Arene–perfluoroarene interactions in crystal engineering. 4.[1] Hexafluorobenzene–*trans*-stilbene (1/1)

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In the title complex, $C_6F_6 \cdot C_{14}H_{12}$, nearly parallel molecules of *trans*-stilbene and librationally disordered hexafluorobenzene form a mixed stack, with each molecule lying on an independent inversion centre. Adjacent stacks pack together in a herring-bone manner.

Comment

While studying arene–perfluoroarene interactions and their possible uses in crystal engineering (Dai *et al.*, 1999; Collings, Batsanov *et al.*, 2001; Collings, Roscoe *et al.*, 2001), we found that arenes and perfluoroarenes of widely mismatched geometry can be cocrystallized. *trans*-Stilbene (TSB) is known to form 1:1 complexes with matching perfluorinated species, *viz. trans*-decafluoroazobenzene–*trans*-stilbene (Bruce *et al.*, 1987) and *trans*-stilbene–*trans*-decafluorostilbene (Coates *et al.*, 1998). On the other hand, TSB forms complexes with electron acceptors of rather disparate geometry, *e.g.* 1:1 complexes with pyromellitic dianhydride (Kodama & Kumakura, 1974) or tetracyanoquinodimethane (Zobel & Ruban, 1983), and 1:2 complexes with 1,2,4,5-tetracyanobenzene (Agostini *et al.*, 1988) or 1,3,5-trinitrobenzene (Bar & Bernstein, 1978). All these are molecular complexes which exhibit no significant charge transfer, and, as most arene–perfluoroarene systems behave in the same way, we expected that TSB could also form complexes with geometrically mismatched perfluoroarenes.

Colourless crystals grown from hexafluorobenzene (HFB) proved to be the 1:1 complex HFB·TSB, (I). Both the TSB and HFB molecules have crystallographic C_i symmetry (Fig. 1). The TSB molecule shows no sign of disorder, unlike the structures of TSB itself (Bouwstra *et al.*, 1984) and most of its molecular complexes, which all display the same mode of

disorder, namely an overlap of two molecular positions, related by a 180° rotation around the $C1 \cdots C1'$ vector. In (I), the TSB molecule is slightly twisted and the planes of the phenyl ring and the olefinic moiety form a dihedral angle (φ) of 7.2 (7)°. Such a conformation is typical for both TSB and its molecular complexes, but contrasts drastically with the twisted conformation observed in the gas phase, where $<\varphi^2>^{1/2} = 31 (5)°$ (Traettenberg *et al.*, 1975). The bond distances in (I) agree with those in pure TSB at 113 K (Hoekstra *et al.*, 1975) or at room temperature, if proper account is taken of the disorder (Bouwstra *et al.*, 1984). Those studies of TSB where the disorder remained unresolved gave spuriously shortened central C=C bond distances (Finder *et al.*, 1974; Bernstein, 1975).

(I)
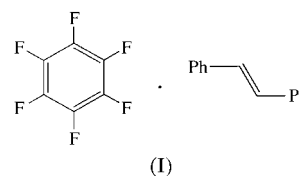
Notwithstanding the low temperature, the HFB molecule shows high atomic displacement parameters, suggesting librational disorder. Attempts to model the disorder by various superpositions of two or three different orientations resulted in unstable refinements if no constraints were applied, or (if severely constrained) converged at much higher R indices than the single-position model. The molecule is probably disordered within one wide flat-bottomed potential well, rather than between separate wells.

The crystal packing of (I) (Fig. 2) comprises mixed stair-like stacks parallel to the crystallographic a axis. Within each stack, the benzene rings of the HFB and TSB molecules are almost parallel [dihedral angle 3.4 (2)°] and overlap with an average interplanar separation of 3.45 (5) Å. Each HFB molecule is sandwiched between two parallel phenyl rings, and each phenyl ring is sandwiched between a parallel HFB molecule on one side and a phenyl ring inclined by 45.9 (2)° on the other. The latter phenyl ring belongs to a TSB molecule of an adjacent stack, related by the operation of a 2_1 screw axis.
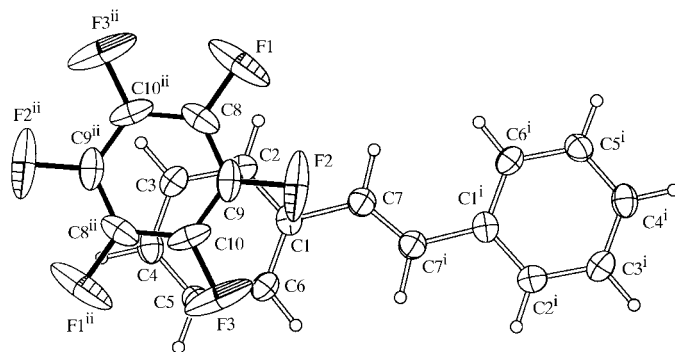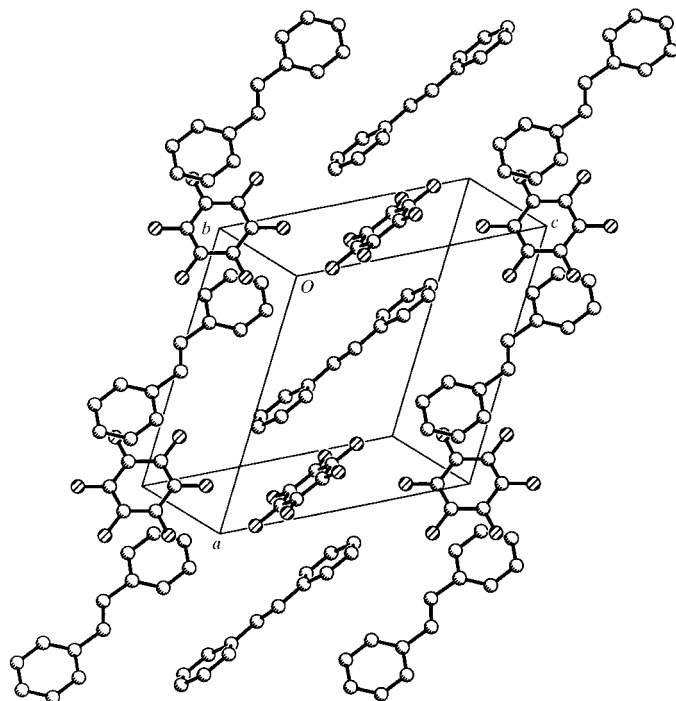

Figure 1
The molecules of HFB (solid bonds) and TSB (hollow bonds) in (I), projected onto their mean planes. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.]

These stacks run in the same direction but have different orientations of the molecular planes, making inter-stack dihedral angles of up to 50.9 (2)° (for HFB/HFB). Thus, the packing of (I) can be described as a combination of stacking

Figure 2
The crystal packing of (I), with H atoms omitted for clarity.

and herring-bone motifs, in contrast with pure HFB (Boden *et al.*, 1973) and pure TSB, both of which display a purely herring-bone packing, with all molecules making T-type (edge-to-face) contacts and with no stacking interactions.

The packing of (I) is relatively loose; the volume per HFB·TSB unit is larger by 3% than the sum of the molecular volumes in solid TSB at 113 K (249.5 $Å^3$; Hoekstra *et al.*, 1975) and in solid HFB at 120 K (147.3 $Å^3$; Boden *et al.*, 1973). Such loose packing may explain the disorder of the HFB molecule in (I).

Experimental

For the preparation of the title adduct, TSB (0.1 g) was dissolved in HFB (1 ml) with warming. Slow evaporation of the solution at room temperature yielded single crystals of (I).

Crystal data

$C_6F_6 \cdot C_{14}H_{12}$	$D_x = 1.488$ Mg m^{-3}
$M_r = 366.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 369
$a = 11.401$ (3) Å	reflections
$b = 6.118$ (2) Å	$\theta = 10.2–24.2°$
$c = 12.262$ (4) Å	$\mu = 0.13$ mm^{-1}
$\beta = 107.09$ (2)°	$T = 120$ (2) K
$V = 817.5$ (4) Å^3	Plate, colourless
$Z = 2$	$0.30 \times 0.30 \times 0.06$ mm

Data collection

SMART 1K CCD area-detector diffractometer	$R_{int} = 0.049$
	$\theta_{max} = 25.4°$
ω scans	$h = -13 \rightarrow 13$
4709 measured reflections	$k = -6 \rightarrow 7$
1501 independent reflections	$l = -14 \rightarrow 8$
1125 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.069P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.078$	$+ 2.177P]$
$wR(F^2) = 0.207$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
1501 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
142 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

C1—C7	1.490 (5)	C8—C10^{ii}	1.370 (7)
C7—C7^i	1.323 (8)	C9—F2	1.342 (5)
C8—F1	1.337 (5)	C9—C10	1.365 (6)
C8—C9	1.359 (7)	C10—F3	1.341 (5)
C2—C1—C6	118.3 (3)	C7^i—C7—C1	125.9 (5)

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

All H atoms were refined and the range of phenyl-ring C—H distances was 0.98 (5)–1.01 (5) Å and the C7—H distance was 1.07 (5) Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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