Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

Crystal structure of 4′-bromo-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile

Ricarda Heckel,[a] Jürg Hulliger,[b] Anke Schwarzer[a]* and Edwin Weber[a]

[a]Institut für Organische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany, and [b]Department of Chemistry and Biochemistry, University of Berne, Freiestrasse 3, CH-3012 Berne, Switzerland. *Correspondence e-mail: anke.schwarzer@chemie.tu-freiberg.de

Received 16 April 2015; accepted 21 April 2015

Edited by W. Imhof, University Koblenz-Landau, Germany

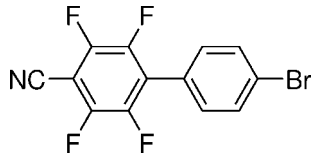
The title compound, $C_{13}H_4BrF_4N$, synthesized from 1,4′-bromoiodobenzene and 4-bromo-2,3,5,6-tetrafluorobenzonitrile in a coupling reaction was found to crystallize in the orthorhombic space group $P2_12_12_1$. The two phenyl rings are rotated with respect to each other by 40.6 (6)°. The molecules interact *via* aryl–perfluoroaryl stacking [3.796 (2) and 3.773 (2) Å], resulting in intermolecular chains along the *a*-axis direction. C—H···F contacts of about 2.45 Å connect these chains. In contrast to the structure of the parent compound 4′-bromobiphenyl-4-carbonitrile, CN···Br contacts that could have given rise to a linear arrangement of the biphenyl molecules desirable for non-linear optical (NLO) materials are not observed in the packing. Instead, several Br···F [3.2405 (17) and 3.2777 (18) Å] and F···F [2.894 (2) Å] contacts of side-on type II form an intermolecular network of zigzag chains. The crystal studied was refined as an inversion twin.

Keywords: crystal structure; biphenyl; tetrafluoro substitution; bromo–cyano substitution; π–π^F stacking; halogen interactions.

CCDC reference: 1060721

1. Related literature

For crystal structures of 4-cyano-4′-halogene substituted biphenyls, see: Gleason *et al.* (1991) for fluorine, Kronebusch *et al.* (1976) for bromine, Britton & Gleason (1991) for iodine. For halogen interactions in molecular crystal structures, see: Ramasubbu *et al.* (1986), Awwadi *et al.* (2006), Brammer *et al.* (2001) and Metrangolo *et al.* (2008). For interactions of halogens with cyano groups, see: Desiraju & Harlow (1989), Süss *et al.* (2005) and Mukherjee *et al.* (2014). For fluorine involved into these interactions, see: Schwarzer *et al.* (2010), Merz & Vasylyeva (2010), Schwarzer & Weber (2008) and Reichenbächer *et al.* (2005).



2. Experimental

2.1. Crystal data

$C_{13}H_4BrF_4N$
M_r = 330.08
Orthorhombic, $P2_12_12_1$
a = 7.3560 (15) Å
b = 12.107 (2) Å
c = 12.723 (3) Å
V = 1133.1 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.66 mm^{-1}
T = 93 K
0.49 × 0.13 × 0.10 mm

2.2. Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
T_{min} = 0.486, T_{max} = 0.718
18347 measured reflections
3234 independent reflections
2930 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.052
S = 0.99
3234 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: refined as an inversion twin.
Absolute structure parameter: 0.011 (9)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···F2	0.95	2.47	2.882 (4)	106
C13—H13···F3	0.95	2.45	2.865 (3)	107

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2015); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *publCIF* (Westrip, 2010) and *SHELXLE* (Hübschle *et al.*, 2011).

Supporting information for this paper is available from the IUCr electronic archives (Reference: IM2464).

References

Awwadi, F. F., Willett, R. D., Peterson, K. A. & Twamley, B. (2006). *Chem. Eur. J.* **12**, 8952–8960.
Brammer, L., Bruton, E. A. & Sherwood, P. (2001). *Cryst. Growth Des.* **1**, 277–290.
Britton, D. & Gleason, W. B. (1991). *Acta Cryst.* C**47**, 2127–2131.
Bruker (2007). *SMART*, *SADABS and SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Desiraju, G. R. & Harlow, R. L. (1989). *J. Am. Chem. Soc.* **111**, 6757–6764.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Gleason, W. B., Brostrom, M., Etter, M. C. & Johnson, R. B. (1991). *Acta Cryst.* C**47**, 2131–2134.
Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). *J. Appl. Cryst.* **44**, 1281–1284.
Kronebusch, P., Gleason, W. B. & Britton, D. (1976). *Cryst. Struct. Commun.* **5**, 17–20.
Merz, K. & Vasylyeva, V. (2010). *CrystEngComm*, **12**, 3989–4002.
Metrangolo, P., Resnati, G., Pilati, T. & Biella, S. (2008). *Halogen Bonding, Structure and Bonding*, Vol. 126, edited by P. Metrangolo & G. Resnati, pp. 105–136. Berlin, Heidelberg: Springer.
Mukherjee, A., Tothadi, S. & Desiraju, G. R. (2014). *Acc. Chem. Res.* **47**, 2514–2524.
Ramasubbu, N., Parthasarathy, R. & Murray-Rust, P. (1986). *J. Am. Chem. Soc.* **108**, 4308–4314.
Reichenbächer, K., Süss, H. I. & Hulliger, J. (2005). *Chem. Soc. Rev.* **34**, 22–30.
Schwarzer, A., Bombicz, P. & Weber, E. (2010). *J. Fluor. Chem.* **131**, 345–356.
Schwarzer, A. & Weber, E. (2008). *Cryst. Growth Des.* **8**, 2862–2874.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Süss, H. I., Neels, A. & Hulliger, J. (2005). *CrystEngComm*, **7**, 370–373.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2015). E**71**, o347–o348 [https://doi.org/10.1107/S2056989015007847]

Crystal structure of 4′-bromo-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile

Ricarda Heckel, Jürg Hulliger, Anke Schwarzer and Edwin Weber

S1. Synthesis and crystallization

Under inert conditions, 1-bromo-4-iodobenzene (22.6 g, 80 mmol) in THF (90 mL) was added dropwise to magnesium shaving (1.8 g, 75 mmol. The reaction mixture was refluxed for 90 min. After cooling to room temperature, CuBr (25.8 g, 180 mmol) was added and the mixture was stirred for 1 h at this temperature. Then 15 ml of 1,4-dioxane was added and the mixture was stirred for an hour followed by dropwise addition of a solution of 4-bromo-2,3,5,6-tetrafluorobenzo-nitrile (6.4 g, 25 mmol) in toluene (50 ml). After refluxing for 2 d, the mixture was cooled to room temperature, filtered over Celite and freed from solvents removed under reduced pressure. The residue was dissolved in toluene and washed with 3M HCl followed by aqueous NaOH solution. The organic phases were collected, dried over Na_2SO_4 and evaporated. The raw product was purified by column chromatography (SiO_2; eluent: CH_2Cl_2/*n*-hexane, 2/1 v/v to yield 1.00 g (12 %) of the title compound. Single crystals suitable for X-ray diffraction were obtained from acetone solution at room temperature. Data for (I): M.p. 133-134 °C. ^{1}H NMR(400 MHz; acetone-d$_6$): δ_H = 7.57 (d, $^3J_{HH}$ = 8.9, 2H, H-9, H-13), 7.82 (d, $^3J_{HH}$ = 8.9, 2H, H-10, H12) ppm. ^{13}C NMR (100 MHz; acetone-d$_6$): δ_C = 94.30 (d, $^2J_{CF}$ = 17.4, C-2), 108.62 (t, $^3J_{CF}$ = -3.7, C-1), 125.52, 126.32 (s, C-8, C11), 127.04 (t, $^2J_{CF}$ = 17.4, C-5), 133.05 (t, $^4J_{CF}$ = 2.5, C-9), 133.32 (s, C-10), 143.39, 146.69 (d, $^1J_{CF}$ = -147.2, C-4), 147.01, 150.43 (d, $^1J_{CF}$ = -265.5, C-3) ppm. ^{19}F NMR(376 MHz; acetone-d$_6$): δ_F = -136.15 (F-1, d, $^3J_{FF}$ = 9.3), -142.53 (F-2, d, $^3J_{FF}$ = 9.3) ppm. GC—MS (m/z) 329 [M]$^+$, 250 [M—Br]$^+$, 231 [-F]$^+$, 200 [-CF]$^+$, 125, 99, 74, 50.

S2. Refinement details

The C-bound H atoms were positioned geometrically and allowed to ride on their parent atoms: C–H = 0.95 Å for aryl H atoms, with [U_{iso}(H) = 1.2U_{eq}(C)].

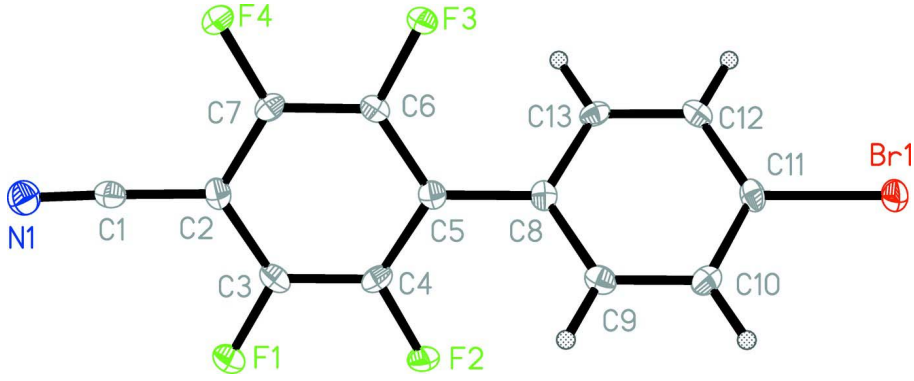


Figure 1

The molecular structure of the title molecule including atom labelling. Displacement ellipsoids drawn at the 50% probability level.

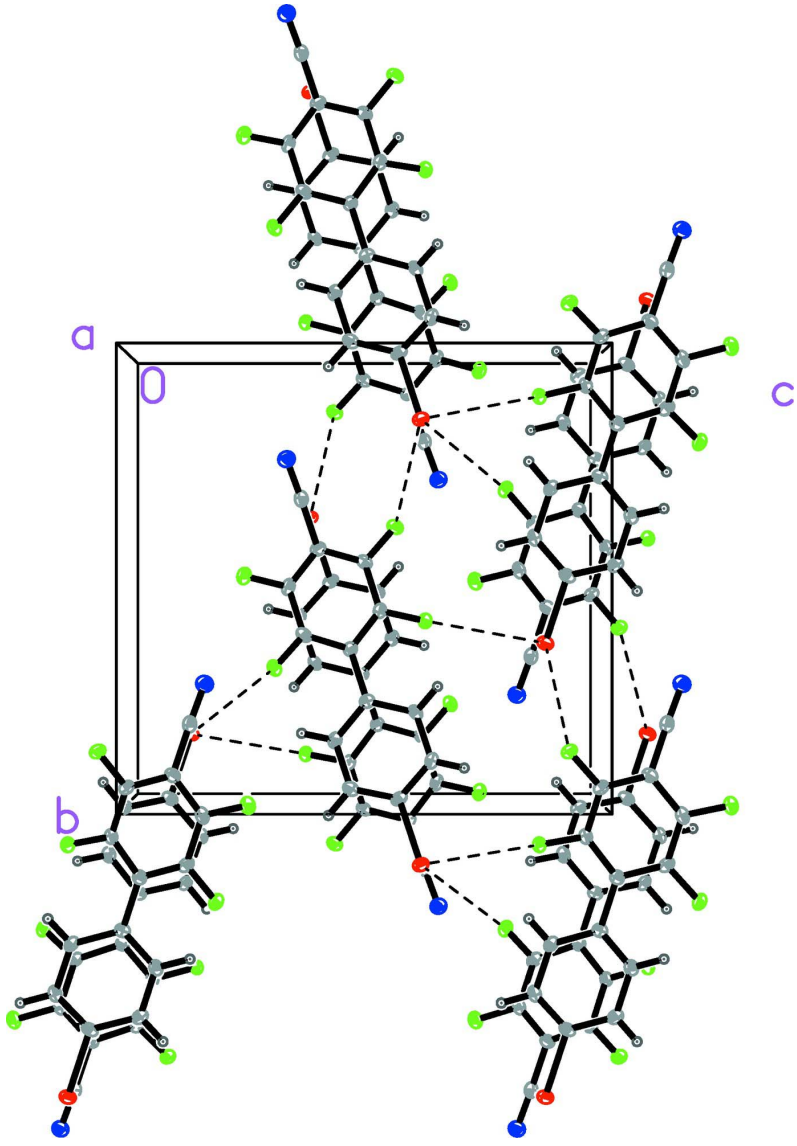


Figure 2

The crystal packing of the title compound showing the stacking interactions along [100].

4′-Bromo-2,3,5,6-tetrafluorobiphenyl-4-carbonitrile

Crystal data

$C_{13}H_4BrF_4N$
$M_r = 330.08$
Orthorhombic, $P2_12_12_1$
$a = 7.3560$ (15) Å
$b = 12.107$ (2) Å
$c = 12.723$ (3) Å
$V = 1133.1$ (4) Å^3
$Z = 4$
$F(000) = 640$

$D_x = 1.935$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4750 reflections
$\theta = 3.2$–28.4°
$\mu = 3.66$ mm^{-1}
$T = 93$ K
Splitter, colorless
0.49 × 0.13 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
T_{min} = 0.486, T_{max} = 0.718
18347 measured reflections
3234 independent reflections
2930 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 29.8°, θ_{min} = 2.3°
h = −10→10
k = −16→16
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.052
S = 0.99
3234 reflections
173 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0144P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Refined as an inversion twin.
Absolute structure parameter: 0.011 (9)

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. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.89811 (4)	0.35795 (3)	0.37922 (2)	0.01853 (8)
F1	0.7744 (2)	1.00596 (16)	0.75920 (12)	0.0196 (4)
F2	0.7639 (2)	0.79698 (15)	0.69387 (12)	0.0179 (4)
F3	1.0359 (2)	0.90632 (14)	0.37137 (13)	0.0163 (4)
F4	1.0323 (2)	1.11450 (14)	0.43493 (13)	0.0196 (4)
N1	0.9005 (4)	1.2681 (2)	0.66563 (19)	0.0208 (6)
C1	0.9026 (4)	1.1790 (2)	0.6343 (2)	0.0161 (6)
C2	0.9029 (5)	1.0664 (2)	0.5984 (2)	0.0153 (6)
C3	0.8371 (4)	0.9812 (3)	0.6627 (2)	0.0154 (7)
C4	0.8354 (4)	0.8729 (3)	0.6295 (2)	0.0147 (6)
C5	0.9004 (4)	0.8418 (2)	0.5296 (2)	0.0131 (6)
C6	0.9650 (4)	0.9283 (3)	0.4667 (2)	0.0129 (6)
C7	0.9665 (4)	1.0369 (3)	0.4992 (2)	0.0144 (6)
C8	0.8998 (5)	0.7249 (2)	0.4938 (2)	0.0133 (6)
C9	0.9476 (4)	0.6389 (3)	0.5620 (2)	0.0145 (6)
H9	0.9807	0.6555	0.6324	0.017*
C10	0.9474 (4)	0.5302 (3)	0.5286 (2)	0.0161 (7)
H10	0.9795	0.4725	0.5756	0.019*
C11	0.8997 (5)	0.5065 (2)	0.4254 (2)	0.0148 (6)

C12	0.8517 (4)	0.5894 (3)	0.3554 (2)	0.0153 (7)
H12	0.8191	0.5720	0.2851	0.018*
C13	0.8520 (4)	0.6986 (3)	0.3898 (2)	0.0142 (6)
H13	0.8196	0.7560	0.3424	0.017*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02368 (15)	0.01300 (14)	0.01890 (13)	−0.00129 (14)	0.00259 (14)	−0.00242 (13)
F1	0.0229 (10)	0.0218 (10)	0.0141 (8)	0.0003 (8)	0.0031 (7)	−0.0022 (7)
F2	0.0213 (10)	0.0185 (10)	0.0138 (8)	−0.0028 (8)	0.0029 (7)	0.0034 (7)
F3	0.0201 (9)	0.0163 (9)	0.0125 (7)	0.0014 (7)	0.0034 (7)	−0.0004 (8)
F4	0.0265 (10)	0.0143 (10)	0.0179 (8)	−0.0015 (7)	0.0042 (7)	0.0030 (7)
N1	0.0216 (14)	0.0193 (15)	0.0215 (12)	0.0015 (14)	0.0011 (13)	−0.0013 (11)
C1	0.0153 (14)	0.0200 (15)	0.0130 (13)	−0.0011 (13)	0.0005 (14)	0.0010 (11)
C2	0.0156 (13)	0.0137 (14)	0.0165 (13)	0.0012 (14)	−0.0020 (13)	−0.0026 (11)
C3	0.0133 (15)	0.0204 (18)	0.0125 (13)	0.0020 (13)	−0.0003 (11)	−0.0034 (12)
C4	0.0121 (13)	0.0149 (16)	0.0169 (13)	−0.0017 (11)	−0.0013 (12)	0.0049 (14)
C5	0.0112 (12)	0.0144 (15)	0.0136 (11)	0.0014 (14)	−0.0040 (12)	−0.0006 (11)
C6	0.0110 (14)	0.0162 (16)	0.0116 (13)	0.0024 (12)	−0.0007 (11)	−0.0012 (12)
C7	0.0136 (14)	0.0138 (16)	0.0160 (14)	0.0003 (12)	−0.0008 (11)	0.0035 (12)
C8	0.0101 (13)	0.0134 (15)	0.0164 (12)	−0.0001 (13)	0.0009 (13)	−0.0013 (11)
C9	0.0117 (14)	0.0187 (16)	0.0133 (12)	−0.0030 (13)	−0.0021 (10)	−0.0017 (14)
C10	0.0155 (17)	0.0149 (16)	0.0178 (14)	0.0010 (12)	0.0008 (12)	0.0033 (13)
C11	0.0125 (13)	0.0136 (15)	0.0183 (13)	−0.0029 (14)	0.0017 (14)	−0.0048 (11)
C12	0.0147 (16)	0.0191 (17)	0.0120 (14)	−0.0006 (12)	0.0002 (10)	−0.0025 (12)
C13	0.0136 (15)	0.0151 (15)	0.0137 (13)	0.0018 (11)	−0.0005 (11)	0.0045 (12)

Geometric parameters (Å, º)

Br1—C11	1.892 (3)	C5—C8	1.487 (4)
F1—C3	1.346 (3)	C6—C7	1.379 (4)
F2—C4	1.339 (3)	C8—C9	1.400 (4)
F3—C6	1.347 (3)	C8—C13	1.406 (4)
F4—C7	1.336 (3)	C9—C10	1.383 (4)
N1—C1	1.150 (4)	C9—H9	0.9500
C1—C2	1.438 (4)	C10—C11	1.389 (4)
C2—C7	1.393 (4)	C10—H10	0.9500
C2—C3	1.402 (4)	C11—C12	1.388 (4)
C3—C4	1.377 (4)	C12—C13	1.392 (4)
C4—C5	1.409 (4)	C12—H12	0.9500
C5—C6	1.401 (4)	C13—H13	0.9500
N1—C1—C2	178.1 (3)	C9—C8—C13	118.6 (3)
C7—C2—C3	117.1 (3)	C9—C8—C5	121.2 (2)
C7—C2—C1	122.1 (3)	C13—C8—C5	120.3 (3)
C3—C2—C1	120.8 (2)	C10—C9—C8	121.1 (3)
F1—C3—C4	119.3 (3)	C10—C9—H9	119.4

F1—C3—C2	119.1 (3)	C8—C9—H9	119.4
C4—C3—C2	121.6 (3)	C9—C10—C11	119.2 (3)
F2—C4—C3	118.0 (3)	C9—C10—H10	120.4
F2—C4—C5	120.1 (3)	C11—C10—H10	120.4
C3—C4—C5	121.9 (3)	C12—C11—C10	121.4 (3)
C6—C5—C4	115.5 (3)	C12—C11—Br1	119.1 (2)
C6—C5—C8	122.5 (2)	C10—C11—Br1	119.5 (2)
C4—C5—C8	122.0 (3)	C11—C12—C13	119.0 (3)
F3—C6—C7	117.1 (3)	C11—C12—H12	120.5
F3—C6—C5	119.8 (3)	C13—C12—H12	120.5
C7—C6—C5	123.0 (3)	C12—C13—C8	120.7 (3)
F4—C7—C6	119.3 (3)	C12—C13—H13	119.6
F4—C7—C2	119.8 (3)	C8—C13—H13	119.6
C6—C7—C2	120.9 (3)		

C7—C2—C3—F1	179.9 (3)	C5—C6—C7—C2	0.2 (5)
C1—C2—C3—F1	−0.5 (4)	C3—C2—C7—F4	−179.4 (3)
C7—C2—C3—C4	0.1 (5)	C1—C2—C7—F4	1.0 (5)
C1—C2—C3—C4	179.7 (3)	C3—C2—C7—C6	−0.3 (4)
F1—C3—C4—F2	2.6 (4)	C1—C2—C7—C6	−179.9 (3)
C2—C3—C4—F2	−177.5 (3)	C6—C5—C8—C9	139.2 (3)
F1—C3—C4—C5	−179.5 (3)	C4—C5—C8—C9	−40.8 (4)
C2—C3—C4—C5	0.3 (5)	C6—C5—C8—C13	−40.4 (5)
F2—C4—C5—C6	177.3 (3)	C4—C5—C8—C13	139.6 (3)
C3—C4—C5—C6	−0.5 (4)	C13—C8—C9—C10	−0.3 (4)
F2—C4—C5—C8	−2.6 (4)	C5—C8—C9—C10	−179.9 (3)
C3—C4—C5—C8	179.6 (3)	C8—C9—C10—C11	0.3 (4)
C4—C5—C6—F3	177.6 (2)	C9—C10—C11—C12	−0.2 (5)
C8—C5—C6—F3	−2.4 (4)	C9—C10—C11—Br1	−179.8 (2)
C4—C5—C6—C7	0.2 (4)	C10—C11—C12—C13	0.1 (5)
C8—C5—C6—C7	−179.8 (3)	Br1—C11—C12—C13	179.7 (2)
F3—C6—C7—F4	1.8 (4)	C11—C12—C13—C8	−0.1 (4)
C5—C6—C7—F4	179.3 (3)	C9—C8—C13—C12	0.2 (4)
F3—C6—C7—C2	−177.3 (3)	C5—C8—C13—C12	179.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···F2	0.95	2.47	2.882 (4)	106
C13—H13···F3	0.95	2.45	2.865 (3)	107