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1-Bromo-2,3,5,6-tetrafluoro-4-nitrobenzene

Mario Stein,^a Anke Schwarzer,^b Jürg Hulliger^c and Edwin Weber^{a*}

^aInstitut für Organische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany, ^bInstitut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany, and ^cDepartment of Chemistry and Biochemistry, University of Berne, Freiestrasse 3, CH-3012 Berne, Switzerland
Correspondence e-mail: Edwin.Weber@chemie.tu-freiberg.de

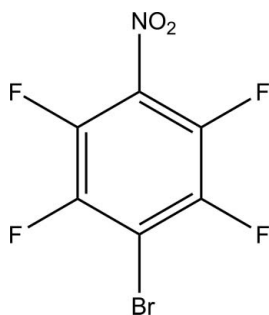
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Key indicators: single-crystal X-ray study; $T = 93$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.023; wR factor = 0.053; data-to-parameter ratio = 12.2.

In the title compound, $\text{C}_6\text{BrF}_4\text{NO}_2$, the nitro group is twisted by 41.7 (3)° with reference to the arene ring mean plane. The main interactions stabilizing the crystal structure include $\text{O}\cdots\text{Br}$ contacts [3.150 (2) and 3.201 (2) Å], while $\text{F}\cdots\text{F}$ interactions are minor [2.863 (3)–2.908 (3) Å].

Related literature

For halogen interactions in molecular crystal structures, see: Awwadi *et al.* (2006); Brammer *et al.* (2001); Metrangolo *et al.* (2008). For fluorine-involved interactions, see: Schwarzer *et al.* (2010); Merz & Vasylyeva (2010); Schwarzer & Weber (2008); Reichenbacher *et al.* (2005). For the synthesis, see: Shtark & Shteingarts (1976).



Experimental

Crystal data

$\text{C}_6\text{BrF}_4\text{NO}_2$	$V = 761.58$ (8) Å ³
$M_r = 273.98$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 5.6718$ (3) Å	$\mu = 5.44$ mm ⁻¹
$b = 10.9476$ (6) Å	$T = 93$ K
$c = 12.2652$ (8) Å	$0.13 \times 0.13 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	4314 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2007)	1550 independent reflections
$T_{\min} = 0.536$, $T_{\max} = 0.612$	1447 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	$\Delta\rho_{\max} = 0.32$ e Å ⁻³
$wR(F^2) = 0.053$	$\Delta\rho_{\min} = -0.53$ e Å ⁻³
$S = 1.00$	Absolute structure: Flack (1983),
1550 reflections	636 Friedel pairs
127 parameters	Flack parameter: 0.026 (10)
1 restraint	

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2278).

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supporting information

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1-Bromo-2,3,5,6-tetrafluoro-4-nitrobenzene

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S1. Comment

Halogen interactions in molecular crystal structures have been the subject of a number of studies (Awwadi *et al.*, 2006; Brammer *et al.*, 2001; Metrangolo *et al.*, 2008). Fluorine involved interactions in particular have been studied by us and others (Schwarzer *et al.*, 2010; Schwarzer & Weber, 2008; Reichenbacher *et al.*, 2005; Merz & Vasylyeva, 2010). In continuation of that work we report herein on the crystal structure of the title tetrafluoro-benzene compound.

In the title compound (Fig. 1) the plane of the nitro group (O1—N1—O2) shows a twist of 41.68 (28)° with reference to the phenyl ring, owing to repulsive interactions between the *ortho*-positioned fluorine (F2 and F3) and oxygen atoms. The N—O bond lengths are different (O1—N1: 1.217 (4) Å; O2—N1: 1.234 (3) Å) as a result of different intermolecular interactions.

In the crystal oxygen O1 is involved in two strong intermolecular contacts to bromine Br1 [3.150 (2) and 3.201 (2) Å], giving rise to the formation of a three-dimensional molecular network (Table 1 and Fig. 2). On the other hand, atom O2 forms a weak contact to atom F3 [2.823 (3) Å].

The fluorine...fluorine contacts [2.863 (3) – 2.908 (3) Å] are close to the sum of their van-der-Waals radii hence, they do not contribute significantly to the stabilization of the crystal packing. Moreover, there is no indication for the presence of either $\pi^F \cdots \pi^F$ stacking or C—X... π^F interactions (X = O, F, Br). Hence, except for the O...Br interactions, the crystal structure is mostly determined by maximum symmetry and close-packing principles, which is reflected in the low melting point of 321 K.

S2. Experimental

The title compound was synthesized according to the published procedure (Shtark & Shteingarts, 1976). 3-bromo-1,2,4,5-tetrafluorobenzene (2.80 g, 12 mmol) and NO₂BF₄ (6.45 g, 48 mmol) were dissolved in 45 ml of sulfolan and stirred for 2 h at 338 K. After cooling the solution to room temperature, 120 ml water was added and the phases separated. The aqueous layer was extracted with chloroform (3 × 50 ml), dried (Na₂SO₄) and evaporated under reduced pressure. The crude product was purified by water steam distillation to yield 2.66 g (81%) of the title compound. Sublimation techniques yielded single crystals suitable for X-ray crystallography.

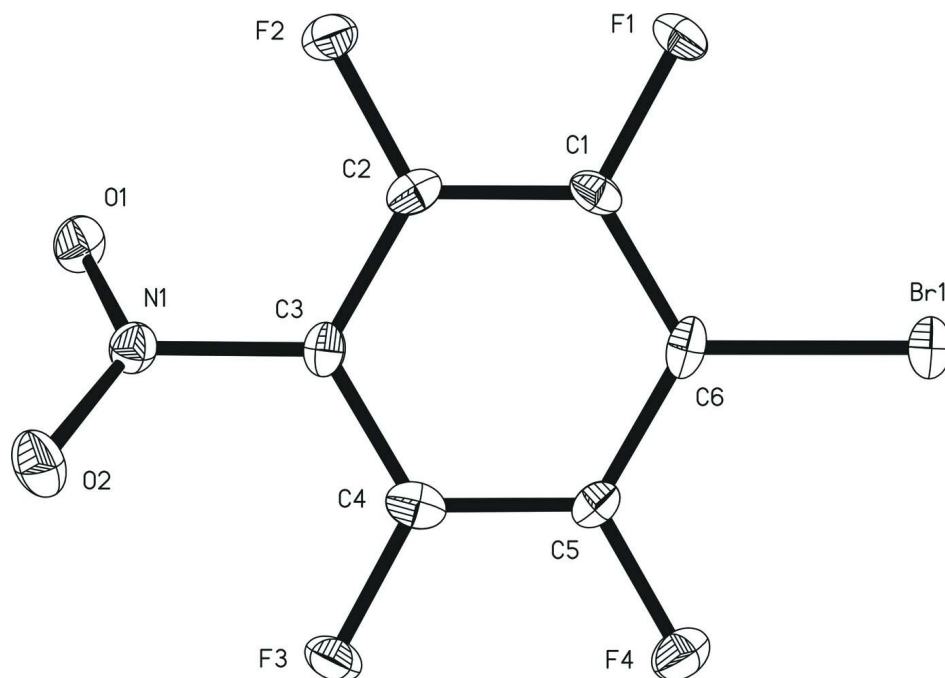
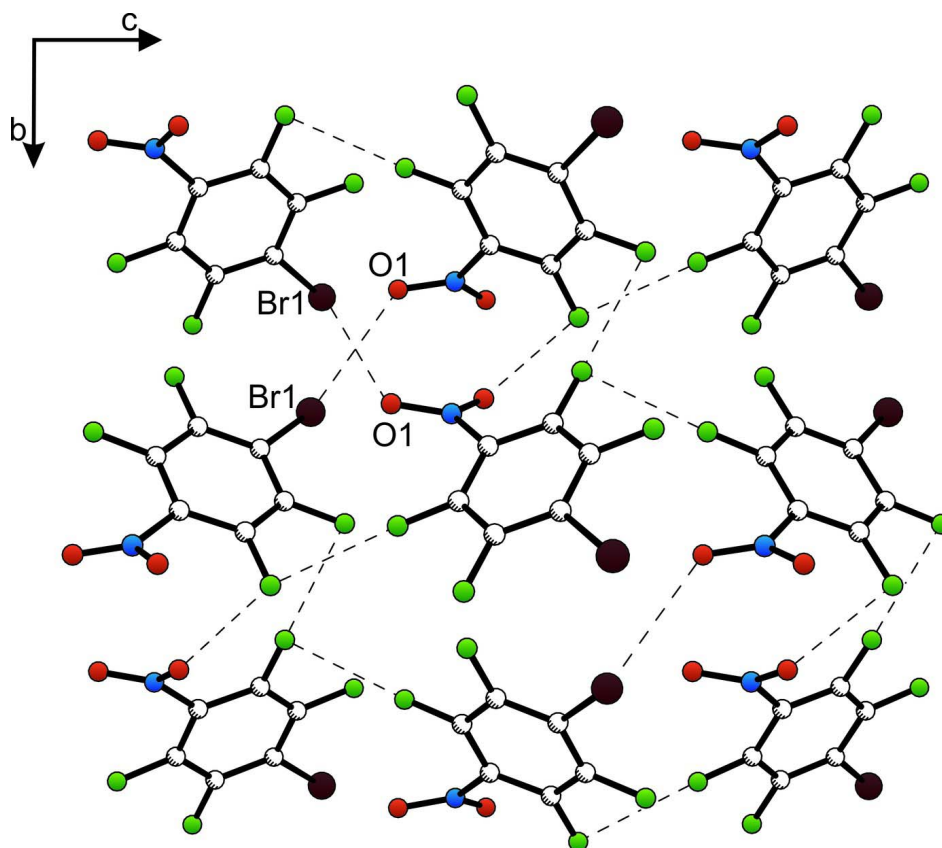


Figure 1

A view of the molecular structure of the title molecule, with the atom numbering and showing 50% probability displacement ellipsoids.

**Figure 2**

A partial view, along the a axis, of the crystal packing of the title compound. The $O\cdots Br$, and potential $O\cdots F$ and $F\cdots F$ contacts are shown as broken lines (see Table 1 for details).

1-Bromo-2,3,5,6-tetrafluoro-4-nitrobenzene

Crystal data

$C_6BrF_4NO_2$

$M_r = 273.98$

Orthorhombic, $Pna2_1$

Hall symbol: $P\ 2c\ -2n$

$a = 5.6718\ (3)\ \text{\AA}$

$b = 10.9476\ (6)\ \text{\AA}$

$c = 12.2652\ (8)\ \text{\AA}$

$V = 761.58\ (8)\ \text{\AA}^3$

$Z = 4$

$F(000) = 520$

$D_x = 2.390\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2319 reflections

$\theta = 3.7\text{--}32.8^\circ$

$\mu = 5.44\ \text{mm}^{-1}$

$T = 93\ \text{K}$

Needle, colourless

$0.13 \times 0.13 \times 0.10\ \text{mm}$

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ϕ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2007)

$T_{\min} = 0.536$, $T_{\max} = 0.612$

4314 measured reflections

1550 independent reflections

1447 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -7 \rightarrow 7$

$k = -14 \rightarrow 12$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.053$

$S = 1.00$

1550 reflections

127 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.008$

$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.53 \text{ e } \text{\AA}^{-3}$

Absolute structure: Flack (1983), 636 Friedel
pairs

Absolute structure parameter: 0.026 (10)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	1.16169 (4)	0.62891 (2)	0.12241 (5)	0.01760 (10)
F1	0.9560 (3)	0.69267 (15)	-0.10033 (17)	0.0188 (4)
F2	0.6066 (3)	0.58458 (16)	-0.20909 (18)	0.0178 (4)
F3	0.5004 (3)	0.30738 (15)	0.08418 (15)	0.0181 (4)
F4	0.8565 (3)	0.41466 (18)	0.19058 (19)	0.0192 (4)
N1	0.3610 (4)	0.3813 (2)	-0.1276 (3)	0.0148 (6)
O1	0.3925 (4)	0.36408 (18)	-0.2245 (2)	0.0181 (5)
O2	0.1833 (3)	0.3518 (2)	-0.0760 (2)	0.0207 (6)
C1	0.8465 (4)	0.5971 (3)	-0.0542 (3)	0.0134 (7)
C2	0.6671 (4)	0.5405 (3)	-0.1118 (3)	0.0136 (7)
C3	0.5498 (4)	0.4424 (3)	-0.0658 (3)	0.0128 (7)
C4	0.6105 (5)	0.4023 (3)	0.0374 (3)	0.0146 (7)
C5	0.7936 (4)	0.4574 (3)	0.0933 (3)	0.0129 (8)
C6	0.9119 (4)	0.5558 (3)	0.0468 (3)	0.0146 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01516 (11)	0.01875 (15)	0.01890 (19)	-0.00140 (8)	-0.00323 (18)	-0.0046 (2)
F1	0.0214 (7)	0.0153 (9)	0.0198 (13)	-0.0066 (6)	0.0011 (8)	0.0038 (8)
F2	0.0241 (8)	0.0159 (9)	0.0135 (13)	-0.0005 (7)	-0.0031 (9)	0.0027 (9)
F3	0.0224 (7)	0.0155 (9)	0.0164 (12)	-0.0057 (6)	0.0040 (8)	0.0017 (7)
F4	0.0256 (9)	0.0177 (10)	0.0142 (14)	0.0018 (7)	-0.0024 (8)	0.0009 (9)
N1	0.0150 (12)	0.0158 (15)	0.014 (2)	-0.0005 (8)	-0.0002 (11)	-0.0015 (13)
O1	0.0205 (8)	0.0206 (12)	0.0133 (16)	-0.0014 (7)	-0.0005 (10)	-0.0048 (10)

O2	0.0134 (9)	0.0245 (14)	0.0241 (17)	-0.0025 (7)	0.0025 (10)	-0.0016 (11)
C1	0.0165 (12)	0.0082 (15)	0.016 (2)	-0.0009 (10)	0.0038 (13)	0.0006 (13)
C2	0.0160 (12)	0.0125 (16)	0.012 (2)	0.0048 (9)	0.0001 (12)	-0.0004 (14)
C3	0.0099 (10)	0.0143 (15)	0.014 (2)	0.0018 (10)	0.0001 (12)	-0.0040 (13)
C4	0.0169 (12)	0.0107 (15)	0.016 (2)	0.0019 (10)	0.0045 (13)	0.0003 (13)
C5	0.0150 (10)	0.0158 (15)	0.008 (2)	0.0030 (9)	0.0001 (11)	-0.0003 (12)
C6	0.0110 (10)	0.0169 (15)	0.016 (2)	0.0014 (10)	-0.0020 (12)	-0.0065 (13)

Geometric parameters (Å, °)

Br1—C6	1.874 (3)	F4—F3 ⁱⁱⁱ	2.877 (2)
Br1—O1 ⁱ	3.150 (2)	F4—F2 ^{vii}	2.901 (2)
Br1—O1 ⁱⁱ	3.201 (2)	N1—O1	1.217 (4)
F3—O2 ⁱⁱⁱ	2.823 (3)	N1—O2	1.234 (3)
F1—C1	1.342 (3)	N1—C3	1.472 (4)
F1—F2 ^{iv}	2.908 (3)	O1—Br1 ^{ix}	3.150 (2)
F2—C2	1.332 (4)	O1—Br1 ^x	3.201 (2)
F2—F3 ^v	2.863 (3)	O2—F3 ^{viii}	2.823 (3)
F2—F4 ^v	2.901 (2)	C1—C6	1.369 (5)
F2—F1 ^{vi}	2.908 (3)	C1—C2	1.385 (4)
F3—C4	1.341 (3)	C2—C3	1.385 (4)
F3—F2 ^{vii}	2.863 (3)	C3—C4	1.383 (5)
F3—F4 ^{viii}	2.877 (2)	C4—C5	1.382 (4)
F4—C5	1.331 (4)	C5—C6	1.391 (4)
C6—Br1—O1 ⁱ	155.87 (10)	N1—O1—Br1 ^{ix}	134.13 (18)
C6—Br1—O1 ⁱⁱ	124.16 (9)	N1—O1—Br1 ^x	133.10 (18)
O1 ⁱ —Br1—O1 ⁱⁱ	73.03 (6)	Br1 ^{ix} —O1—Br1 ^x	75.36 (6)
C1—F1—F2 ^{iv}	169.53 (15)	N1—O2—F3 ^{viii}	144.98 (19)
C2—F2—F3 ^v	176.03 (17)	F1—C1—C6	120.9 (3)
C2—F2—F4 ^v	127.90 (16)	F1—C1—C2	118.2 (3)
F3 ^v —F2—F4 ^v	55.33 (6)	C6—C1—C2	120.8 (3)
C2—F2—F1 ^{vi}	88.19 (17)	F2—C2—C3	121.5 (3)
F3 ^v —F2—F1 ^{vi}	89.86 (7)	F2—C2—C1	119.0 (3)
F4 ^v —F2—F1 ^{vi}	85.76 (7)	C3—C2—C1	119.5 (3)
C4—F3—O2 ⁱⁱⁱ	90.56 (18)	C4—C3—C2	120.0 (3)
C4—F3—F2 ^{vii}	99.04 (18)	C4—C3—N1	120.6 (3)
O2 ⁱⁱⁱ —F3—F2 ^{vii}	161.63 (9)	C2—C3—N1	119.5 (3)
C4—F3—F4 ^{viii}	168.70 (16)	F3—C4—C5	118.4 (3)
O2 ⁱⁱⁱ —F3—F4 ^{viii}	84.17 (8)	F3—C4—C3	121.4 (3)
F2 ^{vii} —F3—F4 ^{viii}	83.52 (8)	C5—C4—C3	120.1 (3)
C5—F4—F3 ⁱⁱⁱ	88.06 (17)	F4—C5—C4	119.5 (3)
C5—F4—F2 ^{vii}	97.86 (13)	F4—C5—C6	120.7 (3)
F3 ⁱⁱⁱ —F4—F2 ^{vii}	116.85 (8)	C4—C5—C6	119.8 (3)
O1—N1—O2	125.5 (3)	C1—C6—C5	119.7 (3)
O1—N1—C3	117.8 (2)	C1—C6—Br1	120.8 (2)
O2—N1—C3	116.6 (3)	C5—C6—Br1	119.5 (2)

O2—N1—O1—Br1 ^{ix}	-164.81 (19)	F4 ^{viii} —F3—C4—C5	-50.3 (12)
C3—N1—O1—Br1 ^{ix}	15.2 (4)	O2 ⁱⁱⁱ —F3—C4—C3	65.5 (3)
O2—N1—O1—Br1 ^x	-49.6 (4)	F2 ^{vii} —F3—C4—C3	-130.3 (3)
C3—N1—O1—Br1 ^x	130.4 (2)	F4 ^{viii} —F3—C4—C3	127.4 (9)
O1—N1—O2—F3 ^{viii}	110.3 (4)	C2—C3—C4—F3	-179.9 (3)
C3—N1—O2—F3 ^{viii}	-69.7 (4)	N1—C3—C4—F3	0.0 (4)
F2 ^{iv} —F1—C1—C6	-133.4 (10)	C2—C3—C4—C5	-2.2 (4)
F2 ^{iv} —F1—C1—C2	47.2 (13)	N1—C3—C4—C5	177.7 (3)
F3 ^v —F2—C2—C3	174 (2)	F3 ⁱⁱⁱ —F4—C5—C4	65.3 (3)
F4 ^v —F2—C2—C3	30.2 (4)	F2 ^{vii} —F4—C5—C4	-51.5 (3)
F1 ^{vi} —F2—C2—C3	113.4 (3)	F3 ⁱⁱⁱ —F4—C5—C6	-113.9 (3)
F3 ^v —F2—C2—C1	-4 (3)	F2 ^{vii} —F4—C5—C6	129.2 (2)
F4 ^v —F2—C2—C1	-147.6 (2)	F3—C4—C5—F4	0.5 (4)
F1 ^{vi} —F2—C2—C1	-64.4 (3)	C3—C4—C5—F4	-177.2 (2)
F1—C1—C2—F2	-1.5 (4)	F3—C4—C5—C6	179.8 (3)
C6—C1—C2—F2	179.1 (3)	C3—C4—C5—C6	2.0 (4)
F1—C1—C2—C3	-179.4 (3)	F1—C1—C6—C5	179.2 (3)
C6—C1—C2—C3	1.2 (4)	C2—C1—C6—C5	-1.4 (4)
F2—C2—C3—C4	-177.2 (3)	F1—C1—C6—Br1	-1.6 (4)
C1—C2—C3—C4	0.6 (4)	C2—C1—C6—Br1	177.8 (2)
F2—C2—C3—N1	2.9 (4)	F4—C5—C6—C1	179.0 (3)
C1—C2—C3—N1	-179.2 (3)	C4—C5—C6—C1	-0.2 (4)
O1—N1—C3—C4	-138.6 (3)	F4—C5—C6—Br1	-0.2 (4)
O2—N1—C3—C4	41.4 (4)	C4—C5—C6—Br1	-179.4 (2)
O1—N1—C3—C2	41.3 (4)	O1 ⁱ —Br1—C6—C1	-143.2 (2)
O2—N1—C3—C2	-138.7 (3)	O1 ⁱⁱ —Br1—C6—C1	86.1 (3)
O2 ⁱⁱⁱ —F3—C4—C5	-112.3 (3)	O1 ⁱ —Br1—C6—C5	36.0 (4)
F2 ^{vii} —F3—C4—C5	52.0 (3)	O1 ⁱⁱ —Br1—C6—C5	-94.7 (2)

Symmetry codes: (i) $-x+2, -y+1, z+1/2$; (ii) $-x+3/2, y+1/2, z+1/2$; (iii) $x+1/2, -y+1/2, z$; (iv) $x+1/2, -y+3/2, z$; (v) $-x+1, -y+1, z-1/2$; (vi) $x-1/2, -y+3/2, z$; (vii) $-x+1, -y+1, z+1/2$; (viii) $x-1/2, -y+1/2, z$; (ix) $-x+2, -y+1, z-1/2$; (x) $-x+3/2, y-1/2, z-1/2$.