

4,4'-Di-*tert*-butyl-2,2'-bipyridine–hexafluorobenzene (1/1)Andrei S. Batsanov,*
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Key indicators

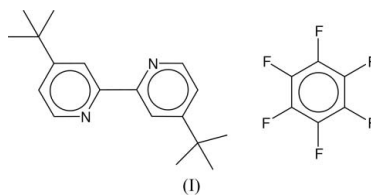
Single-crystal X-ray study
 $T = 120\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.045
 wR factor = 0.138
Data-to-parameter ratio = 13.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title structure, $\text{C}_{18}\text{H}_{24}\text{N}_2\cdot\text{C}_6\text{F}_6$, comprises mixed stacks of alternating 4,4'-di-*tert*-butyl-2,2'-bipyridine and hexafluorobenzene molecules, both lying on crystallographic mirror planes. There are weak $\text{C}-\text{H}\cdots\text{N}$ (2.46–2.51 Å) and $\text{C}-\text{H}\cdots\text{F}$ (2.52–2.74 Å) hydrogen bonds lying on the mirror planes, as well as π - π interactions between stacked aromatic molecules (as indicated by interplanar distances of 3.35 Å).

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actions in crystal engineering.
Part XVI. For Part XV, see
Batsanov *et al.* (2006).

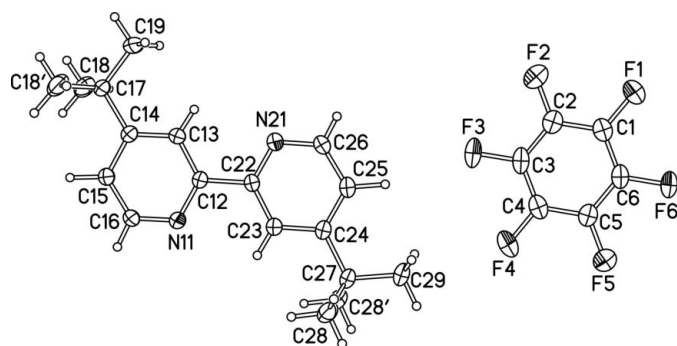
Comment

Numerous arenes and perfluoroarenes readily co-crystallize in a 1:1 stoichiometry with a mixed-stack packing motif (Patrick & Prosser, 1960; Dahl, 1988; Collings *et al.*, 2002). However, only three complexes of pyridine derivatives with perfluoroarenes have been reported to date. In 1:1 complexes of hexafluorobenzene (HFB) with 6-phenyl- or 6,6'-diphenyl derivatives of 4,4'-di-*tert*-butyl-2,2'-bipyridine, DTBPy (Mkhalid *et al.*, 2006), the HFB molecule is stacked with the phenyl substituent rather than with the bipyridine core of the DTBPy. In $Q\cdot 2.5\text{C}_6\text{F}_6$, where $Q = 5,10,15$ -{(1,3,5-triamido-mesitylene)-tris(*o*-phenylene)}-2-(2-pivaloylaminophenyl)porphyrin, $\text{C}_{61}\text{H}_{46}\text{N}_8\text{O}_4$ (Sleboznick *et al.*, 1996), an HFB molecule is in face-to-face contact with the porphyrin, at a distance of 3.21 Å, implying π - π interactions (Hunter & Sanders, 1990; Bacchi *et al.*, 2006), but no continuous stacks exist. Here, we report the title DTBPy·HFB complex, (I), which has infinite heteroarene/HFB mixed stacks.

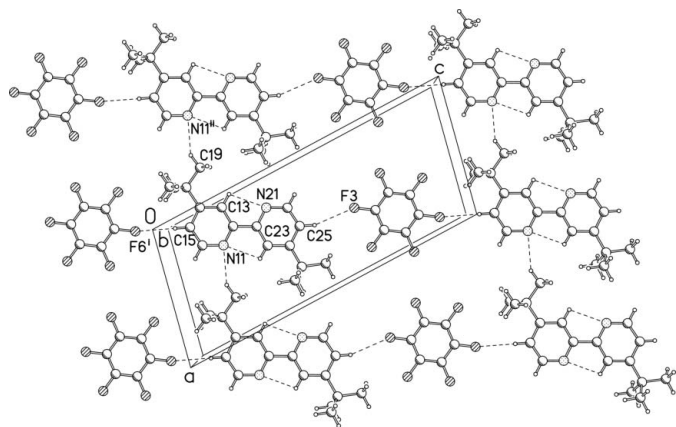


The entire HFB molecule of (I) (Fig. 1) lies on a crystallographic mirror plane (Wyckoff position e), as does the DTBPy molecule, except for the methyl groups $\text{C}18\text{H}_3$ and $\text{C}28\text{H}_3$ and their symmetry equivalents ($\text{C}18'\text{H}_3$ and $\text{C}28'\text{H}_3$ in Fig. 1), as well as two symmetry-related pairs of H atoms on atoms C19 and C29. The DTBPy molecule adopts a *trans* conformation around the central $\text{C}12-\text{C}22$ bond, as in 6-phenyl-DTBPy·HFB, which shows the same motif of alternating molecules lying on mirror planes, whereas in 6,6'-diphenyl-DTBPy·HFB, this unit is twisted by 19° from a perfect *trans* conformation (Mkhalid *et al.*, 2006).

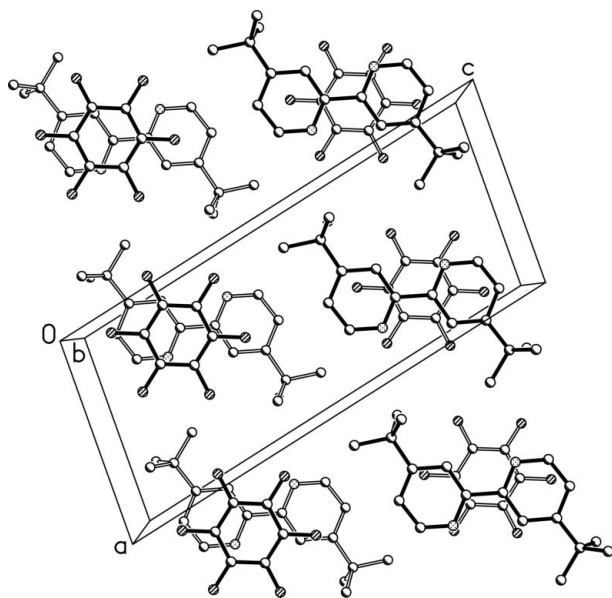
Table 1 lists the shortest intra- (lines 1 and 2) and intermolecular contacts (all located in the mirror plane; Fig. 2),

**Figure 1**

The molecular structure of HFB and DTBPy in (I), viewed down the *b* axis. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are related to unprimed atoms by $(x, \frac{3}{2} - y, z)$.

**Figure 2**

The molecular packing of (I) in the $(x, \frac{3}{4}, z)$ plane. [Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $x - 1, y, z$.]

**Figure 3**

The overlap between molecules of two adjacent layers. H atoms have been omitted for clarity.

which satisfy the definition of ‘weak hydrogen bonds’ as proposed by Taylor & Kennard (1982), Jeffrey (1997) or Desiraju & Steiner (1999). The low dissociation energy of the

shortest C15—H15...F6ⁱ interaction in (I) can be estimated by analogy with the C—H...F—C interactions in the gaseous CH₃·CH₃F complex (Caminati *et al.*, 2005), with similar H...F distances of 2.43 (1) Å. The dissociation energy in the latter compound is only 1.8 kJ mol⁻¹ per H...F link.

The overlap between adjacent layers in (I) is shown in Fig. 3, whereas in the perpendicular direction, [010], runs an infinite columnar (rather than slanted) stack of alternating rigorously parallel HFB and DTBPy molecules with a uniform interplanar separation of 3.35 Å (or *b*/2), which indicates π – π electron interaction between the aromatic rings (see above).

The structure of (I) shows pseudo-symmetry of space group *I2/m* (in the same setting), disturbed by the orientation of the *tert*-butyl groups in DTBPy and by small shifts of the molecular centroids (for HFB, $x = 0.7287$ and $z = 0.7694$; for DTBPy, $x = 0.2751$ and $z = 0.2658$) from the pseudo-*2/m* special positions ($x = z = \frac{3}{4}$ and $x = z = \frac{1}{4}$, respectively).

Experimental

Compound (I) was obtained by hydrolysis of the B—C bond during an attempt to recrystallize the borylation product 4,4′-di-*tert*-butyl-6-Bpin-2,2′-bipyridine (Bpin = BOCMe₂CMe₂O) from HFB solution, which was permitted to evaporate slowly at room temperature. Crystals of (I) were obtained as blocks of irregular shape (with rounded edges) of 0.1 to 0.3 mm in size.

Crystal data

C₁₈H₂₄N₂·C₆F₆
M_r = 454.45
 Monoclinic, *P*2₁/*m*
a = 8.5150 (7) Å
b = 6.6964 (5) Å
c = 19.2756 (18) Å
 β = 102.73 (1)°
V = 1072.08 (16) Å³

Z = 2
D_x = 1.408 Mg m⁻³
 Mo *K*α radiation
 μ = 0.12 mm⁻¹
T = 120 (2) K
 Block, colourless
 0.32 × 0.25 × 0.21 mm

Data collection

Bruker SMART 6K CCD area-
 detector diffractometer
 ω scans
 Absorption correction: none
 12337 measured reflections

2669 independent reflections
 1962 reflections with $I > 2\sigma(I)$
*R*_{int} = 0.047
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.045
wR (*F*²) = 0.138
S = 1.06
 2669 reflections
 193 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0836P)^2 + 0.0675P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$

Table 1

Geometry of C—H...N and C—H...F interactions (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C13—H13...N21	0.95	2.50	2.819 (2)	100
C23—H23...N11	0.95	2.46	2.793 (2)	100
C15—H15...F6 ⁱ	0.95	2.52	3.472 (2)	180
C25—H25...F3	0.95	2.74	3.649 (2)	160
C19—H19...N11 ⁱⁱ	0.98	2.51	3.388 (2)	149

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

All H atoms were observed in a difference Fourier map but were treated as riding in idealized positions, with bond lengths C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aryl H atoms and C–H = 0.98 Å for methyl groups, of which C18H₃ and C28H₃ were permitted to rotate around the C–C bonds and C19H₃ and C29H₃ had fixed orientations due to mirror symmetry. The H atoms of each methyl group were assigned the same $U_{\text{iso}}(\text{H})$ value, which was refined.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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