

C—H·· π interactions in cocrystals of bis(trimethylsilyl)acetylene and diphenylacetylene with benzene

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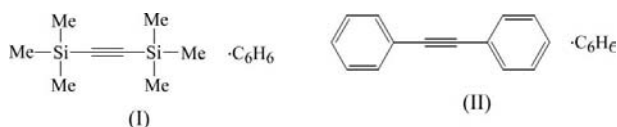
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We present here the crystal structures of two acetylene derivatives cocrystallized with benzene, namely bis(trimethylsilyl)acetylene benzene solvate, $C_8H_{18}Si_2 \cdot C_6H_6$, (I), and diphenylacetylene benzene solvate, $C_{14}H_{10} \cdot C_6H_6$, (II). In (I), both molecules belong to the symmetry point group C_{2h} and are located about special positions with site symmetry $2/m$. In (II), both molecules show crystallographic inversion symmetry. In both structures, there are C—H·· π contacts between aromatic H atoms and the π -electrons of the triple bond. In addition to these, in (II) there are C—H·· π contacts between aromatic H atoms and the π -electron cloud of the benzene molecules.

Comment

The structures of cocrystals of compounds which interact *via* the π -system with other molecules have received increased attention in recent years. As reported by Kirchner *et al.* (2010), the structures of the cocrystals of acetylene, $HC\equiv CH$, and different arenes feature a structural arrangement with C—H·· π contacts as shown in Fig. 1. In all these cases (Figs. 1a, 1b and 1c), the H atoms of the acetylene molecule form C—H·· π interactions with the π -system of the arene rings. It is interesting to note that unusually short triple bonds are reported for the acetylene molecules in these cocrystals.



In this paper, we describe cocrystals of benzene with the alkynes $Me_3SiC\equiv CSiMe_3$ and $PhC\equiv CPh$, (I) and (II), respectively. In contrast to the acetylene arene complexes, the structures of the benzene cocrystals of alkynes (I) and (II) reveal C—H·· π interactions of H atoms of the aromatic rings with the π -system of the alkyne.

Very recently, we have shown that the degradation of $Cl_3SiSiCl_3$ and $Cl_3SiSiCl_2SiCl_3$ in the presence of catalytic amounts of donors, such as amines, in the first step gives dichlorosilylene ($SiCl_2$) and ultimately produces the perchlorinated neopentasilane [$Si(SiCl_3)_4$]. Moreover, we have verified that the donor-induced degradation of $Cl_3SiSiCl_3$ or $Cl_3SiSiCl_2SiCl_3$ in the presence of the silylene-trapping agent 2,3-dimethyl-1,3-butadiene gives the [4+1] cycloadduct (Meyer-Wegner *et al.*, 2009). We are currently interested in cluster compounds consisting of group 14 elements (Wiberg, Lerner, Nöth & Ponikwar, 1999; Wiberg, Lerner, Wagner *et al.*, 1999; Wiberg, Lerner, Vasisht *et al.*, 1999; Lerner, 2005; Lerner *et al.*, 2010), especially those which are composed of two different group 14 elements. To this end, we thought that such cluster compounds could be prepared using the reaction between $SiCl_2$ and $PhC\equiv CPh$ or $Me_3SiC\equiv CSiMe_3$. However, the amine-induced degradation reaction of $Cl_3SiSiCl_3$ in the presence of $PhC\equiv CPh$ or $Me_3SiC\equiv CSiMe_3$ gives, in both cases, exclusively the neopentasilane $Si(SiCl_3)_4$. No trapping product and therefore no cluster was formed. The perchlorinated neopentasilane $Si(SiCl_3)_4$ was identified unambiguously by ^{29}Si NMR spectroscopy. Otherwise single crystals composed of one molecule of benzene and one molecule of $PhC\equiv CPh$ and $Me_3SiC\equiv CSiMe_3$, respectively, could be isolated from these reaction solutions.

Compound (I) crystallizes with just a quarter of each molecule in the asymmetric unit, where these molecules are located about sites with $2/m$ symmetry (Fig. 2). The crystal packing is illustrated in Fig. 3, which shows the C—H·· π

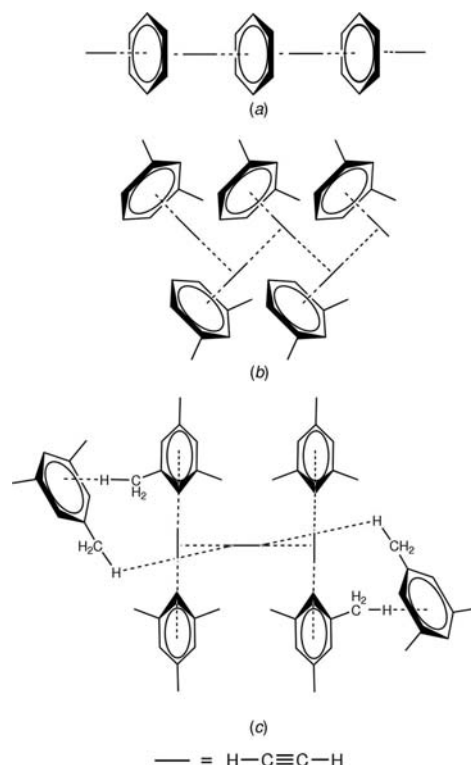


Figure 1
Structural arrangements with C—H·· π contacts.

contacts as dashed lines. There are two symmetry-equivalent contacts. The distance from the H atom (H4) to the centre of the triple bond is 3.013 Å, and the angle at the H atom is exactly 180°. The benzene ring in (I) may be disordered or undergoing libration (elongated ellipsoids and short C—C bonds), so that the current model is just the average structure. Thus, the C—H··· π contact, which appears to be linear, will have an angle slightly less than 180°.

Compound (II) crystallizes with two half molecules in the asymmetric unit, both of which are located on a centre of inversion (Fig. 4). As for (I), there are C—H··· π contacts between aromatic H atoms and the π -electrons of the triple bond

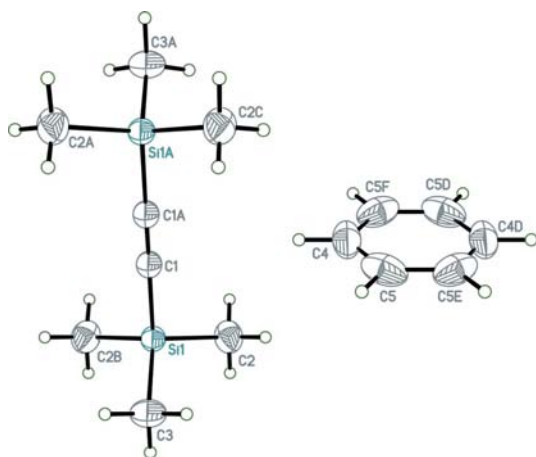


Figure 2

A perspective view of the two distinct molecules in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (A) $-x, -y, -z + 1$; (B) $x, -y, z$; (C) $-x, y, -z + 1$; (D) $-x, -y + 1, -z + 1$; (E) $x, -y + 1, z$; (F) $-x, y, -z + 1$.]

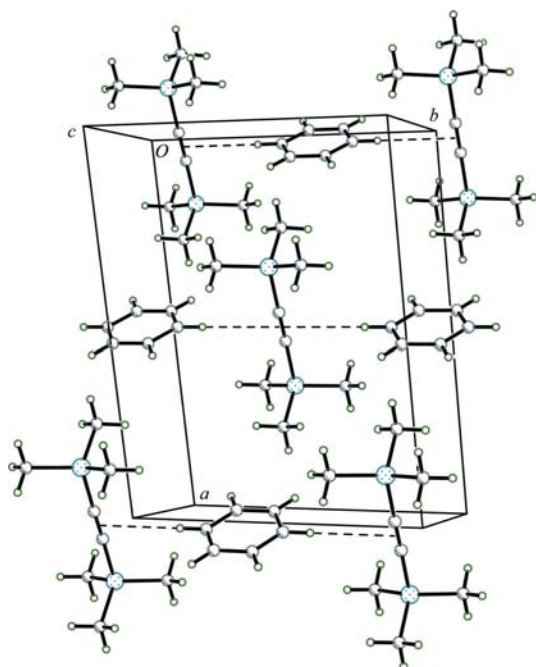


Figure 3

The crystal packing of (I). C—H··· π contacts are shown as dashed lines.

bond (Fig. 5), but in contrast to (I), in this structure, there are four C—H··· π contacts, divided into two symmetry-equivalent pairs. The contact from benzolic atom H8 to the centre of the triple bond has a distance of 3.268 Å and the angle at the H atom is 146°. The second, slightly longer, contact links phenylic atom H5 at a distance of 3.555 Å to the centre of the triple bond and the angle at the H atom is 155°. Furthermore, in this structure, a C—H··· π contact to the centre of the benzene molecule can be observed. The distance from H4 to the centre of the aromatic ring is 2.789 Å and the angle at H4 is 144°.

In order to compare the length of the C≡C bond in (I) and (II) with other structures, two searches of the Cambridge Structural Database (CSD, Version 5.3 of November 2008, plus four updates; Allen, 2002) were performed. For the fragment $C_3Si-C\equiv C-SiC_3$, which was found 27 times, a mean bond length of 1.20 (2) Å was found. This is in good agreement with the value of 1.211 (4) Å found for (I). A second search for diphenylacetylene in which the triple bond does not coordinate to any other atom yielded 34 entries. The mean value of the C≡C bond in these structures was

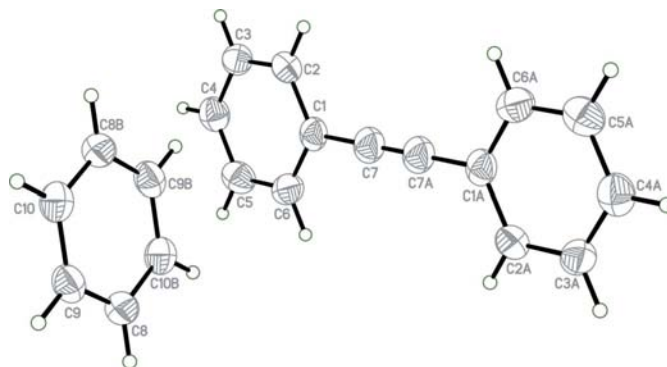


Figure 4

A perspective view of the two distinct molecules in (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (A) $-x, -y, -z + 1$; (B) $-x + 1, -y + 1, -z + 1$.]

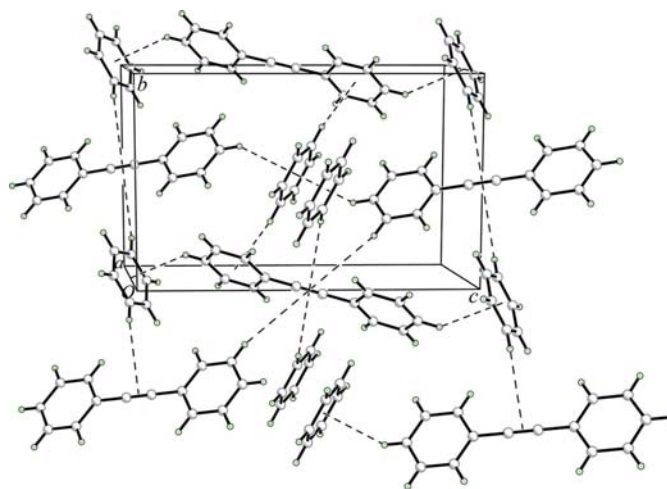


Figure 5

The crystal packing of (II). C—H··· π contacts are shown as dashed lines.

1.19 (3) Å, which agrees well with the value of 1.201 (2) Å found for (II).

It is interesting to note that there are no π - π stacking interactions between aromatic rings in either of the two structures. In (I) the benzene molecules which are the only aromatic rings in this structure are perfectly shielded from each other and in (II) there is no aromatic ring located above another one.

Since neither C atom of the acetylene moiety in (I) and (II) carries an H atom, no C-H... π interaction of the kind encountered by Kirchner *et al.* (2010) could be found either in (I) or in (II). Whereas the distance between an acetylenic H atom and the centre of an aromatic ring was found to be less than 3 Å, all C-H... π contacts to the C \equiv C bond in (I) and (II) are longer than 3 Å.

Both crystal structures presented here show a similar hydrogen-bonding pattern. There are C-H... π contacts from an H atom bonded to an aromatic C atom to the electron cloud of an acetylenic C \equiv C bond. Whereas in (I) there are no C-H... π interactions between two aromatic rings, this kind of interaction can be observed in (II). The reason for the occurrence of these contacts might be that (II) contains significantly more aromatic rings than (I). Both structures lack π - π stacking interactions between aromatic rings.

Experimental

For the synthesis of (I), a solution of Cl₃SiSiCl₃ (0.08 g, 0.29 mmol), *N,N,N',N'*-tetramethylethylenediamine (0.03 g, 0.29 mmol) and Me₃-SiC \equiv CSiMe₃ (0.30 g, 1.74 mmol) in benzene (1 ml) was heated for 110 h to 323 K. After cooling to room temperature, single crystals of the 1:1 adduct of benzene and Me₃SiC \equiv CSiMe₃ were obtained (yield 55%). In the ²⁹Si NMR spectrum of the reaction solution, signals were observed which can be assigned to the perchlorinated neopentasilane Si(SiCl₃)₄. For the synthesis of (II), a mixture of Cl₃SiSiCl₃ (0.08 g, 0.29 mmol), Me₂NEt (0.01 g, 0.15 mmol) and PhC \equiv CPh (0.32 g, 1.78 mmol) were dissolved in benzene (1 ml). After 48 h at room temperature, single crystals of the 1:1 adduct of benzene and PhC \equiv CPh were obtained (yield 60%). In the ²⁹Si NMR spectrum of the reaction solution, signals were observed which can be assigned to the perchlorinated neopentasilane Si(SiCl₃)₄. ²⁹Si NMR (C₆D₆): δ 3.5 [Si(SiCl₃)₄], δ -82.0 [Si(SiCl₃)₄].

Compound (I)

Crystal data

C₈H₁₈Si₂·C₆H₆
M_r = 248.51
 Monoclinic, *C*2/*m*
a = 14.0831 (14) Å
b = 10.6487 (12) Å
c = 5.7225 (6) Å
 β = 106.739 (7)°

V = 821.82 (15) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.19 mm⁻¹
T = 173 K
 0.43 × 0.38 × 0.35 mm

Data collection

Stoe IPDS II two-circle diffractometer
 Absorption correction: multi-scan (MULABS: Spek, 2003; Blessing, 1995)
T_{min} = 0.921, *T_{max}* = 0.935

2358 measured reflections
 808 independent reflections
 754 reflections with *I* > 2σ(*I*)
R_{int} = 0.029

Refinement

R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.090
S = 1.07
 808 reflections

42 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max}$ = 0.21 e Å⁻³
 $\Delta\rho_{\min}$ = -0.25 e Å⁻³

Compound (II)

Crystal data

C₁₄H₁₀·C₆H₆
M_r = 256.35
 Monoclinic, *P*2₁/*c*
a = 5.7078 (6) Å
b = 9.0681 (7) Å
c = 14.4212 (16) Å
 β = 99.741 (9)°

V = 735.66 (13) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.07 mm⁻¹
T = 173 K
 0.41 × 0.35 × 0.32 mm

Data collection

Stoe IPDS II two-circle diffractometer
 3831 measured reflections

1358 independent reflections
 1182 reflections with *I* > 2σ(*I*)
R_{int} = 0.037

Refinement

R[*F*² > 2σ(*F*²)] = 0.036
wR(*F*²) = 0.099
S = 1.08
 1358 reflections

92 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max}$ = 0.15 e Å⁻³
 $\Delta\rho_{\min}$ = -0.12 e Å⁻³

H atoms were located in a difference Fourier map but were included in calculated positions (aromatic and methyl C-H = 0.95 and 0.98 Å, respectively) and refined as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C_{aromatic}) or 1.5*U*_{eq}(C_{methyl}).

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3366). Services for accessing these data are described at the back of the journal.

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