

2,2-Difluoro-4-phenyl-1,3,2-dioxaborolo[4,5-c]chromen-5-ium-2-ide

Michał Wera,^a Alexander D. Roshal^b and Jerzy Błażejowski^{a*}

^aFaculty of Chemistry, University of Gdańsk, J. Sobieskiego 18, 80-952 Gdańsk, Poland, and ^bInstitute of Chemistry, V.N. Karazin National University, Svobody 4, 61077 Kharkiv, Ukraine

Correspondence e-mail: bla@chem.univ.gda.pl

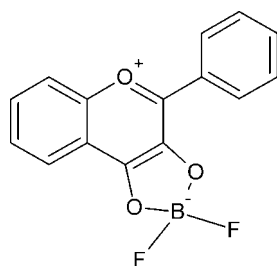
Received 19 November 2010; accepted 23 November 2010

Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.058; wR factor = 0.234; data-to-parameter ratio = 11.7.

In the crystal, the inversely oriented molecules of the title compound, $\text{C}_{15}\text{H}_9\text{BF}_2\text{O}_3$, form stacks along the a axis via $\pi-\pi$ interactions between parallel phenylchromenium fragments. Linked by a network of $\text{C}-\text{H}\cdots\text{F}$ interactions, the stacks form layers in the ac plane that are dispersively stabilized in the crystal structure. Two F atoms bonded to the B atom are located in the plane perpendicular to the planar skeleton of the molecule made rigid by two intramolecular $\text{C}-\text{H}\cdots\text{O}$ interactions.

Related literature

For general background to 3-hydroxy-2-phenyl-4*H*-chromene-4-one (flavonol) and its derivatives, see: Kukhareenko & Avramenko (2001); Petković *et al.* (2010); Roshal *et al.* (1998, 2003); Sytnik *et al.* (1994). For related structures, see: Belogh-Hergovich *et al.* (1999); Farina *et al.* (1995); Kaizer *et al.* (2007); Okabe *et al.* (2003). For intermolecular interactions, see: Choudhury & Guru Row (2004); Hunter *et al.* (2001); Novoa *et al.* (2006); Thalladi *et al.* (1998). For the synthesis, see: Roshal *et al.* (2002).



Experimental

Crystal data

$\text{C}_{15}\text{H}_9\text{BF}_2\text{O}_3$	$\gamma = 71.296$ (11) $^\circ$
$M_r = 286.03$	$V = 627.43$ (15) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.1969$ (10) Å	Mo $K\alpha$ radiation
$b = 9.7054$ (11) Å	$\mu = 0.12$ mm ⁻¹
$c = 9.9986$ (15) Å	$T = 295$ K
$\alpha = 74.310$ (11) $^\circ$	$0.6 \times 0.02 \times 0.02$ mm
$\beta = 75.931$ (13) $^\circ$	

Data collection

Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer	4848 measured reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008)	2218 independent reflections
$T_{\min} = 0.945$, $T_{\max} = 0.979$	996 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	190 parameters
$wR(F^2) = 0.234$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{\max} = 0.22$ e Å ⁻³
2218 reflections	$\Delta\rho_{\min} = -0.24$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}2-\text{H}2\cdots\text{O}3$	0.93	2.37	2.700 (6)	100
$\text{C}6-\text{H}6\cdots\text{O}1$	0.93	2.29	2.967 (6)	129
$\text{C}11-\text{H}11\cdots\text{F}1^i$	0.93	2.44	3.373 (6)	177

Symmetry code: (i) $-x + 1, -y, -z$.

Table 2

$\pi-\pi$ interactions (Å, $^\circ$).

$\text{Cg}1$, $\text{Cg}2$ and $\text{Cg}3$ are the centroids of the $\text{O}3/\text{C}7-\text{C}10/\text{C}15$, $\text{C}10-\text{C}15$ and $\text{C}1-\text{C}6$ rings, respectively. $\text{Cg}I\cdots\text{Cg}J$ is the distance between ring centroids. The dihedral angle is that between the planes of the rings I and J . $\text{Cg}I_{\text{Perp}}$ is the perpendicular distance of $\text{Cg}I$ from ring J . $\text{Cg}I_{\text{Offset}}$ is the distance between $\text{Cg}I$ and the perpendicular projection of $\text{Cg}J$ on ring I .

I	J	$\text{Cg}I\cdots\text{Cg}J$	Dihedral angle	$\text{Cg}I_{\text{Perp}}$	$\text{Cg}I_{\text{Offset}}$
1	1 ⁱⁱ	3.512 (3)	0	3.344 (2)	1.076 (2)
1	3 ⁱⁱⁱ	3.572 (3)	2.3 (3)	3.450 (2)	0.956 (2)
2	3 ⁱⁱ	3.970 (3)	4.3 (3)	3.342 (2)	2.143 (2)
2	3 ⁱⁱⁱ	3.925 (3)	4.3 (3)	3.472 (2)	1.831 (2)
3	1 ⁱⁱⁱ	3.571 (3)	2.3 (3)	3.428 (2)	1.000 (2)
3	2 ⁱⁱ	3.970 (3)	4.3 (3)	3.492 (2)	1.889 (2)
3	2 ⁱⁱⁱ	3.925 (3)	4.3 (3)	3.404 (2)	1.954 (2)

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

Data collection: CrysAlis CCD (Oxford Diffraction, 2008); cell refinement: CrysAlis RED (Oxford Diffraction, 2008); data reduction: CrysAlis RED; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

This study was financed by the State Funds for Scientific Research (grant DS/8220-4-0087-0).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5071).

References

- Belogh-Hergovich, E., Kaizer, J., Speier, G., Argay, G. & Párkányi, L. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3847–3854.
- Choudhury, A. R. & Guru Row, T. N. (2004). *Cryst. Growth Des.* **4**, 47–52.
- Farina, Y., Yamin, B. M., Fun, H.-K., Yip, B.-C. & Teoh, S.-G. (1995). *Acta Cryst.* **C51**, 1537–1540.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hunter, C. A., Lawson, K. R., Perkins, J. & Urch, C. J. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 651–669.
- Kaizer, J., Barath, G., Pap, J., Speier, G., Giorgi, M. & Reglier, M. (2007). *Chem. Commun.* pp. 5235–5237.
- Kukhareenko, A. V. & Avramenko, G. V. (2001). *Russ. J. Gen. Chem.* **71**, 1562–1564.
- Novoa, J. J., Mota, F. & D’Oria, E. (2006). *Hydrogen Bonding – New Insights*, edited by S. Grabowski, pp. 193–244. The Netherlands: Springer.
- Okabe, N., Yamamoto, E. & Yasunori, M. (2003). *Acta Cryst.* **E59**, m715–m716.
- Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.
- Petković, M., Petrović, B., Savić, J., Bugarčić, Ž. D., Dimitrić-Marković, J., Momić, T. & Vasić, V. (2010). *Int. J. Mass Spectrom.* **290**, 39–46.
- Roshal, A. D., Grigorovich, A. V., Doroshenko, A. O., Pivovarenko, V. G. & Demchenko, A. P. (1998). *J. Phys. Chem. A*, **102**, 5907–5914.
- Roshal, A. D., Munoz, A., Sakhno, T. V. & Boisdon, M.-T. (2002). *Chem. Heterocycl. Compd.* **11**, 1597–1604.
- Roshal, A. D., Sakhno, T. V., Verezubova, A. A., Ptiagina, L. M., Musatov, V. I., Wróblewska, A. & Błażejowski, J. (2003). *Funct. Mater.* **10**, 419–426.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Sytnik, A., Gormin, D. & Kasha, M. (1994). *Proc. Natl Acad. Sci. USA*, **91**, 11968–11972.
- Thalladi, V. R., Weiss, H.-C., Bläser, D., Boese, R., Nangia, A. & Desiraju, G. R. (1998). *J. Am. Chem. Soc.* **120**, 8702–8710.

supplementary materials

Acta Cryst. (2010). E66, o3354–o3355 [doi:10.1107/S1600536810048919]

2,2-Difluoro-4-phenyl-1,3,2-dioxaborolo[4,5-*c*]chromen-5-ium-2-ide

M. Wera, A. D. Roshal and J. Blazejowski

Comment

3-Hydroxy-2-phenyl-4*H*-chromene-4-one (flavonol) and its derivatives have been investigated for a long time owing to their unique spectral properties emerging from the excited state intramolecular proton transfer occurring in them (Sytnik *et al.*, 1994). These compounds turned out to be convenient analytical probes because of their considerable ability to complex various chemical entities (molecules, ions) (Roshal *et al.*, 1998; Roshal *et al.*, 2003; Petković *et al.*, 2010). The latter property was the reason for turning our attention to the possibility of applying of flavonol as an analytical spectral probe for boron compounds (Roshal *et al.*, 2002). As part of these investigations we wanted to see how flavonol behaved in the presence of BF₃. Thus we mixed both reagents in dichloromethane, expecting to obtain a molecular complex of flavonol and BF₃. The structure of the crystalline product that was actually separated is presented here. It appears that not complexation but condensation of the two reagents, accompanied by the release of HF, takes place (Kukharenko & Avramenko, 2001) and a molecule of a formally zwitterionic canonical structure was produced. Crystal structures of various flavonol complexes have so far been reported (Farina & Yamin, 1995; Belogh-Hergovich *et al.*, 1999; Okabe *et al.*, 2003; Kaizer *et al.*, 2007), but none of them have contained boron.

The canonical structure of the title compound suggests that the phenylchromenium core of the molecule is aromatic. This is confirmed by analysis of the bond lengths and angles, as well as comparison of the structure determined here with the structures of selected compounds containing flavonol units (Farina *et al.*, 1995; Belogh-Hergovich *et al.*, 1999; Okabe *et al.*, 2003; Kaizer *et al.*, 2007). Furthermore, the average deviation from planarity of the phenylchromenium core is 0.0215 (2) and that of the molecule's skeleton is 0.0373 (2). This implies that both the above-mentioned molecular fragments are planar and that two F atoms at the B atom are located in a plane perpendicular to the molecular one (the dihedral angle between the plane of the molecule's skeleton and the plane of B1–F1–F2 is 89.5 (1)°). Furthermore, two intramolecular C–H···O interactions (Table 1, Fig. 1) stiffen the phenylchromenium core, undoubtedly contributing to its planarity.

In the crystal structure, inversely oriented molecules form stacks along the *a* axis *via* π - π interactions between parallel phenylchromenium fragments (Table 2, Figs. 2 and 3). These stacks are linked by a network of C–H···F interactions arranged in layers in the *ac* plane (Table 1, Figs. 2 and 3). The above-mentioned layers are dispersively stabilized in the crystal lattice. The C–H···O (Novoa *et al.*, 2006) and C–H···F (Thalladi *et al.* (1998); Choudhury & Guru Row (2004)) interactions are of the hydrogen bond type. Like the π - π contacts, they are of an attractive nature (Hunter *et al.*, 2001).

Experimental

The title compound was obtained during the reaction of 3-hydroxy-2-phenyl-4*H*-chromene-4-one (flavonol) with BF₃ (Roshal *et al.*, 2002). Thus, boron trifluoride dissolved in anhydrous diethyl ether was added dropwise, with continuous stirring, to an equimolar amount of a saturated solution of flavonol in anhydrous dichloromethane. After evaporation of the solvents, the residue was recrystallized twice from *N,N*-dimethylformamide yielding yellow fluorescing crystals suitable for X-Ray investigations (m.p. 485 - 487 K).

Refinement

H atoms were positioned geometrically, with C—H = 0.93 Å, and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

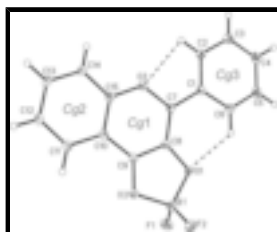


Fig. 1. The molecular structure of the title compound showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 25% probability level, and H atoms are shown as small spheres of arbitrary radius. Cg1, Cg2 and Cg3 denote the ring centroids. The C—H···O hydrogen bonds are represented by dashed lines.

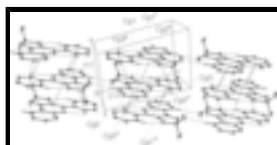


Fig. 2. The arrangement of the molecules in the crystal structure. The C—H···O and C—H···F interactions are represented by dashed lines, the π – π contacts by dotted lines. H atoms not involved in interactions have been omitted. [Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x, -y, -z + 1$.]

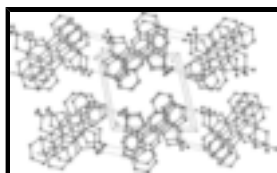


Fig. 3. Molecular stacks in the crystal structure, viewed along the a axis. The C—H···F interactions are represented by dashed lines. H atoms not involved in interactions have been omitted.

2,2-Difluoro-4-phenyl-1,3,2-dioxaborolo[4,5-c]chromen-5-ium-2-ide

Crystal data

$\text{C}_{15}\text{H}_9\text{BF}_2\text{O}_3$	$Z = 2$
$M_r = 286.03$	$F(000) = 292$
Triclinic, $P\bar{1}$	$D_x = 1.514 \text{ Mg m}^{-3}$
Hall symbol: $-P 1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 7.1969 (10) \text{ \AA}$	Cell parameters from 2218 reflections
$b = 9.7054 (11) \text{ \AA}$	$\theta = 3.0\text{--}25.1^\circ$
$c = 9.9986 (15) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$\alpha = 74.310 (11)^\circ$	$T = 295 \text{ K}$
$\beta = 75.931 (13)^\circ$	Needle, yellow
$\gamma = 71.296 (11)^\circ$	$0.6 \times 0.02 \times 0.02 \text{ mm}$
$V = 627.43 (15) \text{ \AA}^3$	

Data collection

Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer	2218 independent reflections
Radiation source: Enhance (Mo) X-ray Source	996 reflections with $I > 2\sigma(I)$

graphite $R_{\text{int}} = 0.034$
 Detector resolution: 10.4002 pixels mm⁻¹ $\theta_{\text{max}} = 25.1^\circ$, $\theta_{\text{min}} = 3.0^\circ$
 ω scans $h = -8 \rightarrow 8$
 Absorption correction: multi-scan $k = -10 \rightarrow 11$
 (*CrysAlis RED*; Oxford Diffraction, 2008)
 $T_{\text{min}} = 0.945$, $T_{\text{max}} = 0.979$ $l = -9 \rightarrow 11$
 4848 measured reflections

Refinement

Refinement on F^2 Primary atom site location: structure-invariant direct methods
 Least-squares matrix: full Secondary atom site location: difference Fourier map
 $R[F^2 > 2\sigma(F^2)] = 0.058$ Hydrogen site location: inferred from neighbouring sites
 $wR(F^2) = 0.234$ H-atom parameters constrained
 $S = 1.10$ $w = 1/[\sigma^2(F_o^2) + (0.0787P)^2 + 0.4107P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 2218 reflections $(\Delta/\sigma)_{\text{max}} < 0.001$
 190 parameters $\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{\AA}^{-3}$
 0 restraints $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
B1	0.4867 (13)	-0.1835 (7)	0.2184 (8)	0.075 (2)
O1	0.3873 (5)	-0.2005 (3)	0.3680 (3)	0.0605 (10)
C1	0.1714 (6)	-0.1185 (5)	0.6585 (5)	0.0395 (11)
F1	0.3869 (6)	-0.2186 (4)	0.1401 (3)	0.1025 (14)
O2	0.4773 (5)	-0.0183 (3)	0.1743 (3)	0.0594 (10)
C2	0.0722 (8)	-0.0564 (6)	0.7748 (5)	0.0600 (15)
H2	0.0499	0.0447	0.7694	0.072*
F2	0.6830 (6)	-0.2651 (4)	0.2068 (4)	0.1059 (14)
O3	0.2079 (5)	0.1167 (3)	0.5341 (3)	0.0480 (9)
C3	0.0071 (9)	-0.1459 (6)	0.8983 (6)	0.0680 (16)
H3	-0.0595	-0.1045	0.9764	0.082*

supplementary materials

C4	0.0389 (8)	-0.2934 (6)	0.9077 (6)	0.0628 (15)
H4	-0.0061	-0.3521	0.9919	0.075*
C5	0.1364 (8)	-0.3559 (6)	0.7946 (6)	0.0601 (15)
H5	0.1595	-0.4574	0.8022	0.072*
C6	0.2010 (7)	-0.2690 (5)	0.6686 (6)	0.0535 (13)
H6	0.2643	-0.3114	0.5907	0.064*
C7	0.2432 (6)	-0.0265 (5)	0.5263 (5)	0.0408 (11)
C8	0.3379 (7)	-0.0667 (5)	0.3996 (5)	0.0436 (12)
C9	0.3902 (7)	0.0404 (5)	0.2829 (5)	0.0453 (12)
C10	0.3501 (7)	0.1903 (5)	0.2890 (5)	0.0414 (11)
C11	0.3933 (7)	0.3038 (5)	0.1770 (5)	0.0549 (14)
H11	0.4525	0.2835	0.0882	0.066*
C12	0.3484 (8)	0.4446 (6)	0.1983 (6)	0.0587 (14)
H12	0.3739	0.5212	0.1237	0.070*
C13	0.2639 (8)	0.4731 (5)	0.3325 (6)	0.0601 (15)
H13	0.2371	0.5689	0.3466	0.072*
C14	0.2191 (7)	0.3639 (5)	0.4443 (6)	0.0566 (14)
H14	0.1636	0.3844	0.5334	0.068*
C15	0.2586 (7)	0.2227 (5)	0.4210 (5)	0.0454 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B1	0.113 (6)	0.055 (4)	0.059 (5)	-0.037 (4)	0.023 (4)	-0.031 (4)
O1	0.090 (3)	0.0377 (19)	0.050 (2)	-0.0213 (18)	0.0070 (19)	-0.0153 (16)
C1	0.037 (3)	0.042 (3)	0.039 (3)	-0.013 (2)	-0.005 (2)	-0.007 (2)
F1	0.189 (4)	0.081 (2)	0.059 (2)	-0.073 (3)	0.000 (2)	-0.0260 (19)
O2	0.086 (3)	0.047 (2)	0.041 (2)	-0.0228 (18)	0.0087 (19)	-0.0157 (17)
C2	0.076 (4)	0.058 (3)	0.048 (3)	-0.026 (3)	0.003 (3)	-0.016 (3)
F2	0.122 (3)	0.062 (2)	0.092 (3)	-0.004 (2)	0.040 (2)	-0.025 (2)
O3	0.059 (2)	0.0383 (18)	0.043 (2)	-0.0122 (15)	0.0004 (16)	-0.0117 (16)
C3	0.093 (4)	0.076 (4)	0.037 (3)	-0.036 (3)	0.005 (3)	-0.014 (3)
C4	0.066 (4)	0.073 (4)	0.043 (3)	-0.032 (3)	-0.001 (3)	0.007 (3)
C5	0.058 (3)	0.054 (3)	0.055 (4)	-0.013 (3)	-0.004 (3)	0.003 (3)
C6	0.056 (3)	0.049 (3)	0.054 (3)	-0.016 (3)	-0.002 (3)	-0.012 (3)
C7	0.041 (3)	0.040 (3)	0.041 (3)	-0.009 (2)	-0.006 (2)	-0.010 (2)
C8	0.044 (3)	0.043 (3)	0.039 (3)	-0.009 (2)	-0.004 (2)	-0.008 (2)
C9	0.047 (3)	0.047 (3)	0.041 (3)	-0.014 (2)	0.000 (2)	-0.014 (2)
C10	0.045 (3)	0.038 (3)	0.043 (3)	-0.012 (2)	-0.005 (2)	-0.011 (2)
C11	0.065 (4)	0.050 (3)	0.049 (3)	-0.022 (3)	0.001 (3)	-0.011 (3)
C12	0.066 (4)	0.047 (3)	0.056 (4)	-0.021 (3)	-0.001 (3)	-0.001 (3)
C13	0.071 (4)	0.038 (3)	0.066 (4)	-0.010 (3)	-0.001 (3)	-0.018 (3)
C14	0.062 (3)	0.042 (3)	0.061 (4)	-0.011 (3)	0.001 (3)	-0.018 (3)
C15	0.046 (3)	0.039 (3)	0.046 (3)	-0.012 (2)	-0.002 (2)	-0.006 (2)

Geometric parameters (\AA , $^\circ$)

B1—F1	1.349 (8)	C5—C6	1.381 (7)
B1—F2	1.375 (9)	C5—H5	0.9300

B1—O1	1.483 (7)	C6—H6	0.9300
B1—O2	1.527 (7)	C7—C8	1.377 (6)
O1—C8	1.336 (5)	C8—C9	1.402 (6)
C1—C6	1.386 (6)	C9—C10	1.405 (6)
C1—C2	1.387 (6)	C10—C11	1.396 (6)
C1—C7	1.462 (6)	C10—C15	1.395 (6)
O2—C9	1.293 (5)	C11—C12	1.363 (7)
C2—C3	1.378 (7)	C11—H11	0.9300
C2—H2	0.9300	C12—C13	1.394 (7)
O3—C7	1.351 (5)	C12—H12	0.9300
O3—C15	1.371 (5)	C13—C14	1.371 (7)
C3—C4	1.356 (7)	C13—H13	0.9300
C3—H3	0.9300	C14—C15	1.380 (6)
C4—C5	1.360 (7)	C14—H14	0.9300
C4—H4	0.9300		
F1—B1—F2	112.0 (5)	O3—C7—C8	117.9 (4)
F1—B1—O1	110.8 (5)	O3—C7—C1	113.2 (4)
F2—B1—O1	110.9 (6)	C8—C7—C1	128.9 (4)
F1—B1—O2	110.6 (6)	O1—C8—C7	128.2 (4)
F2—B1—O2	108.8 (5)	O1—C8—C9	111.7 (4)
O1—B1—O2	103.3 (4)	C7—C8—C9	120.1 (4)
C8—O1—B1	106.4 (4)	O2—C9—C8	111.0 (4)
C6—C1—C2	119.3 (4)	O2—C9—C10	126.5 (4)
C6—C1—C7	120.2 (4)	C8—C9—C10	122.5 (4)
C2—C1—C7	120.6 (4)	C11—C10—C15	119.6 (4)
C9—O2—B1	107.5 (4)	C11—C10—C9	125.9 (5)
C3—C2—C1	119.3 (5)	C15—C10—C9	114.6 (4)
C3—C2—H2	120.3	C12—C11—C10	119.7 (5)
C1—C2—H2	120.3	C12—C11—H11	120.2
C7—O3—C15	122.7 (4)	C10—C11—H11	120.2
C4—C3—C2	120.9 (5)	C11—C12—C13	119.7 (5)
C4—C3—H3	119.5	C11—C12—H12	120.1
C2—C3—H3	119.5	C13—C12—H12	120.1
C3—C4—C5	120.3 (5)	C14—C13—C12	121.9 (5)
C3—C4—H4	119.8	C14—C13—H13	119.1
C5—C4—H4	119.8	C12—C13—H13	119.1
C4—C5—C6	120.2 (5)	C13—C14—C15	118.2 (5)
C4—C5—H5	119.9	C13—C14—H14	120.9
C6—C5—H5	119.9	C15—C14—H14	120.9
C1—C6—C5	119.9 (5)	O3—C15—C14	116.8 (4)
C1—C6—H6	120.1	O3—C15—C10	122.2 (4)
C5—C6—H6	120.1	C14—C15—C10	120.9 (4)
F1—B1—O1—C8	-119.9 (5)	C1—C7—C8—C9	178.1 (4)
F2—B1—O1—C8	114.9 (4)	B1—O2—C9—C8	0.3 (6)
O2—B1—O1—C8	-1.5 (7)	B1—O2—C9—C10	-179.8 (5)
F1—B1—O2—C9	119.3 (5)	O1—C8—C9—O2	-1.4 (6)
F2—B1—O2—C9	-117.2 (5)	C7—C8—C9—O2	-180.0 (4)
O1—B1—O2—C9	0.7 (7)	O1—C8—C9—C10	178.7 (4)

supplementary materials

C6—C1—C2—C3	0.7 (7)	C7—C8—C9—C10	0.2 (7)
C7—C1—C2—C3	-179.7 (5)	O2—C9—C10—C11	1.6 (8)
C1—C2—C3—C4	0.1 (8)	C8—C9—C10—C11	-178.5 (5)
C2—C3—C4—C5	0.1 (8)	O2—C9—C10—C15	-178.4 (5)
C3—C4—C5—C6	-1.0 (8)	C8—C9—C10—C15	1.4 (6)
C2—C1—C6—C5	-1.6 (7)	C15—C10—C11—C12	0.9 (7)
C7—C1—C6—C5	178.7 (4)	C9—C10—C11—C12	-179.1 (5)
C4—C5—C6—C1	1.8 (7)	C10—C11—C12—C13	1.5 (8)
C15—O3—C7—C8	1.5 (6)	C11—C12—C13—C14	-1.8 (8)
C15—O3—C7—C1	-178.3 (4)	C12—C13—C14—C15	-0.5 (8)
C6—C1—C7—O3	-178.3 (4)	C7—O3—C15—C14	-178.3 (4)
C2—C1—C7—O3	2.1 (6)	C7—O3—C15—C10	0.2 (7)
C6—C1—C7—C8	1.9 (7)	C13—C14—C15—O3	-178.5 (4)
C2—C1—C7—C8	-177.7 (5)	C13—C14—C15—C10	2.9 (7)
B1—O1—C8—C7	-179.8 (6)	C11—C10—C15—O3	178.3 (4)
B1—O1—C8—C9	1.8 (6)	C9—C10—C15—O3	-1.6 (7)
O3—C7—C8—O1	-179.9 (4)	C11—C10—C15—C14	-3.2 (7)
C1—C7—C8—O1	-0.2 (8)	C9—C10—C15—C14	176.8 (4)
O3—C7—C8—C9	-1.6 (6)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots O3	0.93	2.37	2.700 (6)	100
C6—H6 \cdots O1	0.93	2.29	2.967 (6)	129
C11—H11 \cdots F1 ⁱ	0.93	2.44	3.373 (6)	177

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

Table 2

π - π interactions (\AA , $^\circ$).

$Cg1$, $Cg2$ and $Cg3$ are the centroids of the O3/C7—C10/C15, C10—C15 and C1—C6 rings, respectively. $CgI\cdots CgJ$ is the distance between ring centroids. The dihedral angle is that between the planes of the rings I and J . CgI_{\perp} is the perpendicular distance of CgI from ring J . CgI_{Offset} is the distance between CgI and the perpendicular projection of CgJ on ring I .

I	J	$CgI\cdots CgJ$	Dihedral angle	CgI_{\perp}	CgI_{Offset}
1	1 ⁱⁱ	3.512 (3)	0	3.344 (2)	1.076 (2)
1	3 ⁱⁱⁱ	3.572 (3)	2.3 (3)	3.450 (2)	0.956 (2)
2	3 ⁱⁱ	3.970 (3)	4.3 (3)	3.342 (2)	2.143 (2)
2	3 ⁱⁱⁱ	3.925 (3)	4.3 (3)	3.472 (2)	1.831 (2)
3	1 ⁱⁱⁱ	3.571 (3)	2.3 (3)	3.428 (2)	1.000 (2)
3	2 ⁱⁱ	3.970 (3)	4.3 (3)	3.492 (2)	1.889 (2)
3	2 ⁱⁱⁱ	3.925 (3)	4.3 (3)	3.404 (2)	1.954 (2)

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

Fig. 1

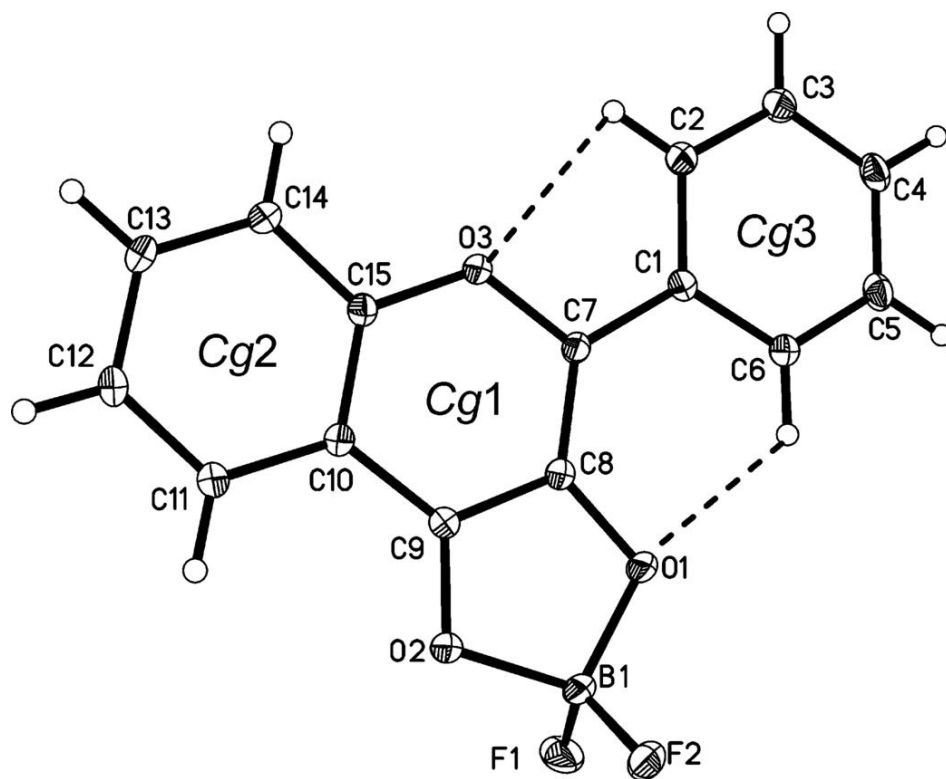


Fig. 2

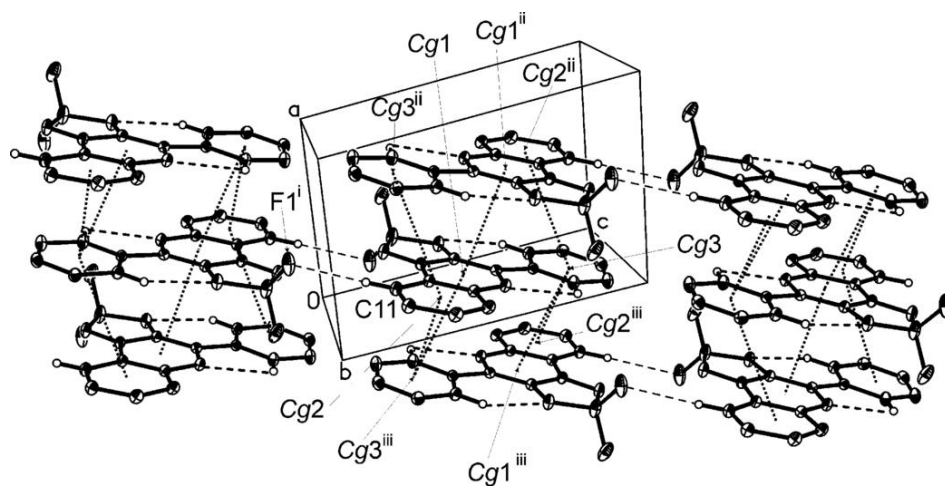


Fig. 3

