of the 1,4-dioxan adduct $(\text{Ph}_3\text{SiOH})_4 \cdot \text{C}_4\text{H}_8\text{O}_2$. However, the structure and composition of this last adduct are entirely different from those of the adduct formed by 1,4-dioxan with triphenylmethanol, Ph_3COH , where a 1:1 adduct is formed containing a two-component aggregate involving just a single O–H...O hydrogen bond (Bourne, Johnson *et al.*, 1991), rather analogous to the structure of (I) (§3.2.1). It is thus pertinent to summarize here the similarities and differences exhibited by the few adducts of Ph_3COH and Ph_3SiOH which


Figure 7

The independent molecular components of (IV), showing the atom-labelling scheme: (a) for the aggregate centred at (0, 0, 0), where the atoms marked 'A' are at the symmetry position $(-x, -y, -z)$; (b) for the aggregate centred at (0, 0, 0.5), where the atoms marked 'A' are at the symmetry position $(-x, -y, 1 - z)$; (c) for the aggregate centred at (0.5, 0.5, 0), where the atoms marked 'A' are at the symmetry position $(1 - x, 1 - y, -z)$; (d) for the aggregate centred at (0.5, 0.5, 0.5), where the atoms marked 'A' are at the symmetry position $(1 - x, 1 - y, 1 - z)$; (e) for the aggregate whose centroid lies near (0.75, 0.25, 0.25); (f) for the aggregate whose centroid lies near (0.75, 0.25, 0.75). Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity only one orientation is shown for each of the disordered components and H atoms bonded to C atoms are omitted.

have been characterized to date. The supramolecular structures of pure Ph_3COH and Ph_3SiOH are entirely different: Ph_3COH forms tetrahedral aggregates $(\text{Ph}_3\text{COH})_4$, containing mobile hydroxyl H atoms (Ferguson *et al.*, 1992; Aliev *et al.*, 1998; Serrano-González *et al.*, 1999), while Ph_3SiOH forms cyclic aggregates $(\text{Ph}_3\text{SiOH})_4$, containing fully ordered hydroxyl H atoms (Bowes *et al.*, 2002). On the other hand, the adducts formed by dimethylsulfoxide with Ph_3COH (Weber *et al.*, 1989) and Ph_3SiOH (Bowes *et al.*, 2002) are isostructural. However, by contrast, Ph_3COH crystallizes from acetone as a 2:1 adduct (Weber *et al.*, 1989), while Ph_3SiOH crystallizes from acetone as the solvent-free cyclic tetramer (Bowes *et al.*, 2002). While Ph_3COH is highly selective for methanol in mixed solvents, crystallizing preferentially as the four-component cyclic aggregate $(\text{Ph}_3\text{COH})_2 \cdot (\text{MeOH})_2$ (Weber *et al.*, 1989), Ph_3SiOH is highly selective for ethanol in mixed solvents, crystallizing preferentially as the five-component cyclic aggregate $(\text{Ph}_3\text{SiOH})_4 \cdot (\text{EtOH})$ (Bourne, Nassimbeni *et al.*, 1991). Further comparison of the adducts and solvates formed by Ph_3COH and Ph_3SiOH seems likely to reveal further similarities and further differences, all based upon the subtle interplay of weak, but long-range direction-specific intermolecular forces, including hard and soft hydrogen bonds, of both $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \pi(\text{arene})$ types, and aromatic $\pi \cdots \pi$ stacking interactions: that is to say, the very forces which are currently least amenable to reliable computational treatment.

X-ray data were collected at the University of Toronto using a Nonius Kappa-CCD diffractometer purchased with funds from NSERC Canada.

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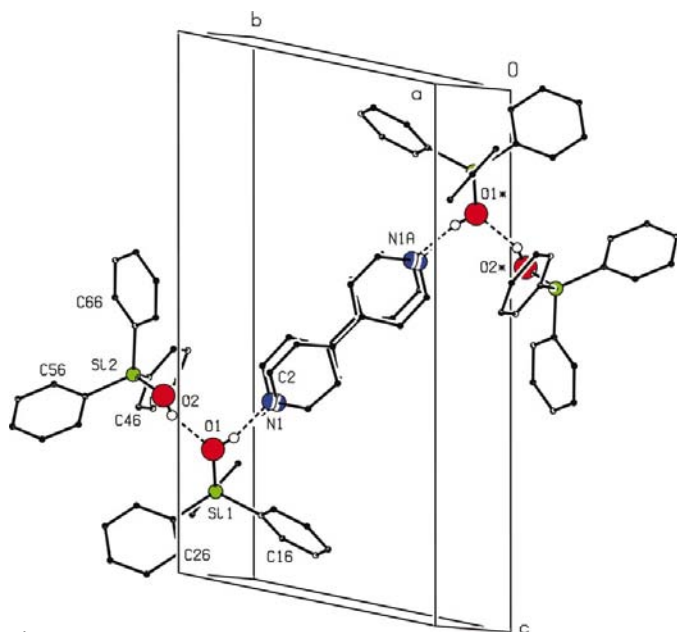


Figure 8

The unit-cell contents of (II). For the sake of clarity H atoms bonded to C are omitted and only one orientation is shown for each of the disordered phenyl rings. The atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

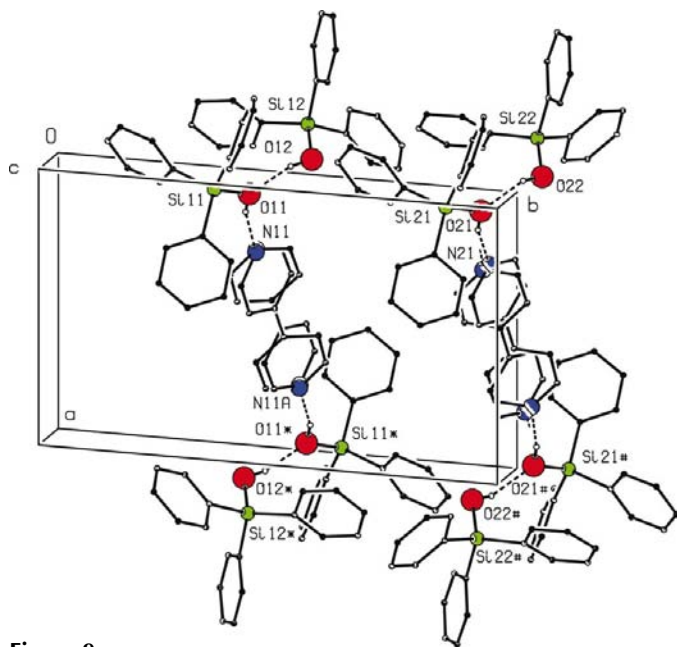


Figure 9

The arrangement of the independent aggregates in the crystal structure of (III). For the sake of clarity H atoms bonded to C are omitted and only one orientation is shown for each of the disordered phenyl rings. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$ and $(1 - x, 2 - y, 1 - z)$, respectively.

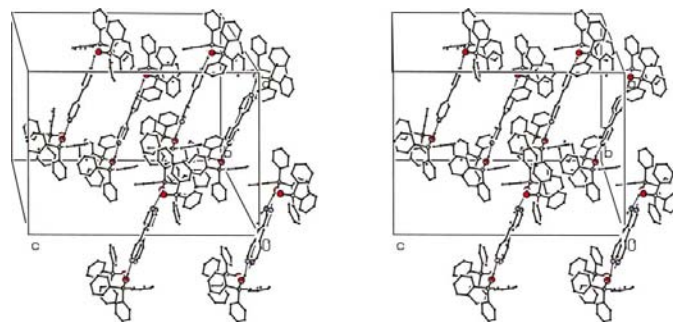


Figure 10

Stereoview of the unit-cell contents of (IV) showing the arrangement of the six independent aggregates. For the sake of clarity H atoms bonded to C are omitted and only one orientation is shown for each of the disordered components.

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