

4,4'-Bis(2,2,2-trifluoroethoxymethyl)-
2,2'-bipyridineNorman Lu,^{a*} Wen-Han Tu,^a Zong-Wei Wu,^a Yuh-Sheng
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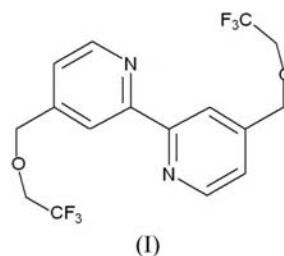
As part of a homologous series of novel polyfluorinated bipyridyl (bpy) ligands, the title compound, C₁₆H₁₄F₆N₂O₂, contains the smallest fluorinated group, *viz.* CF₃. The molecule resides on a crystallographic inversion centre at the mid-point of the pyridine C_{ipso}–C_{ipso} bond. Therefore, the bpy skeleton lies in an *anti* conformation to avoid repulsion between the two pyridyl N atoms. Weak intramolecular C–H···N and C–H···O interactions are observed, similar to those in related polyfluorinated bpy–metal complexes. A π – π interaction is observed between the bpy rings of adjacent molecules and this is probably a primary driving force in crystallization. Weak intermolecular C–H···N hydrogen bonding is present between one of the CF₃CH₂– methylene H atoms and a pyridyl N atom related by translation along the [010] direction, in addition to weak benzyl-type C–H···F interactions to atoms of the terminal CF₃ group. It is of note that the O–CH₂CF₃ bond is almost perpendicular to the bpy plane.

Comment

Bipyridine (bpy) is among the most versatile of ligands in organometallics. It has been used extensively to prepare a variety of chelating compounds with different metals (Haga *et al.*, 2000; Bain, Biebuyck & Whitesides, 1989; Vogelson *et al.*, 2003; Chambron & Sauvage, 1986, 1987). Structures with the motif [4,4'-bis(R_FCH₂OCH₂)-2,2'-bpy]MCl₂ (R_F = C_nF_{2n+1} or HC_nF_{2n}; n = 3 or 4; M = Pd or Pt) are interesting and unusual (Lu *et al.*, 2007; Lu, Tu, Wen *et al.*, 2010; Lu, Tu, Hou *et al.*, 2010). However, the X-ray crystal structures of polyfluorinated bpy compounds (Quici *et al.*, 1999) still remain elusive. We report here the structure of the title compound, (I), the simplest polyfluorinated compound in the series 4,4'-bis(R_FCH₂OCH₂)-2,2'-bpy.

Ruthenium polypyridine complexes have been of particular interest because of their special photophysical properties (Juris *et al.*, 1988; Kalyanasundaram, 1992). By systematically

varying the substituents on different positions of the bpy ring and/or the length of the substituents, one can tune the redox and spin properties. This possibility makes them attractive for use in applications such as dye-sensitized solar cells (DSSC; Grätzel, 2001), molecular electronics and catalysis. Compound (I) has been used to prepare novel fluorinated ruthenium complexes in order to tune the electron density and electrochemical properties at the metal centre (Lagref *et al.*, 2003; Chen *et al.*, 2006; Slattery *et al.*, 1994; Curtright & McCusker, 1999). Additionally, compounds derived from the alkylation of 4,4'-dimethyl-2,2'-bipyridine have also been tested for fungicidal activity against some plant diseases (Kelly-Basetti *et al.*, 1995).



Compound (I) exhibits a crystallographic inversion centre at the mid-point of the pyridine C_{ipso}–C_{ipso} bond and crystallizes in the space group *P*2₁/*n*. Many free bpy ligands described in the literature [Cambridge Structural Database (CSD; Allen, 2002) refcodes EDOXAW and EDOXEA (Maury *et al.*, 2001), FOBRUK and FOBSAR (Iyer *et al.*, 2005), KIDNAP (Vogtle *et al.*, 1990), MILZUC (Heitzler *et al.*, 2002), NAMKAN02 (Zhang *et al.*, 2003), NOFZUD (Sengül *et al.*, 1998), UHIBAO (Viau *et al.*, 2003), VEXQAQ (Spek *et al.*, 2000), VEXQAQ01 (Rice *et al.*, 2002) and VOLLAJ (Butler & Soucy-Breau, 1991)] also possess a crystallographic centre of inversion, two distinctive consequences of which are the planarity of the connected pyridyl units and their *anti* arrangement (Alborés *et al.*, 2004; Iyer *et al.*, 2005). The planar bpy C₁₀N₂ group in (I) has a weak N1···H3ⁱ–C3ⁱ interaction [symmetry code: (i) $-x + 1, -y + 1, -z + 1$], suggested by the N···H distance of 2.49 Å, although the angle

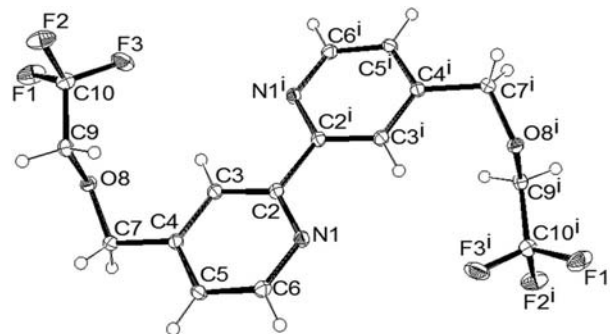


Figure 1

The molecular structure of (I), showing the atom-numbering scheme, displacement ellipsoids drawn at the 35% probability level and H atoms as small spheres of arbitrary radii. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

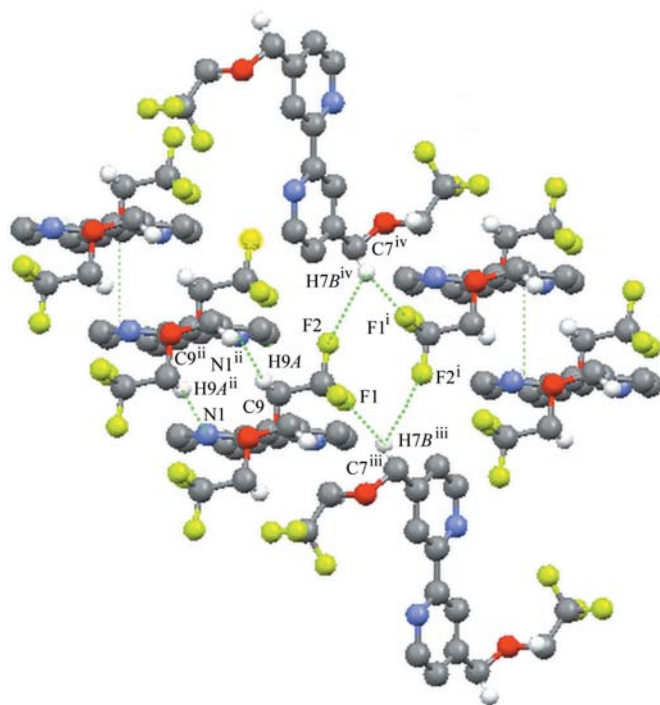


Figure 2

Weak C—H...N and C—H...F interactions involving methylene H atoms; other H atoms have been omitted for clarity. Additional molecules are drawn to highlight the nature of the π – π stacking (dashed lines). [Symmetry codes: (i) $1 - x, -y, 2 - z$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.]

is very acute at 100° . The two polyfluorinated side arms point to opposite sides of the bpy plane.

Fig. 1 shows the molecular structure of (I), which is the first reported example of a polyfluorinated bpy of this type. The special features are the polyfluorinated $\text{CF}_3\text{CH}_2\text{OCH}_2$ tails, with the C9—O8 bond almost perpendicular to the bpy plane [$85.6^\circ(1)$]; a side view is depicted in Fig. 2. There is a weak intramolecular C3—H3...O8 interaction present in the five-membered H3/C3/C4/C7/O8 system, which might provide some support to the vertical side arm. Similar to its metal-containing counterparts (Lu, Tu, Hou *et al.*, 2010), the C3—H3...O8 interaction shows structural parameters of a relatively small C3—C4—C7—O8 torsion angle of $-21.9(2)^\circ$, an H3...O8 distance of 2.52 \AA , shorter than the sum of the van der Waals radii of H and O atoms (2.77 \AA ; Howard *et al.*, 1996), although the C—H...O angle is again very acute at 100° .

The packing of (I) in the solid state is mainly governed by π – π stacking, with a spacing of $3.476(1) \text{ \AA}$ between the planes of the bpy rings of pairs of molecules related by translation along the *b* axis. The bpy ring planes are slanted with respect to the translation direction, so that the distance between the centroids of inversion-related rings in these pairs of molecules is $3.6850(9) \text{ \AA}$ and the slippage of these centroids is 1.22 \AA . Weak intermolecular C9—H9A...N1ⁱⁱ interactions are also found for the above-mentioned *b*-translation related pairs, with H9...N1 = 2.62 \AA . From Fig. 2 and Table 1, two weak

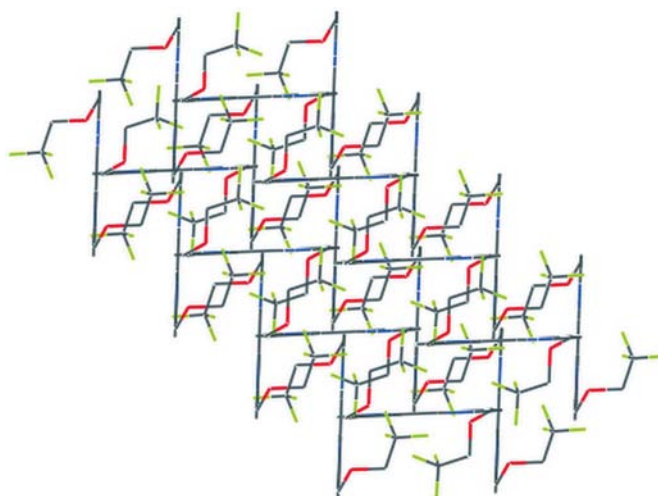


Figure 3

The orthogonal stacking of the bpy molecular planes.

benzyl-type (*i.e.* involving the benzyl CH_2 group and not a ring H atom) C—H...F interactions have been located that give support to the stacking in the crystalline state. These involve the terminal F atoms, with H...F distances of 2.49 and 2.67 \AA , respectively (see Table 1). The sum of the van der Waals radii of H and F atoms is 2.67 \AA (Howard *et al.*, 1996).

The molecules pack such that there are two sets of orientations of the planes of the π – π stacked bpy rings and these sets are almost orthogonal (Fig. 3); the two normals are at a dihedral angle of $85.7(1)^\circ$. The multiple supramolecular interconnections in (I) are consistent with its higher melting point of 356 K ($R_F = \text{C}_2\text{F}_5$, m.p. 313 K ; $R_F = \text{C}_3\text{F}_7$, m.p. 342 K).

In conclusion, one of the elusive polyfluorinated bpy compounds has been crystallized and structurally characterized, showing π – π stacking and weak C—H...F, C—H...O and C—H...N hydrogen-bonding interactions in the solid state.

Experimental

4,4'-Bis($\text{CF}_3\text{CH}_2\text{OCH}_2$)-2,2'-bpy, (I), was prepared according to the general procedure of Lu *et al.* (2007). The crude product was further purified by vacuum sublimation or column chromatography to obtain (I) as a colourless solid. Recrystallization proceeded with dissolution of (I) in dimethyl sulfoxide to form a saturated solution, to which a water overlayer (5 ml) was added. Solvent diffusion over a period of a week at 298 K afforded white needle-shaped crystals of (I).

Analytical data for (I): yield 86% , m.p. 356 K ; $^1\text{H NMR}$ (500 MHz, *d*-DMSO, room temperature): δ 8.68 (*d*, H₆, $^3J_{\text{HH}} = 5.0 \text{ Hz}$, 2H), 8.38 (*s*, H₃, 2H), 7.41 (*d*, H₅, $^3J_{\text{HH}} = 5.0 \text{ Hz}$, 2H), 4.83 (*s*, bpy-CH₂, 4H), 4.22 (*q*, $-\text{OCH}_2\text{CF}_3$, $^3J_{\text{HF}} = 9.2 \text{ Hz}$, 4H); $^{19}\text{F NMR}$ (470.5 MHz, *d*-DMSO, room temperature): δ -73.2 (*t*, $-\text{CH}_2\text{CF}_3$, $^3J_{\text{HF}} = 8.6 \text{ Hz}$, 6F); $^{13}\text{C NMR}$ (126 MHz, *d*-DMSO, room temperature): δ 155.2, 149.4, 147.6, 122.1, 118.3 (*s*, bpy, 10C), 124.5 (127.8–121.1, *q*, $-\text{CF}_3$, $^1J_{\text{CF}} = 280.4 \text{ Hz}$, 2C), 71.7 (*s*, bpy-CH₂, 2C), 67.1 (*q*, $-\text{CH}_2\text{CF}_3$, $^2J_{\text{CF}} = 32.3$, 2C); GC/MS (*M/e*): $M^+ = 380$, ($M - \text{C}_2\text{H}_3\text{F}_3\text{O}$)⁺ = 281, [$M - (\text{C}_2\text{H}_3\text{F}_3\text{O})_2$]⁺ = 182, ($M - \text{C}_2\text{H}_3\text{F}_3\text{OC}_6\text{H}_5\text{N}$)⁺ = 91; FT-IR (cm^{-1}): 1603, 1560, 1440 (bpy-ring, *m*), 1178, 1153 (CF_2 stretch, *s*).

Crystal data

$C_{16}H_{14}F_6N_2O_2$	$V = 782.91 (9) \text{ \AA}^3$
$M_r = 380.29$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 12.9726 (9) \text{ \AA}$	$\mu = 0.16 \text{ mm}^{-1}$
$b = 4.7485 (3) \text{ \AA}$	$T = 100 \text{ K}$
$c = 14.1782 (10) \text{ \AA}$	$0.28 \times 0.2 \times 0.18 \text{ mm}$
$\beta = 116.309 (3)^\circ$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	5975 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1587 independent reflections
$T_{\min} = 0.692$, $T_{\max} = 0.745$	1332 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	119 parameters
$wR(F^2) = 0.082$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
1587 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

All H atoms were generated geometrically, with C—H = 0.93 Å for CH groups on bpy and 0.97 Å for CH₂ groups on side chains, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT (Bruker, 2001); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3229). Services for accessing these data are described at the back of the journal.

References

- Alborés, P., Baraldo, L. M., Ibañez, A. & Baggio, R. (2004). *Acta Cryst.* **C60**, o850–o852.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Bain, C. D., Biebuyck, H. A. & Whitesides, G. M. (1989). *Langmuir*, **5**, 723–727.
- Bruker (2001). SAINT and SMART. Bruker AXS Inc., Madison, Wisconsin, USA.
- Butler, I. R. & Soucy-Breau, C. (1991). *Can. J. Chem.* **69**, 1117–1123.
- Chambron, J.-C. & Sauvage, J.-P. (1986). *Tetrahedron Lett.* **27**, 865–868.
- Chambron, J.-C. & Sauvage, J.-P. (1987). *Tetrahedron*, **43**, 895–904.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	D—H	H···A	$D \cdots A$	$D-H \cdots A$
C9—H9A···N1 ⁱⁱ	0.97	2.62	3.573 (2)	166
C7—H7B···F1 ⁱⁱⁱ	0.97	2.49	3.116 (2)	122
C7—H7B···F2 ^{iv}	0.97	2.67	3.328 (2)	126

Symmetry codes: (ii) $-x + 1, -y, -z + 1$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x - \frac{1}{2}, -y - \frac{1}{2}, z - \frac{1}{2}$.

- Chen, C. Y., Wu, S. J., Wu, C. G., Chen, J. G. & Ho, K. C. (2006). *Angew. Chem. Int. Ed.* **45**, 5822–5825.
- Curtright, A. E. & McCusker, J. K. (1999). *J. Phys. Chem. A*, **103**, 7032–7041.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Grätzel, M. (2001). *Nature (London)*, **414**, 338–344.
- Haga, M., Hong, H., Shiozawa, Y., Kawata, Y., Monjushiro, H., Fukuo, T. & Arakawa, R. (2000). *Inorg. Chem.* **39**, 4566–4573.
- Heirtzler, F., Neuburger, M. & Kulike, K. (2002). *J. Chem. Soc. Perkin Trans. 1*, pp. 809–820.
- Howard, J. A. K., Hoy, V. J., O'Hagan, D. & Smith, G. T. (1996). *Tetrahedron*, **52**, 12613–12622.
- Iyer, V. M., Stoeckli-Evans, H., D'Aléo, A., Cola, L. D. & Belsler, P. (2005). *Acta Cryst.* **C61**, o259–o261.
- Juris, A., Balzani, V., Barigelletti, F., Campagna, S., Belsler, P. & Von Zelewsky, A. (1988). *Coord. Chem. Rev.* **84**, 85–277.
- Kalyanasundaram, K. (1992). *Photochemistry of Polypyridine and Porphyrin Complexes*. London: Academic Press.
- Kelly-Basetti, B. M., Cundy, D. J., Pereira, S. M., Sasse, W. H. F., Savage, G. P. & Simpson, G. W. (1995). *Bioorg. Med. Chem. Lett.* **5**, 2989–2992.
- Lagref, J. J., Nazeeruddin, M. K. & Grätzel, M. (2003). *Synth. Met.* **138**, 333–339.
- Lu, N., Lin, Y. C., Chen, J. Y., Chen, T. C., Chen, S. C., Wen, Y. S. & Liu, L. K. (2007). *Polyhedron*, **26**, 3045–3053.
- Lu, N., Tu, W. H., Hou, H. C., Lin, C. T., Li, C. K. & Liu, L. K. (2010). *Polyhedron*, **29**, 1123–1129.
- Lu, N., Tu, W. H., Wen, Y. S., Liu, L. K., Chou, C. Y. & Jiang, J. C. (2010). *CrystEngComm*, **26**, 538–542.
- Maury, O., Guegan, J.-P., Renouard, T., Hilton, A., Dupau, P., Sandon, N., Toupet, L. & Le Bozec, H. (2001). *New J. Chem.* **25**, 1553–1566.
- Quici, S. M., Cavazzini, M., Ceragioli, S., Montanari, F. & Pozzi, G. (1999). *Tetrahedron Lett.* **40**, 3647–3650.
- Rice, C. R., Onions, S., Vidal, N., Wallis, J. D., Senna, M.-C., Pilkington, M. & Stoeckli-Evans, H. (2002). *Eur. J. Inorg. Chem.* **8**, 1985–1997.
- Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Slattery, S. J., Gokaldas, N., Mick, T. & Goldsby, K. A. (1994). *Inorg. Chem.* **33**, 3621–3624.
- Spek, A. L., Lakin, M. T., Palmans, A. & Meijer, E. W. (2000). Private communication (refcode: VEXQAQ). CCDC, Cambridge, England.
- Sengül, A., Hursthouse, M. B., Coles, S. J. & Gillard, R. D. (1998). *Acta Cryst.* **C54**, 661–662.
- Viau, L., Senechal, K., Maury, O., Guegan, J.-P., Dupau, P., Toupet, L. & Le Bozec, H. (2003). *Synthesis*, **4**, 577–583.
- Vogelsson, C. T., Keys, A., Edwards, C. L. & Barron, A. R. (2003). *J. Mater. Chem.* **13**, 291–296.
- Vogtle, F., Hochberg, R., Kochendorfer, F., Windscheif, P.-M., Volkmann, M. & Jansen, M. (1990). *Chem. Ber.* **123**, 2181–2185.
- Zhang, Y. A. W., Maverick, A. W. & Fronczek, F. R. (2003). Private communication (refcode: NAMKAN02). CCDC, Cambridge, England.