

## 2,3-5,6-Tetrafluoro-1,4-di-4-pyridylbenzene

Montserrat Ferrer,<sup>a</sup> Albert Gutiérrez,<sup>a</sup> Mounia Mounir,<sup>a</sup> Xavier Solans<sup>b</sup> and Mercè Font-Bardia<sup>b\*</sup>

<sup>a</sup>Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain, and <sup>b</sup>Departament de Cristal·lografia, Universitat de Barcelona, Martí i Franquès, sn, E-08028 Barcelona, Spain

Correspondence e-mail: xavier@geo.ub.es

## Key indicators

Single-crystal X-ray study  
T = 294 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
R factor = 0.059  
wR factor = 0.137  
Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

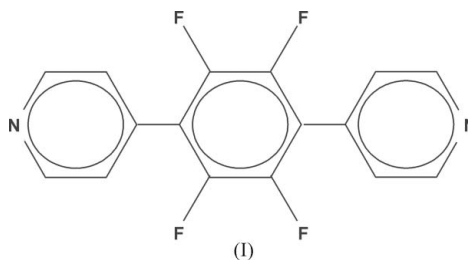
In the title centrosymmetric molecule,  $\text{C}_{16}\text{H}_8\text{F}_4\text{N}_2$ , the dihedral angle between the pyridine and benzene rings is  $50.47(5)^\circ$ , which is intermediate between those observed when the central ring is benzene and when it is an anthracene. The crystal structure consists of layers of molecules parallel to  $(20\bar{1})$ .

Received 28 June 2006

Accepted 30 June 2006

## Comment

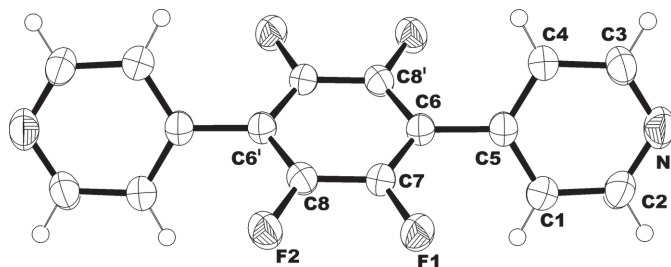
One of the most important targets in crystal engineering is the rational design and preparation of molecular architectures with desired topologies and functions. Dipyridyl ligands have been widely used as versatile building blocks or tectons to obtain a great variety of supramolecules, from coordination polymers to those involving non-covalent  $\pi$ - $\pi$  stacking or hydrogen-bond networks (Roesky & Andruh, 2003; Barnett & Champness, 2003).



Over the last five years we have been using the title compound, (I), as organic linker in self-assembly reactions with different  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  units in order to build molecular squares and/or triangles (Ferrer *et al.*, 2003). Given the difficulty in growing crystals of these supramolecular species, we decided to investigate the crystal structures of their building blocks in order to estimate the size of the generated cavity. The knowledge of this size will allow us to select the species with appropriate dimensions to establish host-guest interactions within the cavity.

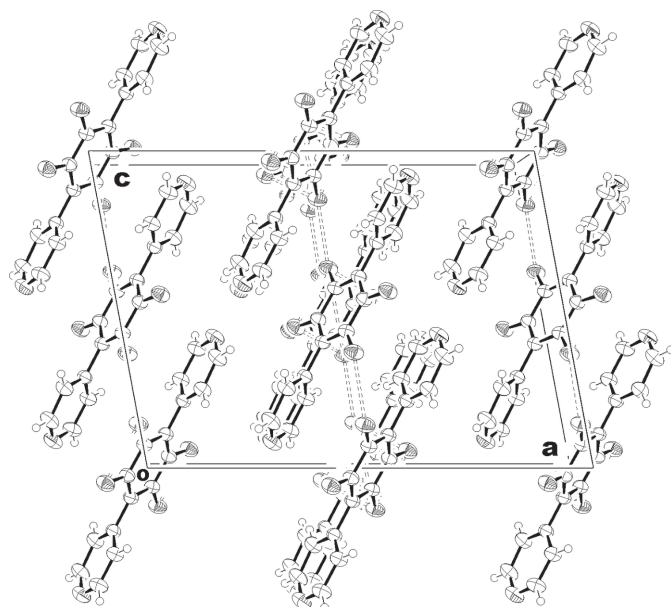
27 crystal structures with the 1,4-di-4-pyridylbenzene unit have been found in the Cambridge Structural Database (CSD, May 2006 version; Allen *et al.*, 2002). They can be classified in three groups: (i) structures with a central benzene ring and no substituents on the pyridyl groups, (ii) structures with a central benzene ring but with substituents in the 3- and/or 5- positions of the pyridyl group and (iii) structures with a central anthracene ring system. Compound (I) is the first structure with a central tetrafluorobenzene ring; there is a centre of inversion at the centre of the benzene ring.

The dihedral angle between the benzene ring and the pyridine ring is  $50.47(5)^\circ$ . This has a mean value of  $35(3)^\circ$  (range  $25.09$ – $47.59^\circ$ ) for the structures with benzene as the



**Figure 1**

A view of the molecular structure of (I), showing 50% probability displacement ellipsoids and the labelling of the non-H atoms. H atoms are drawn as small circles of arbitrary radius. Atoms labelled with a prime are generated by the symmetry operation  $(-x, 1 - y, -z)$ .



**Figure 2**

Packing of the molecules, showing short F...F contacts (dashed lines).

central ring and  $79(2)^\circ$  (range  $64.98\text{--}90^\circ$ ) for the structures with an anthracene ring system.

In the crystal structure, molecules are located in layers parallel to  $(20\bar{1})$ . Each benzene ring has as next neighbour in the adjacent layer a pyridyl ring, with a distance between ring centroids of  $3.869(3)\text{ \AA}$ . The shortest intermolecular F...F contacts,  $F1\cdots F1(-x, y, \frac{1}{2} - z) = 2.752(2)\text{ \AA}$  are observed between the layers and  $F1\cdots F2(-x, -y, -z)$  of  $2.849(3)\text{ \AA}$  (Fig.2) is found within the layer. 5756 F...F intermolecular distances in the range  $2.50\text{--}2.94\text{ \AA}$  ( $2.94\text{ \AA}$  = sum of van der Waals radii) have been found in the CSD.

## Experimental

Reactions and manipulations were performed under a prepurified  $N_2$  atmosphere using standard Schlenk techniques. Solvents (unless otherwise stated) and other chemicals were used as received. The synthesis of compound (I) was carried out according to a  $[PdCl_2(PPh_3)_2]/LiCl$ -promoted cross-coupling reaction (Fujita *et al.*, 1995) between 4-(trimethylstannyl)pyridine (Phillips & Herber, 1984) and 1,4-dibromotetrafluorobenzene.  $[PdCl_2(PPh_3)_2]$  (30.3 mg, 0.04 mmol) and LiCl (170 mg, 4 mmol) were added to a dry toluene

solution of 4-(trimethyltin)pyridine (314 mg, 1.29 mmol) and 1,4-dibromotetrafluorobenzene (133 mg, 0.43 mmol). After 72 h under reflux, the reaction mixture was treated with  $H_2O$  (50 ml). The organic phase was removed, and the aqueous layer was extracted with  $CH_2Cl_2$  ( $3 \times 40\text{ ml}$ ). The combined organic layers were dried ( $MgSO_4$ ) and concentrated under reduced pressure until a yellow precipitate was formed. The solid was purified by column chromatography on silica gel using first  $CH_2Cl_2$ , and subsequently  $CH_2Cl_2/CH_3OH$  (98:2) as eluent, giving compound (I) as a white solid (45% yield). Slow evaporation of a tetrahydrofuran solution of (I) yielded single crystals suitable for X-ray diffraction.

## Crystal data

$C_{16}H_8F_4N_2$	$Z = 4$
$M_r = 304.24$	$D_x = 1.639\text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.126(10)\text{ \AA}$	$\mu = 0.14\text{ mm}^{-1}$
$b = 5.919(5)\text{ \AA}$	$T = 294\text{ K}$
$c = 12.376(8)\text{ \AA}$	Prism, white
$\beta = 100.56(3)^\circ$	$0.3 \times 0.2 \times 0.1\text{ mm}$
$V = 1233.3(15)\text{ \AA}^3$	

## Data collection

Mar Research MAR345 image-plate diffractometer	1693 independent reflections
$\varphi$ scans	1473 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.026$
6143 measured reflections	$\theta_{max} = 30.0^\circ$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0816P)^2 + 0.0195P]$
$R[F^2 > 2\sigma(F^2)] = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.137$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.21$	$\Delta\rho_{max} = 0.49\text{ e \AA}^{-3}$
1693 reflections	$\Delta\rho_{min} = -0.42\text{ e \AA}^{-3}$
101 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: $0.014(3)$

H atoms were positioned geometrically and treated as riding atoms, with  $C\text{--}H = 0.93\text{ \AA}$  and  $U_{iso}(H) = 1.2U_{eq}(C)$ .

Data collection: *MARXDS* (Klein, 2000); cell refinement: *AUTOMAR* (Klein & Bartels, 2000); data reduction: *MARSCALE* (Klein, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2003); software used to prepare material for publication: *PLATON* (Spek, 2003).

## References

- Allen, F. H. (2002). *Acta Cryst B* **58**, 380–388.  
 Barnett, S. A. & Champness, N. R. (2003). *Coord. Chem. Rev.* **246**, 145–168.  
 Farrugia, L. G. (2003). *ORTEP-3 for Windows*. Version 1.075. University of Glasgow, Scotland.  
 Ferrer, M., Mounir, M., Rossell, O., Ruiz, E. & Maestro, M. A. (2003). *Inorg. Chem.* **42**, 5890–5899.  
 Fujita, M., Oka, H. & Ogura, K. (1995). *Tetrahedron Lett.* **36**, 5247–5250.  
 Klein, C. (1998). *MARSCALE*. Marresearch, Hamburg, Germany.  
 Klein, C. (2000). *MARXDS*. Marresearch, Hamburg, Germany.  
 Klein, C. & Bartels, K. (2000). *AUTOMAR*. X-Ray Research GmbH, Germany.  
 Phillips, J. E. & Herber, R. H. (1984). *J. Organomet. Chem.* **268**, 39–47.  
 Roesky, H. W. & Andruh, M. (2003). *Coord. Chem. Rev.* **236**, 91–119.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97* (release 97-2). University of Göttingen, Germany.  
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.