# Constructing a short C−H···O hydrogen bond: the crystalline complex of triphenylsilylacetylene with triphenylphosphineoxide. A very unusual crystal structure with *Z* = 7 and *Z*′ = 3.5

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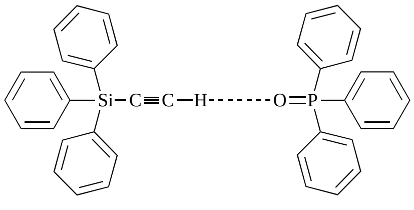
**The crystalline complex of triphenylsilylacetylene ($Ph_3Si{-}C{\equiv}C{-}H$) and triphenylphosphineoxide ($Ph_3P{=}O$) contains four symmetry independent molecular dimers which are connected by C≡C−H···O=P hydrogen bonds. These hydrogen bond have H···O separations between 1.99 and 2.05 Å, and are the shortest reported for acetylenic donors. This reflects the fact that the hydrogen bonds are formed between one of the strongest known C−H donors and one of the strongest O acceptors. The red-shift of the acetylenic IR C−H stretching vibration compared to an apolar solution is $-149\ cm^{-1}$, the largest reported for a known crystal structure. The crystal packing in space group $P\bar{1}$ is complex with the very rare unit cell content of 3.5 formula units per asymmetric crystal unit ($Z' = 3.5$).**

## Introduction

In recent years, C−H···O hydrogen bonding has become one of the main subjects of hydrogen bond research.[1–3] It has been shown that the properties of this interaction depend critically on the nature of the C−H donor and of the O acceptor: early spectroscopic experiments indicate that the 'strength' of a C−H donor depends on the C hybridization as $C(sp^1){-}H > C(sp^2){-}H > C(sp^3){-}H$ and increases with the number of electron-withdrawing substituents.[4] Structurally, this is reflected in a shortening of the H···O separations. In crystals, the observed average C−H···O distances correlate with the conventional C−H acidity, *i.e.* the H···O distance reduces systematically with increasing acidity.[5] Analogously, C−H···O distances reduce with increasing O basicity.[6] Apart from these direct influences of donor and acceptor nature, C−H···O hydrogen bonds can experience appreciable influences from the surroundings, such as strengthening by cooperativity effects.[7–9]

C−H···O hydrogen bonds in general are much weaker interactions than conventional O/N−H···O hydrogen bonds, and have much longer donor–acceptor separations. However, if the most polarized of the C−H donors are involved [$CHCl_3$, $CH(NO_2)_3$, −C≡C−H, N≡C−H, imidazolium ions, *etc.*], there seems to be an overlap in geometries and strengths with conventional hydrogen bonds.[3] Examples are the adduct of trinitromethane to dioxane[10] (H···O = 2.00 Å based on an idealized C−H bond distance), or 2-ethynyladamantan-2-ol (H···O = 2.07 Å).[7,8,11]

The shortest known C−H···O bonds were found by accident,[10,11] leading to the challenge to design and produce crystals containing C−H···O bonds with equal or even shorter donor–acceptor separations. A promising strategy is available: if acidic C−H donors are in a crystal structure combined with very basic O acceptors, short C−H···O bonds might be obtained. To avoid competitive effects, the molecule(s) should carry no strong O−H or N−H donors. Both the acidic C−H donor and the O acceptor should be sterically easily accessible. Following this strategy, a relevant molecular assembly was, indeed, produced: the crystalline 1:1 complex of triphenylsilylacetylene (TPSiA) and triphenylphosphineoxide (TPPO), **1**, which is described below.



Complex **1**

## Experimental

### General

Attempts were made to cocrystallize the very strong hydrogen bond acceptor TPPO with a number of terminal alkynes, and with chloroform. In most cases, the substances would not cocrystallize, but with TPSiA, plate-shaped colourless crystals of **1** were obtained (slow evaporation of an equimolar MeOH solution of TPSiA, obtained from Aldrich, and TPPO, obtained from Lancaster). Crystals are stable under ambient conditions. From EtOH and propan-1-ol, crystals of the same kind were obtained.

### Crystallography

Formula $C_{20}H_{16}Si{\cdot}C_{18}H_{15}OP$, $M_w = 562.3$. All tested crystals exhibit high mosaicity and relatively high background intensities. X-Ray diffraction data were measured at room temperature on an Enraf-Nonius Turbo-CAD4 diffractometer (FR571 rotating anode X-ray generator, Ni-filtered Cu-Kα radiation, ω-scan mode, $\lambda/2 \sin\theta_{max} = 0.89$ Å, no absorption correction). The space group is triclinic $P\bar{1}$ (No. 2) with $Z = 7$, 3.5 formula units per asymmetric crystal unit ($Z' = 3.5$); further crystal data is given in Table 1.

The structure was solved with direct methods[12] and refined on $F^2$ of all reflections using the program SHELXL93.[13] Due to disorder and pseudosymmetries (see main text), refinement was troublesome and several restraints had to be used (Si−C≡C−H groups were restrained to be linear, all Si−C≡C−H groups refined with equal bond lengths, phenyl groups treated as ideal hexagons, H-atoms refined in the riding model with $U_{iso} = 1.2 \times U_{eq}$ of the atom they are bonded to;[13] for the disordered pairs **C** and **D** (see Fig. 1), alternative Si and P atoms

**Table 1** Crystallographic data for **1**, 1:1 TPSiA–TPPO

| | |
|---|---|
| Crystal data | |
| Formula | $C_{20}H_{16}Si{\cdot}C_{18}H_{15}OP$ |
| $M_w$ | 562.3 |
| Temperature | Room temp. |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ (No. 2) |
| $Z$ | 7 |
| $Z'$ | 3.5 |
| $a$/Å | 14.098(6) |
| $b$/Å | 12.221(3) |
| $c$/Å | 28.80(2) |
| $\alpha$/° | 80.68(5) |
| $\beta$/° | 78.48(9) |
| $\gamma$/° | 85.55(6) |
| $V$/Å$^3$ | 5576(5) |
| $D_c$/g cm$^{-3}$ | 1.17 |
| $\mu$/mm$^{-3}$ | 1.33 |
| $F$(000) | 2072 |
| Crystal size/mm$^3$ | 0.4 × 0.4 × 0.1 |
| Data collection | |
| $\lambda$/Å | 1.541 76 |
| $\lambda$/2 sin $\theta_{max}$/Å | 0.89 |
| Measured reflections | 16 835 |
| $R_{merge}$ ($F^2$) | 0.023 |
| Unique reflections | 16 452 |
| Unique refl. with $F^2 > 2\sigma(F^2)$ | 11 558 |
| Refinement | |
| Program | SHELXL93 |
| Data/parameters | 16 427/1013 |
| $\Delta\rho_{max}$/e Å$^{-3}$ | 0.60 |
| $wR(F^2)$ [for $F^2 > 2\sigma(F^2)$] | 0.270 |
| $R(F^2)$ [for $F^2 > 2\sigma(F^2)$] | 0.092 |

were placed in the same sites with the same anisotropic displacement parameters and alternative Si–C≡C and P=O vectors were restrained to be colinear; this is reasonable because in TPSiA and TPPO, the Si–C≡C and P=O bonds have the same orientation with respect to the phenyl groups). Anisotropic refinement converged with $R = 0.092$ [for $I > 2\sigma(I)$],† which is high for normal small molecule structures, but not unusual for a structure of the present complexity ($Z' = 3.5$, 143.5 symmetry-independent non-H atoms).

### Vibrational spectroscopy

Solution spectra of TPSiA and of TPPO in $CCl_4$ (J. T. Baker) were recorded in a 1.0 mm NaCl cell at concentrations less than $10^{-2}$ mM. Solid state spectra of microcrystalline **1** were recorded at ambient temperature as KBr pellets (Merck, Uvasol). In addition, the mull technique [poly(chlorotrifluoroethylene) oil, Merck, Uvasol] was applied to check for polymorphic interference. Spectra were recorded on a Perkin-Elmer Model 2000 FTIR spectrometer equipped with a DTGS detector and connected to a PC under GRAMS Research software. Scanning parameters: resolution 2 cm$^{-1}$, eight scans and medium apodization. A low temperature spectrum of a mull sample of **1** was also recorded, which is very similar to the room temperature spectrum, and not indicative of a phase transition upon cooling (−184 °C, SPECAC 21525 variable temperature vacuum cell with liquid nitrogen as coolant).

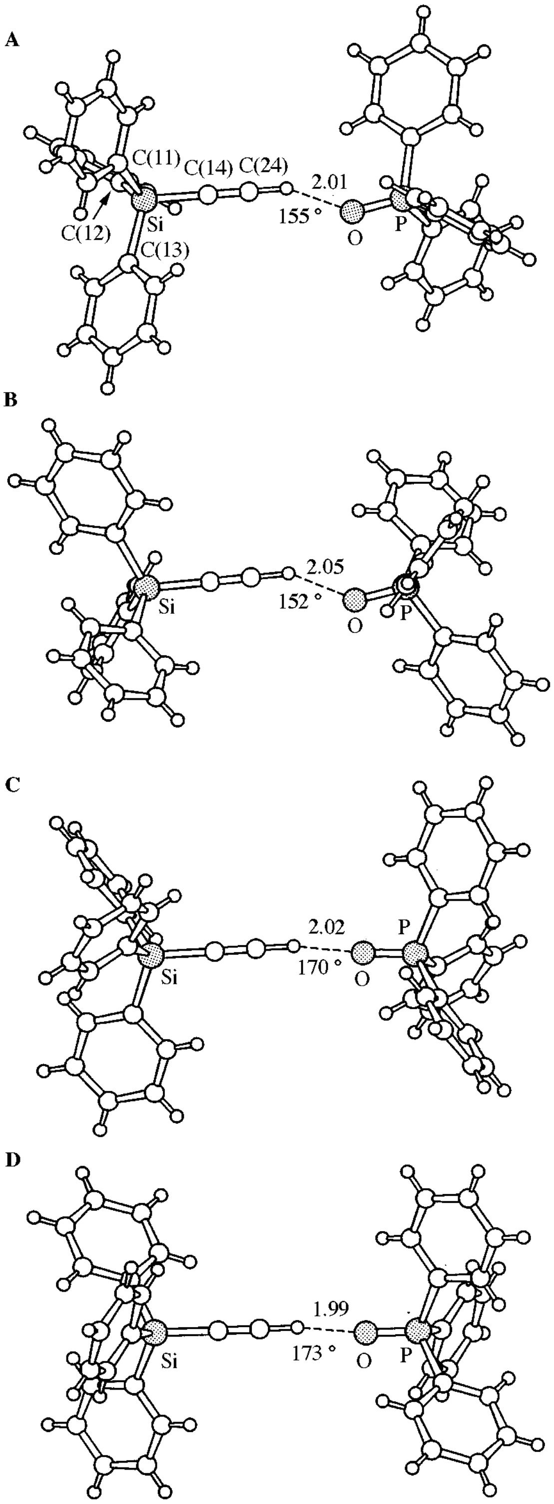


**Fig. 1** The four symmetry-independent pairs of molecules triphenylsilylacetylene (TPSiA)–triphenylphosphineoxide (TPPO) in the crystal structure of **1**. The dimers are labelled **A**–**D**. All dimers are drawn in projections on the Si–C≡C···P plane. The pair **D** is placed on a crystallographic inversion centre, *i.e.* the orientation is reversed for 50% of all pairs (TPPO 'left', TPSiA 'right'). The orientation of the pair **C** is disordered with 54% of all pairs orientated as shown, and 46% reserved.

## Results

### C≡C–H···O=P hydrogen bonding

The crystal structure of **1** contains four symmetry-independent quasi-centrosymmetric C–H···O hydrogen bonded dimers TPSiA–TPPO, **A**–**D**, shown in Fig. 1. All dimers have somewhat different geometries, as shown by the Si···P distances and the inclination angles of the $XPh_3$ moieties with respect to the Si···P line, $\omega$, given in Table 2 ($\omega$ defined in the table heading). Dimers **A** and **B** have shorter Si···P distances and are less linear than **C** and **D**. Dimers **A** and **B** are ordered, whereas **C** and **D** are disordered with two possible orientations of the hydrogen bond (*i.e.* TPSiA can be left and TPPO right, as

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† Atomic coordinates, displacement parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Instructions for Authors (1997)', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/71.

**Table 2** Dimer geometry. $\omega_1$ = angle between the normal of the plane through the three phenyl(Si) pivot atoms C11, C12 and C13, and the Si···P line; $\omega_2$ = as $\omega_1$ for the three phenyl(P) pivot C-atoms

| Dimer | Si···P/Å | $\omega_1$/° | $\omega_2$/° |
|---|---|---|---|
| **A** | 7.39 | 5 | 14 |
| **B** | 7.39 | 9 | 14 |
| **C** | 7.57 | 4 | 2 |
| **D** | 7.55 | 2 | — |

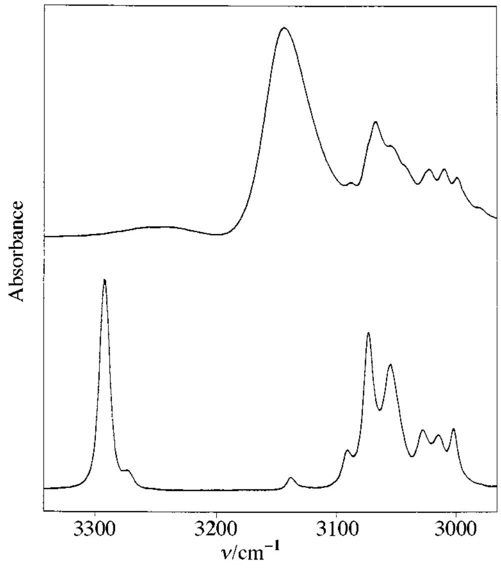


**Fig. 2** The C–H stretching region of the IR spectra of crystalline **1** (top) and a dilute solution of TPSiA in $CCl_4$ (bottom). Numerical values are given in Table 4.

shown in Fig. 1, or reverse). **D** is placed on an inversion centre relating the left and right molecules, so that both are populated 50% with TPSiA and 50% with TPPO. For **C**, the occupancies refine to 54 and 46% for the alternative orientations, which is not significantly different from 50%. Apparently, there is a relation between geometry and disorder property: the more symmetrical dimers are disordered whereas the less symmetrical are not.‡ Giving a reason for this behaviour would be speculative and is therefore not attempted here.

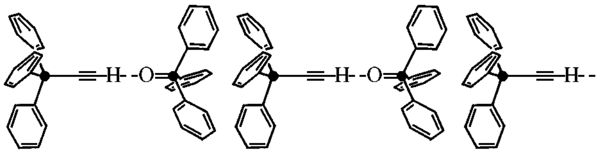
The hydrogen bond geometries of the symmetry-independent dimers are given in Table 3. The combination of the acidic donor Si–C≡C–H with the basic P=O acceptor has actually resulted in unusually short C–H···O contacts: the H···O distances are between 1.99 and 2.05 Å (standard deviations presumably *ca.* 0.02 Å), mean value 2.02 Å. This means that **1** contains the shortest C≡C–H···O bonds reported as yet. With C($sp^3$)–C≡C–H donors and C=O acceptors, C–H···O bonds have a mean H···O separation of 2.24(3) Å, and with C–O–C acceptors of even 2.44(6) Å.[6] Although the H···O distances in **1** are in a narrow range, the C–H···O angles vary over a rather wide range, 152–176°, and the angles at O over even 143–176°. This variability of angles is a consequence of the well known flexibility of hydrogen bonds in general: they tend to be linear, but can be easily bent without much of a loss in bond energy.

A highly sensitive tool to probe C≡C–H moieties for hydrogen bonding effects is infrared (IR) spectroscopy.[7,9,14] Due to weakening of the C–H bond in a C≡C–H···O interaction, the frequency of the C–H stretching vibration $\nu_{\equiv C-H}$ is lowered for hydrogen bonding C≡C–H compared to 'free' C≡C–H. To see if the very short H···O separations in **1** are associated with very large red shifts of $\nu_{\equiv C-H}$, IR spectra were recorded for crystals of **1**, and for a dilute solution of TPSiA in $CCl_4$. The relevant spectral region is shown in Fig. 2, numerical data is given in Table 4. The solution spectrum shows the 'free' ≡C–H stretching vibration at 3293 cm$^{-1}$; for crystalline **1**, this band is much broader and more intense, with the peak position shifted to 3144 cm$^{-1}$. This is lower than for any terminal alkyne with a known crystal structure,§ indicating considerable weakening of the C–H bond. The band must be composed of signals from the different dimers, which due to the different geometries should be centred at slightly different wavenumbers. The individual components, however, cannot be resolved here.

## Crystal packing with $Z = 7$

The intention of the study has been to engineer a short C–H···O hydrogen bond. Unexpectedly, this led to the formation of a complex crystal packing mode with $Z = 7$ and $Z' = 3.5$ (7 dimers per unit cell, 3.5 per asymmetric crystal unit). A search through the Cambridge Crystallographic Database[15] showed only one previously published example with $Z = 7$ (out of 152 464 entries in 1996): hydrated 2-(2-hydroxyphenyl)pyridin-3-ol,[16] also with space group $P\bar{1}$ and $Z' = 3.5$ (uniqueness of $Z = 7$ not discussed in the original publication). Therefore, crystal packing with $Z = 7$ is highly exceptional, and the packing mode observed for **1** deserves more detailed discussion.

As shown in Fig. 1, TPSiA and TPPO form quasi-centrosymmetric dimers. In the crystal lattice, these are arranged in columns where translation related dimers are connected by multiple edge-to-face phenyl–phenyl contacts involving all six phenyl rings of the contacting molecules, Scheme 1.



**Scheme 1**

Since there are four symmetry-independent dimers, four symmetry-independent molecular columns **A**–**D** are formed. As mentioned above, dimers **A** and **B** are ordered, whereas **C** and **D** are disordered with two alternative orientations. This means that in columns **A** and **B**, all dimers have the same orientation, as in Scheme 1, whereas in columns **C** and **D**, dimers are incorporated with both possible orientations. At this point, it is helpful to refer to the concept of supramolecular synthons introduced by Desiraju.[17] 'Supramolecular synthons' are integral units of intermolecular interaction patterns, which can be regarded as building blocks of the interaction pattern as a whole. The molecular columns in **1** are built employing two distinct supramolecular synthons, shown as boxes in Scheme 2.

Synthon **I** is the C≡C–H···O interaction joining the polar

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‡ One could argue that the relation is in fact reversed: the linear geometry of **C** and **D** is a refinement artefact because disordered dimers falsely refine to a more symmetrical geometry. However, there is no apparent disorder of the phenyl orientations in **C** and **D**. Since the inclination angles $\omega$ in Table 2 are based on planes through the pivot atoms of phenyl groups, they are little affected by the SiCCH/PO disorder. The Si···P distances are not affected at all by disorder (because for a disordered pair, Si···P = P···Si). This means that the geometrical data in Table 2 and the more linear geometry of dimers **C** and **D** are 'true'.

§ For substances with published crystal structures, the lowest acetylenic $\nu_{\equiv C-H}$ for a non-ionic compound known to us is in 2-ethynyladamantan-2-ol, $\nu = 3181$ cm$^{-1}$ at room temp. (3161 cm$^{-1}$ at 100 K).[14] For ionic compounds, the lowest $\nu_{\equiv C-H}$ is in triphenylprop-2-ynlphosphonium bromide, $\nu = 3150$ cm$^{-1}$ at room temp., which contains a $P^+$–C≡C–H···$Br^-$ interaction with H···$Br^-$ = 2.58 Å.[21] One substance with an even lower acetylenic $\nu_{C-H}$ is known: dibutyl(ethynyl)phosphineoxide with $\nu_{\equiv C-H} = 3115$ cm$^{-1}$, compared to 3295 cm$^{-1}$ in $CCl_4$.[14] Presumably, the interaction responsible for this dramatic red shift of 180 cm$^{-1}$ is a O=P–C≡C–H···O=P hydrogen bond. Very poor crystallinity of the substance prevents structure determination.

**Table 3** Hydrogen bond geometry,[a] based on a linear Si–C≡C–H group with C–H = 1.08 Å

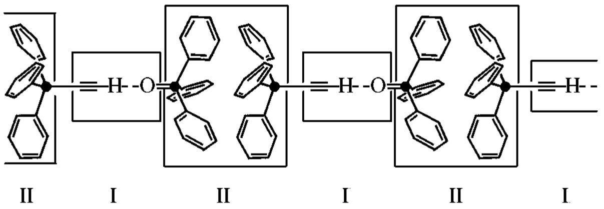
| H-bond | H···O/Å | C···O/Å | C–H···O/° | H···O=P/° |
|---|---|---|---|---|
| (**A**)C≡C–H···O=P(**A**) | 2.01 | 3.02 | 155 | 145 |
| (**B**)C≡C–H···O=P(**B**) | 2.05 | 3.04 | 152 | 143 |
| (**C**)C≡C–H···O=P(**C**) | 2.02 | 3.09 | 170 | 175 |
| (**C**)P=O···H–C≡C(**C**) | 2.01 | 3.09 | 176 | 176 |
| (**D**)C≡C–H···O=P(**D**′) | 1.99 | 3.06 | 173 | 173 |

[a] Due to restrained refinement, standard deviations of the given parameters based on standard deviations of atomic coordinates are not realistic, and are therefore not given. Realistic estimates for standard deviations might be *ca.* 0.02 Å for distances and *ca.* 2° for angles for the ordered dimers **A** and **B**, and ⩾0.02 Å and ⩾2°, respectively, for the disordered dimers **C** and **D** (for ordered small molecule structures, standard deviations are normally ⩽0.01 Å for distances and ⩽1° for angles).

**Table 4** Relevant IR stretching frequencies for TPSiA and TPPO solutions in $CCl_4$ and for microcrystalline samples of **1** at room temp.

| | TPSiA in $CCl_4$ | TPPO in $CCl_4$ | **1** crystal | $\Delta\nu_{\text{cryst-soln}}$ |
|---|---|---|---|---|
| $\nu_{\equiv C-H}/cm^{-1}$ | 3293 | | 3144[a] | −149 |
| $\nu_{C\equiv C}/cm^{-1}$ | 2039 | | 2022 | −17 |
| $\nu_{P=O}/cm^{-1}$ | | 1202 | 1191 | −11 |

[a] At −184 °C: 3129 $cm^{-1}$.



**Scheme 2**

ends of TPSiA and TPPO. This interaction is specific in discriminating the two molecular species: it obviously does not allow association of homo-pairs TPSiA–TPSiA or TPPO–TPPO *via* their polar ends. Synthon **II** is the entity of Ph–Ph interactions joining the apolar ends of the molecules ('sextuple phenyl embrace'[18]). Since the Si–$C_{Ph}$ and P–$C_{Ph}$ bond lengths are very similar (at room temp. 1.86 Å in pure TPSiA,[19] 1.79 Å in pure TPPO[20]), the geometries of $SiPh_3$ and $PPh_3$ moieties are almost identical. Therefore, the geometry of synthon **II** is very poor in discriminating the possible pairs TPSiA–TPPO, TPSiA–TPSiA and TPPO–TPPO. The different partial charges on the P and Si centres, however, should slightly favour hetero-association for synthon **II**.

In this situation, it is easy to understand that the formation of the molecular columns is prone to exhibit disorder with dimers incorporated 'the wrong way', *i.e.* with homo-pairs forming synthon **II**. It remains difficult to understand, however, why this affects only two of the four independent columns; it can only be assumed that this is due to subtleties of the dimer geometries which favour hetero-association for bent dimer geometry (**A** and **B**) and allow homo-association for linear dimers (**C** and **D**). A different reason could be that the four different columns are engaged in different lateral contacts (see below) which might induce different disorder properties. A further problem is that the crystal structure cannot tell whether the disordered chains are composed of dimers incorporated in both orientations completely at random, or if there are short (or possibly even long) ordered sequences. A systematic preference of synthon **II** to form hetero-dimers would suggest the latter case.

In the crystal lattice, the four independent columns form a quasi-hexagonal arrangement, which does not seem to be governed by specific intermolecular interactions, but by close-packing requirements. This is commonly observed in columnar structures. At a first glance, this arrangement seems to be simple, Fig. 3(*a*). If the orientation of the columns is taken into account, however, the picture becomes highly complex, Fig. 3(*b*): column **A** is surrounded by one parallel, two antiparallel and three disordered columns, **B** by one parallel, one antiparallel and four disordered columns, the disordered column **C** by five ordered and one disordered column, and finally **D** by four ordered and two disordered columns. This means that the intermolecular surroundings of all four columns are different. To show the lateral contacts of the columns, a suitable section of the crystal packing is drawn in Fig. 4. The side-contacts involve Ph–Ph interactions as well as contacts from phenyl rings to the hydrogen bonding groups of neighbouring dimers.

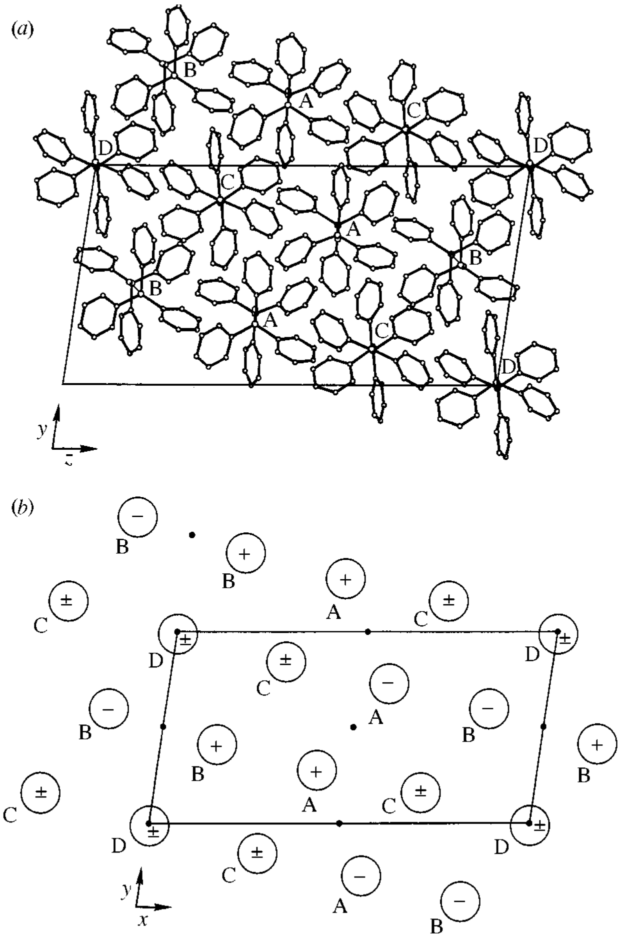


**Fig. 3** Crystal packing of **1**. (*a*) Projection along the *x*-axis, which is the column axis. (*b*) As above, with columns schematically represented by circles centred at the Si atoms. The orientation of the columns is indicated by symbols: + denotes Si–C≡C–H parallel with the *x*-axis; − denotes Si–C≡C–H antiparallel with the *x*-axis; ± denotes columns with disordered dimer orientation. Crystallographic inversion centres are marked by dots.

## Conclusions

To create a short C–H···O hydrogen bond, a molecule carry-

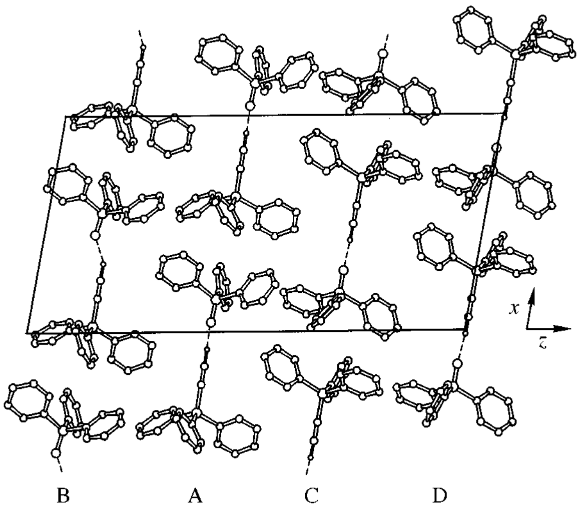


**Fig. 4** Crystal packing of **1** projected along the *y*-axis. One layer of columns is shown (those with centres at $0 \leqslant y < 0.5$). For disordered columns **C** and **D**, only one of the alternative dimer orientations is shown.

ing the strongly polarized donor Si−C≡C−H was cocrystallized with a molecule carrying the strong hydrogen bond acceptor P=O. Competitive effects and effects from steric hindrance were avoided by suitable selection of the carrier molecules. Indeed, C−H · · · O bonds were formed with H · · · O separations in the range 1.99–2.05 Å, which are the shortest observed yet for C≡C=H donors. This supports published views that in C−H · · · O interactions, mean donor–acceptor separations are primarily governed by donor acidity and acceptor basicity.[5,6] The unusually short hydrogen bond distance is associated with an unusually pronounced red shift of the IR C−H stretching vibration, again supporting published (but not undisputed) views that these parameters are closely correlated.

The crystal packing of **1** with seven formula units per crystal unit ($Z = 7$), and its disorder properties are highly exceptional, even intriguing to the crystallographer. Crystalline **1** is composed of columns built of molecular dimers. This is what has to be expected, and this is apparently very simple. Looking at the architecture of the columns, Scheme 2, it is also easy to rationalize orientational disorder within the columns. It is very difficult to understand, however, why this does not affect all columns in a similar way, and why ordered and disordered columns arrange themselves in such an awkwardly complicated fashion as shown in Fig. 3(*b*). The crystal packing as a whole is apparently determined by a very large number of weak and weakest directional and non-directional intermolecular interactions which cannot be disentangled with reasonable efforts.

## Acknowledgements

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