organic compounds

A new polymorph and two inclusion compounds of 9,9′-spirobifluorene

Richard E. Douthwaite,* Andrew Taylor and Adrian C. Whitwood

Department of Chemistry, University of York, Heslington, York YO10 5DD, England
Correspondence e-mail: red4@york.ac.uk

Two new inclusion compounds of 9,9′-spirobifluorene (SBF) incorporating benzene [(I), $C_{25}H_{16}\cdot C_6H_6$] and biphenyl [(II), $C_{25}H_{16}\cdot C_{12}H_{10}$], and a new polymorph of SBF [(III), $C_{25}H_{16}$] are reported. All three exhibit $C-H\cdots\pi$(arene) hydrogen bonds between adjacent SBF molecules. Compound (II) also contains biphenyl $C-H$ to SBF π-arene interactions. Collectively, hydrogen bonding gives rise to a chain and a layered motif in compounds (I) and (II), respectively.

Comment

The synthesis of 9,9′-spirobifluorene (SBF) was first reported by Clarkson & Gomberg in 1930, and the first single-crystal structure determination was reported four decades later by Schenk (1972). Exhibiting D_{2d} point symmetry, SBF is an unusual structural motif, which has prompted its use in molecular recognition (Alcazar & Diederich 1992) and catalytic applications (Poriel *et al.*, 2003), and its incorporation into materials that exhibit unusual optoelectronic properties (Wong *et al.*, 2002). We have recently been interested in using SBF as a structural motif in molecular solids and report here the structures of two inclusion compounds, (I) and (II), incorporating benzene and biphenyl, respectively. In the course of our study, we also determined the structure of a new polymorph of SBF, (III).
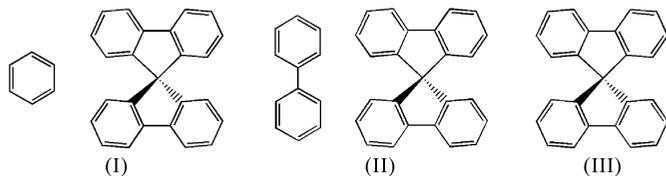
One of our initial aims had been to prepare co-crystals of SBF and fluorinated aromatics, including hexafluorobenzene, perfluoronaphthalene and perfluorobiphenyl, with the intention of investigating supramolecular structures akin to those derived from co-crystallization between planar hydro- and fluoroaromatics. However, in no case did co-crystals between SBF and fluoroaromatics result. We tentatively assigned this

observation to repulsive (steric) interactions between SBF and fluoroaromatics, preventing the attractive molecular electric quadrupole moment interactions that result in parallel stacking in many perhydro/perfluoro aromatic co-crystals (Williams, 1993). However, we rationalized that it may be possible to prepare inclusion compounds incorporating SBF and hydroaromatics, because the relative quadrupole moments would give rise to attractive edge-to-face electrostatic interactions (Lowden & Chandler 1974; Shi & Bartell 1988) that could be sterically accessible for SBF. Indeed, co-crystallization of SBF and the hydroaromatics benzene and biphenyl gave the inclusion compounds (I) and (II), respec-
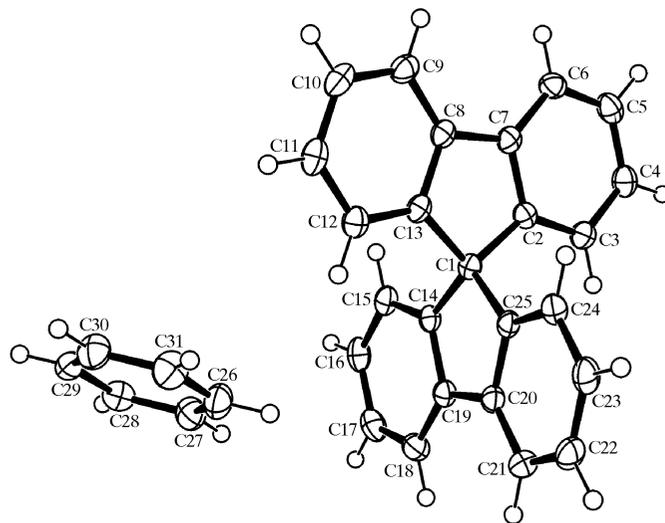
Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.
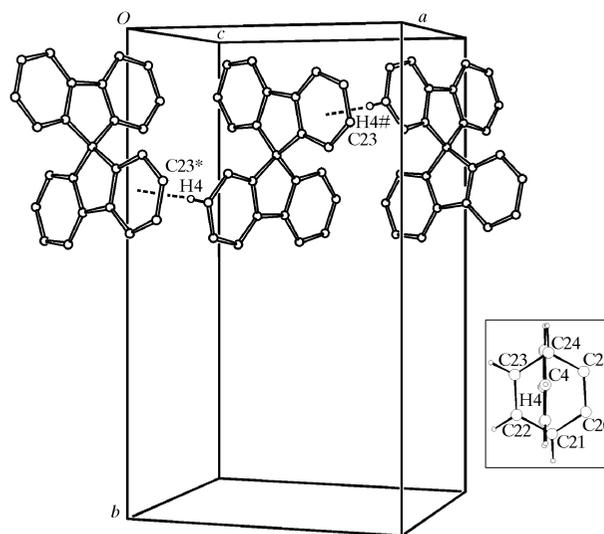
Figure 2
The hydrogen bonding in (I). Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ and $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, respectively. Inset: a view down the C4—H4 bond axis, showing the relative π-arene position.

tively, which exhibit a range of edge-to face C—H···π(arene) hydrogen bonds between the aromatic moieties.

The bond lengths and angles of the constituent molecules of (I)–(III) are not exceptional. Examination of the packing diagrams reveals structural motifs resulting from C—H···π(arene) interactions and, based on the C—H···A (A = acceptor) angles and H···A bond lengths, these are considered here as weak hydrogen bonds.

Compound (I) contains one molecule of SBF and one molecule of benzene in the asymmetric unit (Fig. 1). Hydrogen bonds are present between adjacent SBF molecules, resulting in an infinite chain motif (Fig. 2). The benzene molecules do not participate in any directional bonding, and there is no
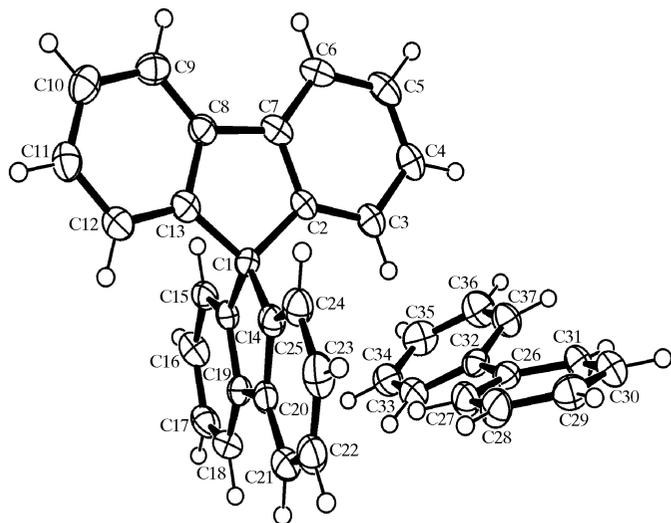
Figure 3
A view of the asymmetric unit of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids.
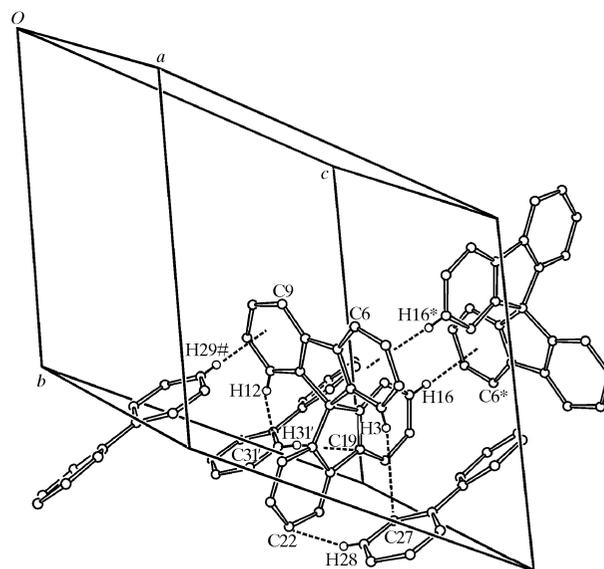
Figure 4
The hydrogen bonding in (II). Atoms marked with an asterisk (*), a hash (#) or a prime (′) are at the symmetry positions $(1 - x, 1 - y, 2 - z)$, $(1 - x, 2 - y, -z)$ and $(-1 + x, y, z)$, respectively.
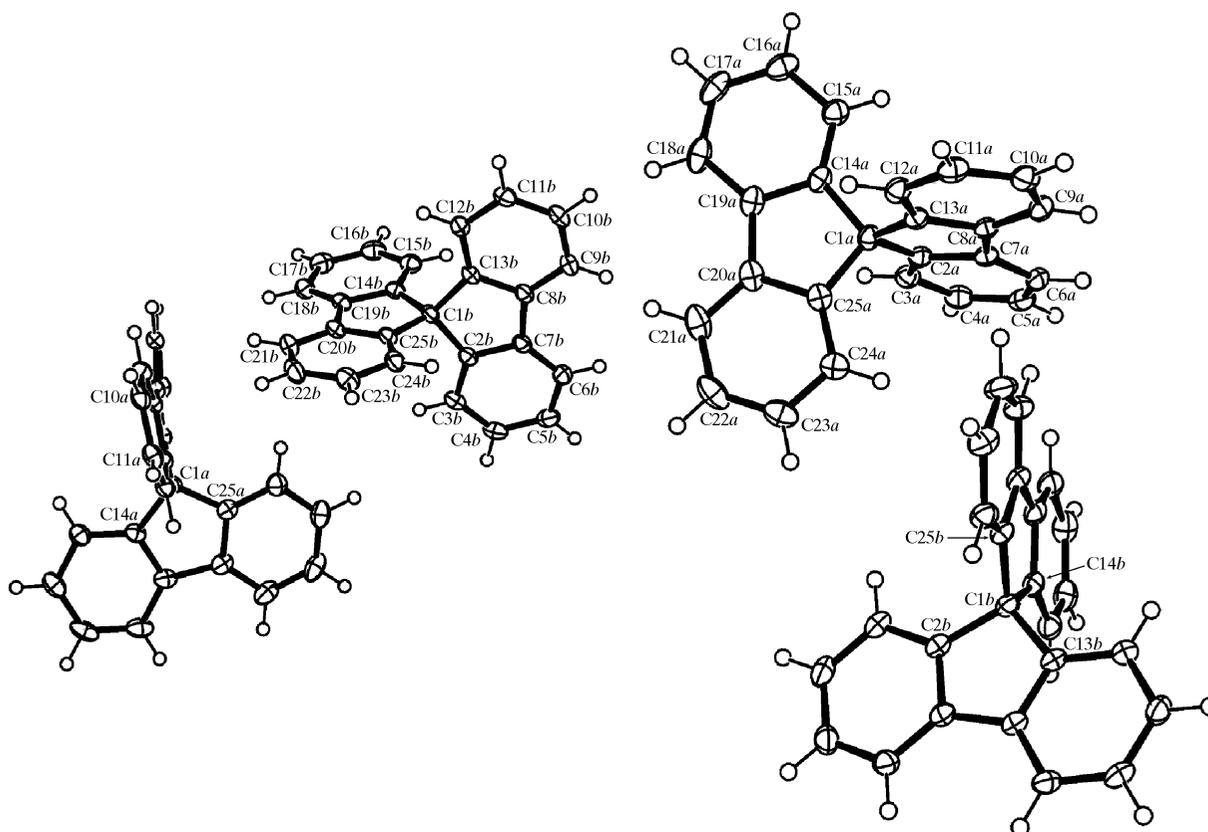
Figure 5
A view of the asymmetric unit of (III), showing both SBF moieties and the atom-numbering scheme, with 50% probability displacement ellipsoids.

directional bonding nor any short contacts between the chains. Hydrogen-bonding details are shown in Fig. 2, and the distance between atom H4 in the molecule at (x, y, z) and $Cg1$ (the centroid of the C20–C25 benzene ring) in the symmetry-related molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ is 2.67 Å (Table 1).

Compound (II) contains one molecule of SBF and one molecule of biphenyl in the asymmetric unit (Fig. 3) and exhibits several C—H$\cdots\pi$(arene) hydrogen-bonding motifs (Fig. 4), which collectively result in a layered structure with planes parallel to the (011) direction (Table 2). In contrast with (I), adjacent SBF molecules at (x, y, z) and $(1 - x, 1 - y, 2 - z)$ are connected via a pair of hydrogen bonds between atom H16 and the C2–C7 benzene ring (Fig. 4), with a H16$\cdots$Cg2 (ring centroid of the C2–C7 ring) distance of 2.65 Å. Biphenyl distance of molecules connect SBF pairs via a series of C—H$\cdots\pi$-arene interactions. Atom H29 in a biphenyl molecule at $(1 - x, 2 - y, 1 - z)$ interacts in an asymmetric hydrogen bond with the arene moiety C8–C13 (centroid $Cg3$) of an SBF molecule at (x, y, z). In addition, biphenyl–SBF hydrogen bonding is present between atoms H3 and C27 of an SBF molecule at (x, y, z), and atoms C22 and H28, respectively, of a biphenyl molecule at (x, y, z), connecting pairs of SBF molecules into a chain motif. The chains can then be interpreted as precursors to a layer in the [011] plane via interaction of SBF and biphenyl atoms.

Compound (III) contains two molecules of SBF in the asymmetric unit (Fig. 5), in contrast to a single molecule observed by Schenk (1971), which aggregates through very short intermolecular C—C distances (3.22, 3.35 and 3.45 Å) from edge–edge π-interactions between phenyl groups. The new polymorph, (III), does not exhibit short C—C contacts, but SBF molecules of (III) participate in C—H$\cdots\pi$ interac-

tions to give centrosymmetric SBF dimers (Fig. 6), with a H11A$\cdots$Cg4 distance of 2.59 Å [$Cg4$ is the centroid of the C20A–C25A ring at $(1 - x, -y, 1 - z)$; C11A—H11A = 0.95 Å, C11A$\cdots$Cg4 = 3.495 Å and C11A—H11A$\cdots$Cg4 = 160°]. Examination of the packing shows that layers of discrete SBF dimers are present parallel to the bc plane, separated by layers of SBF molecules that do not exhibit directional bonding (Fig. 6). In our study, all other solvent mixtures that we examined led to crystallization of the polymorph identified by Schenk (1971). This suggests that polymorph (III) is possibly metastable with respect to that described by Schenk (1971).
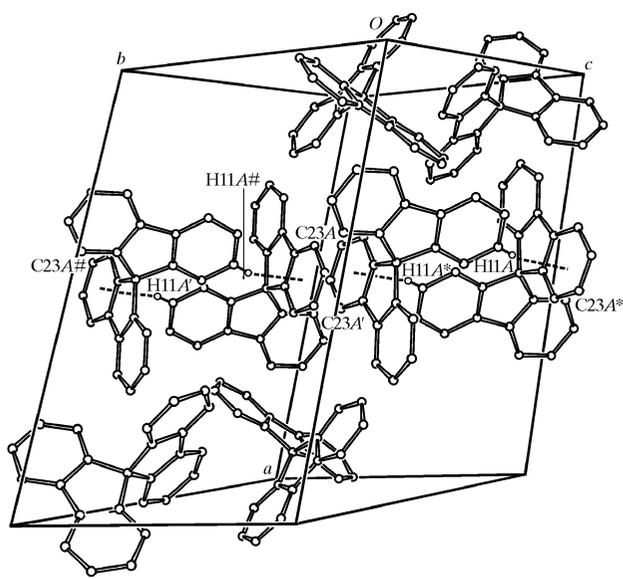
It is anticipated that the weak hydrogen-bonding motifs observed in compounds (I)–(III) are likely to be an important factor in determining the structures of molecular solids derived from SBF.

Experimental

Single crystals of (I)–(III) were grown by slow evaporation of SBF (20 mg) dissolved in benzene for (I), in pentane containing 1 equivalent of biphenyl for (II), and in a 1:1 mixture of hexafluorobenzene and dichloromethane for (III). All compounds melted in the range 470–473 K.

Compound (I)

Crystal data

$C_{25}H_{16}\cdot C_6H_6$	$D_x = 1.219$ Mg m^{-3}
$M_r = 394.49$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4471
$a = 10.7900$ (6) Å	reflections
$b = 18.4004$ (10) Å	$\theta = 2.2$–27.4°
$c = 10.8403$ (6) Å	$\mu = 0.07$ mm^{-1}
$\beta = 92.8770$ (10)°	$T = 115$ (2) K
$V = 2149.5$ (2) Å^3	Block, colourless
$Z = 4$	$0.2 \times 0.2 \times 0.2$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	4921 independent reflections
φ and ω scans	3949 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$R_{int} = 0.024$
	$\theta_{max} = 27.5°$
$T_{min} = 0.893, T_{max} = 0.990$	$h = -14 \rightarrow 13$
14 724 measured reflections	$k = -23 \rightarrow 23$
	$l = -14 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.056P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.5085P]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
4921 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
280 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
H-atom parameters constrained	

Figure 6
The hydrogen bonding in (III). Atoms marked with an asterisk (*), a hash (#) or a prime (') are at the symmetry positions $(1 - x, -y, 1 - z)$, $(x, 1 + y, z)$ and $(1 - x, 1 - y, 1 - z)$, respectively.

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$Cg1$ is the centroid of the C20–C25 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$\cdots$Cg1^i	0.95	2.67	3.61	172
C11—H11$\cdots$C16^{ii}	0.95	2.74	3.6196 (18)	154

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Compound (II)

Crystal data

$C_{25}H_{16} \cdot C_{12}H_{10}$
$M_r = 470.58$
Triclinic, $P\bar{1}$
$a = 9.774 (4)$ Å
$b = 11.427 (4)$ Å
$c = 13.075 (5)$ Å
$\alpha = 71.339 (8)°$
$\beta = 83.106 (9)°$
$\gamma = 67.030 (7)°$
$V = 1273.8 (8)$ Å^3

$Z = 2$
$D_x = 1.227$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 944
  reflections
$\theta = 2.4–24.2°$
$\mu = 0.07$ mm^{-1}
$T = 115 (2)$ K
Block, colourless
$0.14 \times 0.11 \times 0.04$ mm

Data collection

Bruker SMART CCD area detector
  diffractometer
φ and ω scans
Absorption correction: multi-scan
  (SADABS; Bruker, 2000)
  $T_{min} = 0.985$, $T_{max} = 0.998$
6971 measured reflections

4476 independent reflections
2416 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 25.1°$
$h = -11 \rightarrow 6$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.079$
$wR(F^2) = 0.248$
$S = 0.92$
4476 reflections
335 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2)]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: SHELXL97
Extinction coefficient: 0.022 (6)

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$Cg2$ is the centroid of the C2–C7 ring and $Cg3$ is the centroid of the C8–C13 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C16—H16$\cdots Cg2^i$	0.95	2.65	3.57	162
C29—H29$\cdots Cg3^{ii}$	0.95	2.63	3.56	163
C3—H3$\cdots$C27	0.95	2.80	3.692 (5)	157
C28—H28$\cdots$C22	0.95	2.84	3.658 (6)	147
C12—H12$\cdots$C31^{iii}	0.95	2.87	3.783 (5)	161
C31—H31$\cdots$C19^{iv}	0.95	2.80	3.708 (5)	159

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x + 1, -y + 2, -z$; (iii) $x - 1, y, z$; (iv) $x + 1, y, z$.

Compound (III)

Crystal data

$C_{25}H_{16}$
$M_r = 316.38$
Monoclinic, $P2_1/c$
$a = 18.2491 (17)$ Å
$b = 11.1522 (10)$ Å
$c = 18.6918 (17)$ Å
$\beta = 117.907 (2)°$
$V = 3361.7 (5)$ Å^3
$Z = 8$

$D_x = 1.250$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7135
  reflections
$\theta = 2.2–25.0°$
$\mu = 0.07$ mm^{-1}
$T = 115 (2)$ K
Block, colourless
$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector
  diffractometer
φ and ω scans
Absorption correction: multi-scan
  (SADABS; Bruker, 2000)
  $T_{min} = 0.970$, $T_{max} = 0.987$
18 394 measured reflections

5925 independent reflections
4923 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 25.0°$
$h = -16 \rightarrow 21$
$k = -13 \rightarrow 13$
$l = -22 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.119$
$S = 1.05$
5925 reflections
451 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.075P)^2$
  $+ 0.6111P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

H atoms were placed in calculated positions and treated as riding, with C—H distances of 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Compound (II) contains zero values in the weighting scheme, resulting from weak diffraction by this sample.

For all compounds, data collection: SMART (Bruker, 2000); cell refinement: SAINT-Plus (Bruker, 2000); data reduction: SAINT-Plus; structure solution: SHELXS97 (Sheldrick, 1997); structure refinement: SHELXL97 (Sheldrick, 1997); molecular graphics: CAMERON (Watkin et al., 1996); publication software: SHELXTL (Bruker, 2001).

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