(E)-2-{2-[4-(Trifluoromethyl)phenyl]-ethenyl}-1,3,2-benzodioxaborole

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Key indicators

Single-crystal X-ray study
$T = 160$ K
Mean σ(C–C) = 0.007 Å
R factor = 0.090
wR factor = 0.279
Data-to-parameter ratio = 10.0

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

Molecules of the twinned and disordered title compound, $C_{15}H_{10}BF_3O_2$, are essentially planar with a high degree of conjugation. The molecular geometry is similar to that of closely related analogues. Molecules pack parallel in the triclinic crystal structure, with some π-stacking interaction.
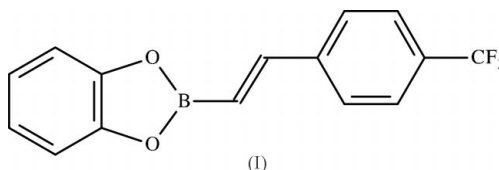
Comment

The title compound, (I), is one of a series of 2-styrylboronate esters prepared in a study of hydroboration reactions of alkynes, with a variety of *para* substituents (Wiesauer, 1997). We have previously reported the structure of the parent compound with no substituent in the *para* position (Clegg *et al.*, 2001). The title compound is the trifluoromethyl analogue. Structures have also been determined for the SMe (Yuan *et al.*, 1990), OMe (Nguyen *et al.*, 2002) and Me (Clegg *et al.*, 2004) derivatives.

(I)

The molecule of the title compound (Fig. 1) is approximately planar, except for the F atoms of the CF_3 group (which is disordered), with a high degree of conjugation. The r.m.s. deviation of the ordered atoms from their mean plane is 0.147 Å; this is rather greater than for the corresponding methyl-substituted compound and the parent compound. All torsion angles for non–F atoms are close to 0 and 180°, the largest corresponding to twists of about 5 and 9° around the B—C and C—C bonds linking the alkene double bond to the benzodioxaborole (Bcat) group and the trifluoromethylphenyl group (Table 1). As well as these small twisting distortions, the molecule is slightly bowed along its length.

The molecular geometry of this series of compounds has been discussed in the previous paper (Clegg *et al.*, 2004).
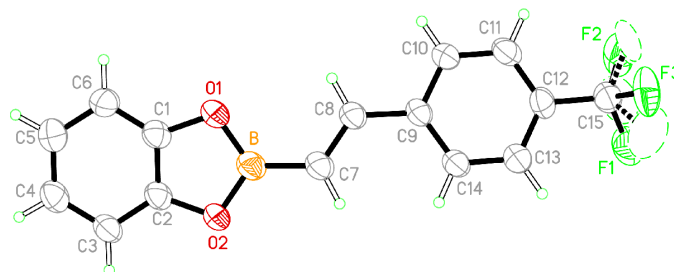

Figure 1
The molecular structure, with atom labels and 50% probability ellipsoids for non-H atoms. Minor disorder component atoms are not labelled.

organic papers

All the molecules in the triclinic crystal structure are parallel, with a separation of about 3.66 Å between pairs of adjacent molecules, indicating some π-stacking interaction (Figs. 2 and 3). This is different from the herring-bone packing arrangement found in other compounds in this series and typical of many planar organic molecules.

Experimental

4–Trifluoromethylphenylethyne (0.371 g, 2.18 mmol) and catecholborane (0.288 g, 2.4 mmol) were heated at 353 K for 3 h in a vial under a nitrogen atmosphere. The resulting yellow solid was recrystallized three times from diethyl ether/n-hexane, in a final yield of 380 mg (56%). Analysis calculated: C 62.12, H 3.47%; found: C 62.10, H 3.45%. Mass spectrum: 290 (M^+, 100%), 264 (7.1%), 172 (10.8%), 151 (8.2%), 145 (8.1%), 120 (23.0%). ^{1}H NMR (200 MHz): δ 6.56 (d, J = 18.4 Hz, 1H, H8), 7.12 (m, 2H, two of H3–H6), 7.27 (m, 2H, two of H3–H6), 7.67 (apparent s, 4H, H10–H14), 7.77 (d, J = 18.4 Hz, 1H, H7) (using the crystallographic numbering scheme of Fig. 1). ^{13}C{^{1}H} NMR (50 MHz): δ 112.5 (2C, C3 and C6), 122.9 (4C, C4, C5 and two of C10, C11, C13, C14), 125.7 (1C, C15), 126.7 (1C, C9), 127.5 (2C, two of C10, C11, C13, C14), 140.2 (1C, C12), 148.2 (2C, C1 and C2), 150.1 (1C, C8), resonance of C7 too broad to be observed. ^{11}B{^{1}H} NMR (64 MHz): δ 31.3.

Crystal data

$C_{15}H_{10}BF_3O_2$	$Z = 2$
$M_r = 290.04$	$D_x = 1.479$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.757$ (4) Å	Cell parameters from 2228
$b = 7.768$ (4) Å	reflections
$c = 12.578$ (7) Å	$\theta = 1.6–27.1°$
$\alpha = 93.581$ (12)°	$\mu = 0.12$ mm^{-1}
$\beta = 98.600$ (16)°	$T = 160$ (2) K
$\gamma = 91.084$ (15)°	Block, colourless
$V = 651.2$ (6) Å^3	$0.45 \times 0.40 \times 0.10$ mm

Data collection

Bruker SMART 1 K CCD diffractometer	1352 reflections with $I > 2\sigma(I)$
Thin-slice ω scans	$\theta_{max} = 25.0°$
Absorption correction: none	$h = -8 \rightarrow 7$
2252 measured reflections	$k = -9 \rightarrow 9$
2252 independent reflections	$l = -3 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1961P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.091$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.279$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
2252 reflections	$\Delta\rho_{min} = -0.40$ e Å^{-3}
225 parameters	Extinction correction: SHELXTL
H-atom parameters constrained	Extinction coefficient: 0.04 (2)

Table 1
Selected geometric parameters (Å, °).

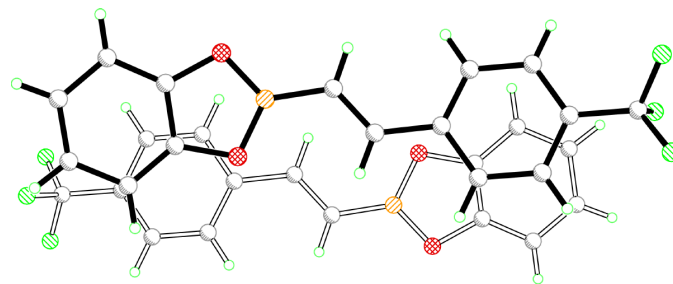|			
B—O1	1.405 (6)	B—C7	1.522 (7)
B—O2	1.394 (6)	C7—C8	1.339 (6)
O1—B—O2	110.9 (4)	B—O2—C2	104.7 (4)
O1—B—C7	124.6 (4)	B—C7—C8	123.9 (4)
O2—B—C7	124.5 (4)	C7—C8—C9	126.5 (4)
B—O1—C1	105.4 (3)		
O1—B—C7—C8	−5.2 (7)	C7—C8—C9—C10	170.2 (4)
O2—B—C7—C8	175.5 (5)	C7—C8—C9—C14	−8.2 (7)
B—C7—C8—C9	−175.4 (4)		

Figure 2
The overlap of adjacent molecules related by inversion symmetry, seen in projection normal to the mean plane of one molecule. One molecule is shown with filled bonds, and the other with hollow bonds.
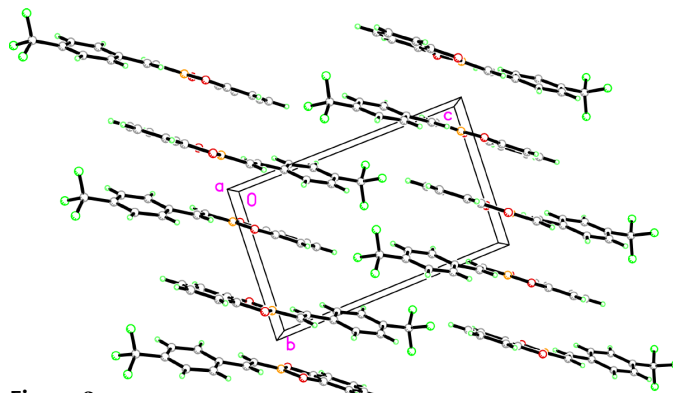

Figure 3
The crystal packing, viewed along the a axis.

H atoms were positioned geometrically and refined with a riding model, with C—H = 0.95 Å and with U_{iso}(H) = 1.2U_{eq}(C). The trifluoromethyl group is disordered, the two components being rotated by about 60° from each other around the C—C bond, with occupancy factors that refined to 0.883 (9):0.117 (9); restraints were applied to the geometry and displacement parameters. The crystal was found to be non-merohedrally twinned by 180° rotation about the [001] reciprocal lattice vector, with approximately equal contributions of the two components. The twinning was resolved with the aid of the programs ROTAX (Cooper et al., 2002) and ROTWIN (Pink & Young, 2000), and involved the refinement of six twin-component parameters applied to groups of reflections with different degrees of overlap; because of the twinning, equivalent reflections could not be merged before the refinement. The combination of twinning and disorder leads to relatively high R factors.

Data collection: SMART (Bruker, 2001); cell refinement: local programs; data reduction: SAINT (Bruker, 2001) and ROTWIN (Pink & Young, 2000); program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and local programs.

References

Bruker (2001). SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Clegg, W., Marder, T. B., Scott, A. J., Wiesauer, C. & Weissensteiner, W. (2001). Acta Cryst. E**57**, o63–o65.

Clegg, W., Scott, A. J., Marder, T. B., Wiesauer, C. & Weissensteiner, W. (2004). *Acta Cryst.* E**60**, o1172–o1174.

Cooper, R. I., Gould, R. O., Parson, S. & Watkin, D. J. (2002). *J. Appl. Cryst.* **35**, 168–174.

Nguyen, P., Coapes, R. B., Woodward, A. D., Taylor, N. J., Burke, J. M., Howard, J. A. K. & Marder, T. B. (2002). *J. Organomet. Chem.* **652**, 77–85.

Pink, M. & Young, V. G., Jr. (2000). *ROTWIN.* University of Minnesota, USA.

Sheldrick, G. M. (2001). *SHELXTL.* Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.

Wiesauer, C. (1997). Doctoral thesis, University of Vienna, Austria.

Yuan, Z., Taylor, N. J., Marder, T. B., Williams, I. D., Kurtz, S. K. & Cheng, L.-T. (1990). *J. Chem. Soc. Chem. Commun.* pp. 1489–1492.

supporting information

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$C_{15}H_{10}BF_3O_2$	$Z = 2$
$M_r = 290.04$	$F(000) = 296$
Triclinic, $P\bar{1}$	$D_x = 1.479$ Mg m^{-3}
$a = 6.757$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.768$ (4) Å	Cell parameters from 2228 reflections
$c = 12.578$ (7) Å	$\theta = 1.6$–27.1°
$\alpha = 93.581$ (12)°	$\mu = 0.12$ mm^{-1}
$\beta = 98.600$ (16)°	$T = 160$ K
$\gamma = 91.084$ (15)°	Block, colourless
$V = 651.2$ (6) Å^3	$0.45 \times 0.40 \times 0.10$ mm

Data collection

Bruker SMART 1K CCD diffractometer	2252 independent reflections
Radiation source: sealed tube	1352 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.000$
Detector resolution: 8.192 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.6°$
thin–slice ω scans	$h = -8 \rightarrow 7$
2252 measured reflections	$k = -9 \rightarrow 9$
	$l = -3 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.091$	$w = 1/[\sigma^2(F_o^2) + (0.1961P)^2]$
$wR(F^2) = 0.279$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2252 reflections	$\Delta\rho_{max} = 0.47$ e Å^{-3}
225 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
114 restraints	Extinction correction: SHELXTL, $Fc^* = kFc[1+0.001 x Fc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.04 (2)
Secondary atom site location: difference Fourier map	

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
B	0.1954 (8)	0.1947 (7)	0.4681 (4)	0.0454 (13)	
O1	0.3266 (4)	0.2942 (4)	0.5465 (2)	0.0465 (9)	

O2	−0.0021 (4)	0.2099 (4)	0.4863 (2)	0.0461 (9)	
C1	0.2049 (6)	0.3745 (5)	0.6139 (4)	0.0423 (11)	
C2	0.0086 (7)	0.3250 (5)	0.5764 (4)	0.0418 (11)	
C3	−0.1482 (7)	0.3849 (6)	0.6264 (4)	0.0483 (12)	
H3	−0.2834	0.3505	0.6006	0.058*	
C4	−0.0959 (7)	0.4987 (6)	0.7168 (4)	0.0502 (12)	
H4	−0.1981	0.5439	0.7539	0.060*	
C5	0.1016 (8)	0.5473 (6)	0.7539 (4)	0.0514 (13)	
H5	0.1322	0.6239	0.8163	0.062*	
C6	0.2567 (7)	0.4864 (6)	0.7017 (4)	0.0478 (12)	
H6	0.3922	0.5213	0.7262	0.057*	
C7	0.2603 (7)	0.0836 (6)	0.3761 (4)	0.0455 (12)	
H7	0.1612	0.0136	0.3307	0.055*	
C8	0.4489 (6)	0.0787 (5)	0.3554 (4)	0.0415 (11)	
H8	0.5474	0.1427	0.4049	0.050*	
C9	0.5190 (6)	−0.0160 (5)	0.2636 (3)	0.0401 (11)	
C10	0.7156 (7)	0.0144 (6)	0.2453 (4)	0.0439 (11)	
H10	0.8030	0.0888	0.2948	0.053*	
C11	0.7844 (7)	−0.0627 (6)	0.1556 (4)	0.0467 (12)	
H11	0.9169	−0.0386	0.1428	0.056*	
C12	0.6584 (7)	−0.1756 (5)	0.0844 (4)	0.0438 (11)	
C13	0.4648 (7)	−0.2103 (6)	0.1034 (4)	0.0487 (12)	
H13	0.3792	−0.2880	0.0552	0.058*	
C14	0.3965 (7)	−0.1321 (6)	0.1922 (4)	0.0446 (11)	
H14	0.2643	−0.1577	0.2048	0.054*	
C15	0.7339 (7)	−0.2619 (6)	−0.0099 (4)	0.0502 (12)	
F1	0.5875 (6)	−0.2947 (7)	−0.0955 (3)	0.0810 (17)	0.883 (9)
F2	0.8691 (9)	−0.1688 (6)	−0.0485 (4)	0.092 (2)	0.883 (9)
F3	0.8060 (8)	−0.4152 (5)	0.0083 (3)	0.0761 (16)	0.883 (9)
F1X	0.937 (2)	−0.277 (5)	0.016 (2)	0.085 (11)	0.117 (9)
F2X	0.675 (7)	−0.422 (3)	−0.038 (3)	0.116 (14)	0.117 (9)
F3X	0.716 (6)	−0.178 (4)	−0.096 (2)	0.092 (12)	0.117 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B	0.037 (3)	0.046 (3)	0.054 (3)	0.007 (2)	0.009 (2)	0.001 (2)
O1	0.0338 (18)	0.0529 (19)	0.0534 (19)	0.0065 (14)	0.0102 (15)	−0.0030 (15)
O2	0.0317 (17)	0.0528 (19)	0.0540 (19)	0.0039 (13)	0.0119 (14)	−0.0092 (15)
C1	0.037 (3)	0.038 (2)	0.052 (3)	0.0083 (19)	0.008 (2)	0.002 (2)
C2	0.038 (3)	0.036 (2)	0.053 (3)	0.0053 (18)	0.013 (2)	0.000 (2)
C3	0.039 (3)	0.052 (3)	0.056 (3)	0.002 (2)	0.017 (2)	0.000 (2)
C4	0.047 (3)	0.048 (3)	0.058 (3)	0.010 (2)	0.018 (2)	0.000 (2)
C5	0.057 (3)	0.049 (3)	0.050 (3)	0.006 (2)	0.014 (2)	0.002 (2)
C6	0.041 (3)	0.050 (3)	0.052 (3)	0.003 (2)	0.005 (2)	−0.002 (2)
C7	0.036 (3)	0.044 (3)	0.057 (3)	0.0062 (19)	0.009 (2)	−0.001 (2)
C8	0.035 (3)	0.039 (2)	0.050 (3)	0.0041 (18)	0.009 (2)	−0.001 (2)
C9	0.034 (2)	0.041 (2)	0.047 (2)	0.0073 (18)	0.009 (2)	0.001 (2)

C10	0.034 (2)	0.047 (3)	0.051 (3)	−0.0015 (19)	0.012 (2)	−0.002 (2)
C11	0.034 (3)	0.045 (3)	0.062 (3)	0.0060 (19)	0.012 (2)	0.004 (2)
C12	0.047 (3)	0.036 (2)	0.051 (3)	0.008 (2)	0.017 (2)	0.002 (2)
C13	0.043 (3)	0.048 (3)	0.057 (3)	0.001 (2)	0.014 (2)	−0.004 (2)
C14	0.035 (2)	0.043 (2)	0.057 (3)	0.0015 (19)	0.014 (2)	−0.002 (2)
C15	0.049 (3)	0.046 (3)	0.058 (3)	0.001 (2)	0.018 (2)	−0.002 (2)
F1	0.068 (3)	0.111 (4)	0.062 (2)	0.022 (2)	0.0093 (19)	−0.016 (2)
F2	0.112 (4)	0.078 (3)	0.099 (4)	−0.029 (3)	0.074 (4)	−0.023 (3)
F3	0.104 (4)	0.060 (3)	0.069 (3)	0.041 (2)	0.025 (3)	−0.002 (2)
F1X	0.061 (10)	0.13 (3)	0.065 (17)	0.045 (14)	0.017 (13)	−0.028 (17)
F2X	0.16 (3)	0.068 (14)	0.13 (3)	−0.04 (2)	0.07 (3)	−0.019 (16)
F3X	0.11 (3)	0.09 (2)	0.087 (18)	0.04 (2)	0.032 (18)	0.034 (16)

Geometric parameters (Å, º)

B—O1	1.405 (6)	C8—C9	1.472 (6)
B—O2	1.394 (6)	C9—C10	1.400 (6)
B—C7	1.522 (7)	C9—C14	1.398 (6)
O1—C1	1.395 (5)	C10—H10	0.950
O2—C2	1.391 (5)	C10—C11	1.390 (6)
C1—C2	1.378 (6)	C11—H11	0.950
C1—C6	1.361 (6)	C11—C12	1.393 (6)
C2—C3	1.384 (6)	C12—C13	1.388 (6)
C3—H3	0.950	C12—C15	1.486 (6)
C3—C4	1.395 (7)	C13—H13	0.950
C4—H4	0.950	C13—C14	1.382 (6)
C4—C5	1.383 (7)	C14—H14	0.950
C5—H5	0.950	C15—F1	1.357 (6)
C5—C6	1.392 (7)	C15—F2	1.322 (5)
C6—H6	0.950	C15—F3	1.316 (6)
C7—H7	0.950	C15—F1X	1.368 (14)
C7—C8	1.339 (6)	C15—F2X	1.308 (14)
C8—H8	0.950	C15—F3X	1.295 (14)
O1—B—O2	110.9 (4)	C8—C9—C14	123.0 (4)
O1—B—C7	124.6 (4)	C10—C9—C14	118.3 (4)
O2—B—C7	124.5 (4)	C9—C10—H10	119.6
B—O1—C1	105.4 (3)	C9—C10—C11	120.8 (4)
B—O2—C2	104.7 (4)	H10—C10—C11	119.6
O1—C1—C2	108.5 (4)	C10—C11—H11	120.1
O1—C1—C6	129.3 (4)	C10—C11—C12	119.8 (4)
C2—C1—C6	122.2 (4)	H11—C11—C12	120.1
O2—C2—C1	110.4 (4)	C11—C12—C13	119.9 (4)
O2—C2—C3	127.5 (4)	C11—C12—C15	119.7 (4)
C1—C2—C3	122.1 (4)	C13—C12—C15	120.4 (4)
C2—C3—H3	122.0	C12—C13—H13	119.9
C2—C3—C4	116.0 (4)	C12—C13—C14	120.2 (4)
H3—C3—C4	122.0	H13—C13—C14	119.9

C3—C4—H4	119.3	C9—C14—C13	121.0 (4)
C3—C4—C5	121.4 (5)	C9—C14—H14	119.5
H4—C4—C5	119.3	C13—C14—H14	119.5
C4—C5—H5	119.3	C12—C15—F1	112.6 (4)
C4—C5—C6	121.5 (5)	C12—C15—F2	113.9 (4)
H5—C5—C6	119.3	C12—C15—F3	113.7 (4)
C1—C6—C5	116.8 (4)	C12—C15—F1X	108.1 (11)
C1—C6—H6	121.6	C12—C15—F2X	117.9 (17)
C5—C6—H6	121.6	C12—C15—F3X	116.2 (15)
B—C7—H7	118.1	F1—C15—F2	103.8 (5)
B—C7—C8	123.9 (4)	F1—C15—F3	103.2 (4)
H7—C7—C8	118.1	F2—C15—F3	108.6 (5)
C7—C8—H8	116.7	F1X—C15—F2X	101.8 (18)
C7—C8—C9	126.5 (4)	F1X—C15—F3X	103.2 (17)
H8—C8—C9	116.7	F2X—C15—F3X	107.6 (19)
C8—C9—C10	118.7 (4)		

O2—B—O1—C1	−0.8 (5)	C7—C8—C9—C14	−8.2 (7)
C7—B—O1—C1	179.8 (4)	C8—C9—C10—C11	−175.6 (4)
O1—B—O2—C2	1.5 (5)	C14—C9—C10—C11	2.9 (7)
C7—B—O2—C2	−179.0 (4)	C9—C10—C11—C12	−1.8 (7)
B—O1—C1—C2	−0.3 (5)	C10—C11—C12—C13	0.0 (7)
B—O1—C1—C6	−179.1 (4)	C10—C11—C12—C15	−178.3 (4)
O1—C1—C2—O2	1.2 (5)	C11—C12—C13—C14	0.5 (7)
O1—C1—C2—C3	−179.6 (4)	C15—C12—C13—C14	178.8 (4)
C6—C1—C2—O2	−179.8 (4)	C12—C13—C14—C9	0.7 (7)
C6—C1—C2—C3	−0.6 (7)	C8—C9—C14—C13	176.1 (4)
B—O2—C2—C1	−1.7 (5)	C10—C9—C14—C13	−2.3 (7)
B—O2—C2—C3	179.2 (5)	C11—C12—C15—F1	−149.5 (5)
O2—C2—C3—C4	179.2 (4)	C11—C12—C15—F2	−31.6 (7)
C1—C2—C3—C4	0.2 (6)	C11—C12—C15—F3	93.5 (5)
C2—C3—C4—C5	−0.3 (7)	C11—C12—C15—F1X	28 (2)
C3—C4—C5—C6	0.8 (7)	C11—C12—C15—F2X	142 (2)
O1—C1—C6—C5	179.8 (4)	C11—C12—C15—F3X	−88 (2)
C2—C1—C6—C5	1.1 (7)	C13—C12—C15—F1	32.2 (6)
C4—C5—C6—C1	−1.2 (7)	C13—C12—C15—F2	150.1 (5)
O1—B—C7—C8	−5.2 (7)	C13—C12—C15—F3	−84.8 (6)
O2—B—C7—C8	175.5 (5)	C13—C12—C15—F1X	−151 (2)
B—C7—C8—C9	−175.4 (4)	C13—C12—C15—F2X	−36 (3)
C7—C8—C9—C10	170.2 (4)	C13—C12—C15—F3X	94 (2)