organic compounds

4-Fluoro-2-[(3-methylphenyl)imino-methyl]phenol

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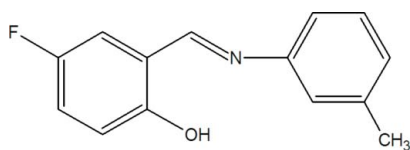
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The title compound, $C_{14}H_{12}FNO$, crystallizes as the *trans* phenol–imine tautomer. The two benzene rings are essentially coplanar, being inclined to one another by 9.28 (7)°. This is at least in part due to the intramolecular O—H···N hydrogen bond between the hydroxy O atom and the imine N atom. The crystal structure is stabilized by an array of weak C—H···O and C—H···F interactions, which link the molecules into a stable three-dimensional network.

Related literature

For related structures, see: Karakaş *et al.* (2004); Arod *et al.* (2005); Cheng *et al.* (2005); Brink *et al.* (2009). For related rhenium tricarbonyl complexes containing salicylaldimines, see: Brink *et al.* (2011). For related *N,O*-bidentate ligands coordinated to a rhenium tricarbonyl core, see: Schutte *et al.* (2011).

Experimental

Crystal data

$C_{14}H_{12}FNO$	$V = 548.37$ (5) Å^3
$M_r = 229.25$	$Z = 2$
Monoclinic, Pc	Mo $K\alpha$ radiation
$a = 10.2655$ (6) Å	$\mu = 0.10$ mm^{-1}
$b = 4.6738$ (2) Å	$T = 100$ K
$c = 12.3561$ (8) Å	$0.19 \times 0.1 \times 0.06$ mm
$\beta = 112.331$ (3)°	

Data collection

Bruker X8 APEXII 4K Kappa CCD diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2004) $T_{min} = 0.981$, $T_{max} = 0.994$
	7009 measured reflections

1319 independent reflections
1203 reflections with $I > 2\sigma(I)$

$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	2 restraints
$wR(F^2) = 0.095$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{max} = 0.19$ e Å^{-3}
1319 reflections	$\Delta\rho_{min} = -0.19$ e Å^{-3}
156 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1B···N1	0.84	1.85	2.601 (2)	147
C1—H1A···O1^i	0.95	2.6	3.467 (3)	151
C16—H16···O1^i	0.95	2.65	3.495 (3)	149
C13—H13···F1^{ii}	0.95	2.6	3.472 (3)	153
C231—H23A···F1^{iii}	0.98	2.73	3.321 (3)	119
C231—H23C···F1^{iv}	0.98	2.67	3.193 (2)	114

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: WingGX (Farrugia, 1999).

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4-Fluoro-2-[(3-methylphenyl)iminomethyl]phenol

Alice Brink, Hendrik G. Visser and Andreas Roodt

Comment

Schiff-base ligands have played a significant role in the development of coordination chemistry as stable organometallic complexes are readily formed with a variety of transition metals. In continuation of our research on the coordination of various bifunctional chelate systems on the *fac*-[*M*(CO)$_3$]$^+$ moiety (*M* = Re(I), Tc(I)) (Brink *et al.*, 2011; Schutte *et al.*, 2011) the title compound was synthesized and is reported here.

The title compound (Figure 1) is essentially co-planar with a dihedral angle of 9.28 (7)° between the aromatic rings. The bond distances and angles in the title compound are in accord with those reported for related salicylaldimine-based ligand systems (Karakaş *et al.*, 2004; Arod *et al.*, 2005; Cheng *et al.*, 2005; Brink *et al.*, 2009).

The compound crystallizes as the *trans* phenol-imine tautomer. A strong intramolecular hydrogen bond occurs between the O—H⋯N atoms in each unique molecule. The crystal structure is stabilized by an array of weak C—H⋯O and C—H⋯F interactions. The bifurcated acceptor, O1, experiences weak hydrogen bond interactions with H16 and H1A. As a result, the two independent molecules pack nearly perpendicular to each other with a dihedral angle of 88.01 (5)° between planes drawn through the C1 aromatic ring systems (Figures 2 and 3). All the interactions serve to link the molecules into a stable three-dimensional supramolecular network. The molecular packing, viewed along the *c*-axis, illustrates the cube-like tunnel formation resulting from the various interactions (Figure 4).
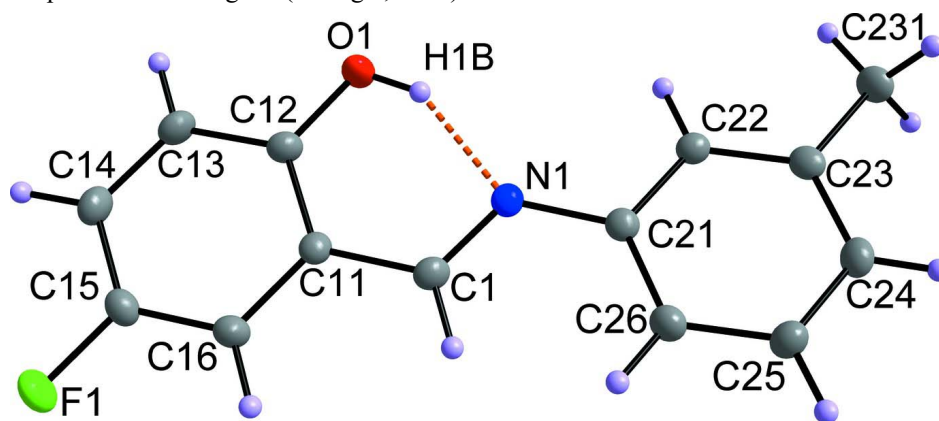
Experimental

The reaction was performed under Schlenk conditions using a nitrogen atmosphere. To a solution of 5-fluorosalicyl-aldehyde (0.50 g, 3.57 mmol) in methanol, a solution of *m*-toluidine (0.382 g, 3.57 mmol) was added. The reaction was refluxed at 80°C for 3 h. The solvent was removed under reduced pressure. The product was obtained as an orange solid which was washed with cold methanol and filtered. Crystals suitable for X-ray diffraction were grown from the filtrate. Yield 82.1%. ^{1}H NMR [acetone-d_6, 600 MHz, δ (p.p.m.)] 13.04 (s, 1H), 8.90 (s, 1H), 7.40 (dd, 1H, *J* = 3.1, 8.7 Hz), 7.35 (t, 1H, *J* = 7.7 Hz), 7.25 (s, 1H), 7.24–7.20 (m, 2H), 7.16 (d, 1H, *J* = 7.7 Hz), 6.96 (dd, 1H, *J* = 4.5, 9.1 Hz), 2.39 (s, 3H, CH$_3$).

Refinement

The aromatic H atoms and hydroxy H atom were placed in geometrically idealized positions and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C) and 1.5$_{eq}$(O).The aliphatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C) and 1.5$_{eq}$(C), respectively for the methyl-ene and methyl carbon atoms. The methyl groups were generated to fit the difference electron density and the groups were then refined as rigid rotors. The absolute structure parameter is meaningless and has been removed from the CIF. The Friedel opposites have been merged as the compound is a weak anomalous scatterer.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: WingGX (Farrugia, 1999).

Figure 1

Representation of the molecular structure of the title compound, showing the numbering scheme and displacement ellipsoids drawn at the 50% probability level.

Figure 2

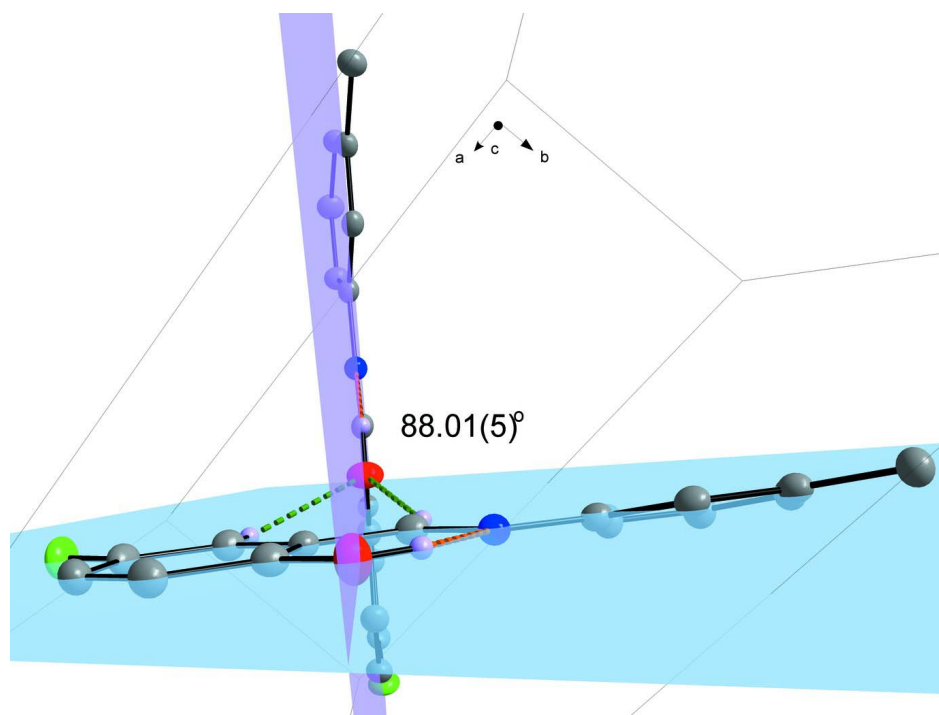Representation of the hydrogen-bond interactions (only relevant H atoms are shown).

Figure 3

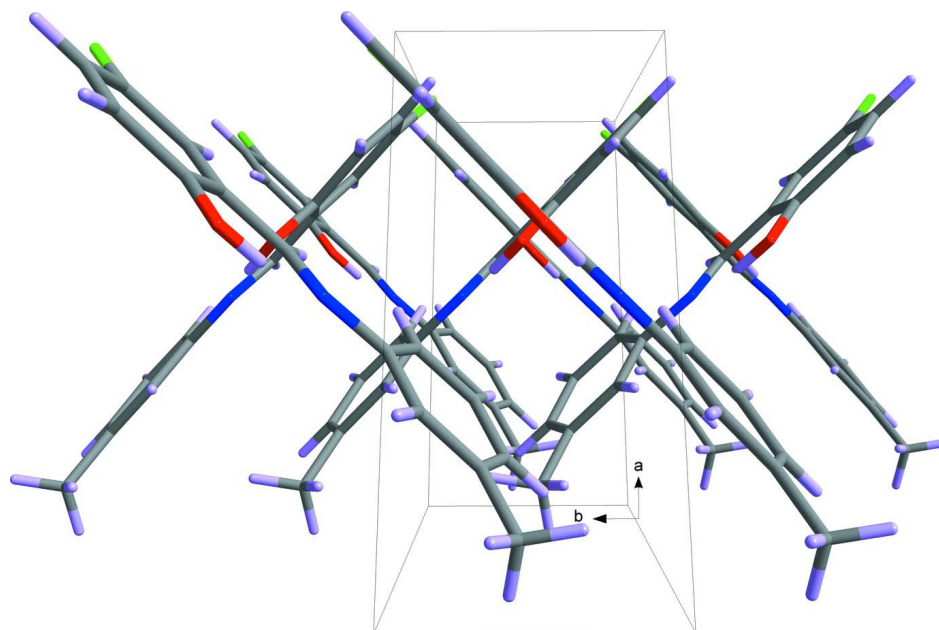Representation of the perpendicular orientation of molecules.

Figure 4

Molecular packing of the unit cell illustrating the cube-like formation as viewed along the *c*-axis.

4-Fluoro-2-[(3-methylphenyl)iminomethyl]phenol

Crystal data

$C_{14}H_{12}FNO$	$F(000) = 240$
$M_r = 229.25$	$D_x = 1.388$ Mg m^{-3}
Monoclinic, Pc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P -2yc	Cell parameters from 2573 reflections
$a = 10.2655$ (6) Å	$\theta = 3.4–28.3°$
$b = 4.6738$ (2) Å	$\mu = 0.10$ mm^{-1}
$c = 12.3561$ (8) Å	$T = 100$ K
$\beta = 112.331$ (3)°	Cuboid, orange
$V = 548.37$ (5) Å^3	$0.19 × 0.1 × 0.06$ mm
$Z = 2$	

Data collection

Bruker X8 APEXII 4K Kappa CCD diffractometer	7009 measured reflections
Graphite monochromator	1319 independent reflections
Detector resolution: 512 pixels mm^{-1}	1203 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.028$
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	$\theta_{max} = 28.0°$, $\theta_{min} = 3.4°$
$T_{min} = 0.981$, $T_{max} = 0.994$	$h = -13\rightarrow13$
	$k = -5\rightarrow6$
	$l = -16\rightarrow16$

Refinement

Refinement on F^2	2 restraints
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.0513P]$
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
1319 reflections	$\Delta\rho_{max} = 0.19$ e Å^{-3}
156 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Experimental. Intensity data was collected on a Bruker X8 Apex II 4 K Kappa CCD diffractometer using an exposure time of 55 s/frame. A total of 1495 frames were collected with a frame width of 0.5° covering up to $\theta = 28.0°$ with 99.6% completeness accomplished

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.

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

	x	y	z	U_{iso}*/U_{eq}
N1	0.51676 (18)	0.7931 (4)	0.51611 (15)	0.0170 (4)
O1	0.62483 (16)	0.5330 (3)	0.71672 (14)	0.0229 (4)
H1B	0.571	0.6442	0.666	0.034*
F1	0.95777 (14)	−0.0665 (3)	0.54083 (13)	0.0276 (3)
C1	0.5962 (2)	0.6410 (4)	0.47953 (19)	0.0178 (4)
H1A	0.5897	0.6626	0.4012	0.021*
C11	0.6955 (2)	0.4372 (4)	0.55563 (18)	0.0161 (4)
C12	0.7069 (2)	0.3900 (4)	0.67131 (18)	0.0183 (4)

C13	0.8048 (2)	0.1934 (5)	0.74184 (18)	0.0211 (5)
H13	0.8132	0.1637	0.8203	0.025*
C14	0.8897 (2)	0.0416 (5)	0.6980 (2)	0.0219 (5)
H14	0.9567	−0.0919	0.7458	0.026*
C15	0.8756 (2)	0.0873 (4)	0.5839 (2)	0.0195 (5)
C16	0.7817 (2)	0.2812 (5)	0.51227 (19)	0.0181 (4)
H16	0.7753	0.3092	0.4343	0.022*
C21	0.4220 (2)	0.9970 (4)	0.44138 (18)	0.0168 (4)
C22	0.3265 (2)	1.1211 (4)	0.48298 (18)	0.0171 (4)
H22	0.3286	1.0669	0.5577	0.021*
C23	0.2280 (2)	1.3232 (5)	0.41733 (18)	0.0189 (4)
C24	0.2290 (2)	1.4038 (5)	0.30877 (18)	0.0209 (5)
H24	0.163	1.541	0.2625	0.025*
C25	0.3257 (2)	1.2853 (5)	0.26779 (19)	0.0223 (5)
H25	0.3258	1.3445	0.1943	0.027*
C26	0.4219 (2)	1.0818 (4)	0.33261 (19)	0.0205 (5)
H26	0.4871	1.0008	0.3036	0.025*
C231	0.1250 (2)	1.4526 (5)	0.4626 (2)	0.0227 (5)
H23A	0.1367	1.3641	0.5377	0.034*
H23B	0.0289	1.4194	0.4063	0.034*
H23C	0.1422	1.6588	0.4736	0.034*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0165 (8)	0.0168 (8)	0.0174 (9)	−0.0004 (6)	0.0061 (7)	0.0005 (6)
O1	0.0264 (8)	0.0271 (8)	0.0181 (7)	0.0081 (6)	0.0116 (7)	0.0032 (6)
F1	0.0278 (7)	0.0264 (7)	0.0320 (7)	0.0092 (5)	0.0154 (6)	0.0010 (6)
C1	0.0200 (10)	0.0174 (8)	0.0165 (10)	−0.0022 (8)	0.0075 (8)	0.0011 (8)
C11	0.0166 (10)	0.0141 (9)	0.0164 (10)	−0.0015 (7)	0.0050 (8)	−0.0008 (8)
C12	0.0190 (10)	0.0193 (10)	0.0170 (10)	−0.0024 (8)	0.0074 (9)	−0.0012 (8)
C13	0.0228 (11)	0.0231 (10)	0.0157 (10)	−0.0005 (9)	0.0053 (9)	0.0034 (8)
C14	0.0201 (11)	0.0207 (10)	0.0212 (11)	0.0009 (8)	0.0036 (9)	0.0019 (8)
C15	0.0166 (10)	0.0191 (10)	0.0244 (12)	0.0003 (8)	0.0096 (9)	−0.0018 (8)
C16	0.0194 (10)	0.0192 (10)	0.0178 (10)	−0.0010 (8)	0.0095 (8)	−0.0006 (7)
C21	0.0171 (10)	0.0154 (9)	0.0177 (10)	−0.0020 (8)	0.0063 (8)	−0.0010 (7)
C22	0.0184 (10)	0.0163 (9)	0.0165 (10)	−0.0023 (7)	0.0066 (8)	−0.0006 (8)
C23	0.0168 (10)	0.0188 (10)	0.0200 (11)	−0.0025 (8)	0.0059 (8)	−0.0034 (8)
C24	0.0181 (11)	0.0193 (10)	0.0219 (11)	0.0017 (8)	0.0039 (9)	0.0011 (8)
C25	0.0240 (12)	0.0248 (11)	0.0186 (10)	0.0027 (8)	0.0086 (9)	0.0038 (8)
C26	0.0206 (10)	0.0217 (10)	0.0209 (11)	0.0022 (8)	0.0098 (9)	0.0001 (8)
C231	0.0192 (10)	0.0244 (10)	0.0247 (11)	0.0015 (8)	0.0086 (9)	−0.0019 (9)

Geometric parameters (Å, º)

N1—C1	1.287 (3)	C21—C22	1.395 (3)
N1—C21	1.422 (3)	C21—C26	1.401 (3)
O1—C12	1.353 (3)	C21—N1	1.422 (3)
O1—H1B	0.84	C22—C23	1.396 (3)
F1—C15	1.361 (2)	C22—H22	0.95

C1—C11	1.450 (3)	C23—C24	1.397 (3)
C1—H1A	0.95	C23—C231	1.499 (3)
C11—C16	1.401 (3)	C24—C25	1.389 (3)
C11—C12	1.407 (3)	C24—H24	0.95
C12—C13	1.396 (3)	C25—C26	1.386 (3)
C13—C14	1.385 (3)	C25—H25	0.95
C13—H13	0.95	C26—H26	0.95
C14—C15	1.377 (3)	C231—H23A	0.98
C14—H14	0.95	C231—H23B	0.98
C15—C16	1.373 (3)	C231—H23C	0.98
C16—H16	0.95		
C1—N1—C21	120.69 (16)	C26—C21—N1	124.30 (18)
C12—O1—H1B	109.5	C22—C21—N1	116.25 (17)
N1—C1—C11	121.23 (18)	C26—C21—N1	124.30 (18)
N1—C1—H1A	119.4	C21—C22—C23	121.53 (18)
C11—C1—H1A	119.4	C21—C22—H22	119.2
C16—C11—C12	119.11 (19)	C23—C22—H22	119.2
C16—C11—C1	118.98 (18)	C22—C23—C24	118.16 (18)
C12—C11—C1	121.91 (18)	C22—C23—C231	120.94 (18)
O1—C12—C13	118.70 (18)	C24—C23—C231	120.90 (19)
O1—C12—C11	121.31 (19)	C25—C24—C23	120.63 (19)
C13—C12—C11	119.99 (19)	C25—C24—H24	119.7
C14—C13—C12	120.27 (19)	C23—C24—H24	119.7
C14—C13—H13	119.9	C26—C25—C24	120.94 (19)
C12—C13—H13	119.9	C26—C25—H25	119.5
C15—C14—C13	118.9 (2)	C24—C25—H25	119.5
C15—C14—H14	120.5	C25—C26—C21	119.3 (2)
C13—C14—H14	120.5	C25—C26—H26	120.4
F1—C15—C16	118.91 (19)	C21—C26—H26	120.4
F1—C15—C14	118.57 (19)	C23—C231—H23A	109.5
C16—C15—C14	122.5 (2)	C23—C231—H23B	109.5
C15—C16—C11	119.17 (19)	H23A—C231—H23B	109.5
C15—C16—H16	120.4	C23—C231—H23C	109.5
C11—C16—H16	120.4	H23A—C231—H23C	109.5
C22—C21—C26	119.44 (19)	H23B—C231—H23C	109.5
C22—C21—N1	116.25 (17)		
N1—N1—C1—C11	0.0 (6)	N1—N1—C21—C22	0.0 (6)
C21—N1—C1—C11	178.58 (17)	C1—N1—C21—C22	171.08 (18)
N1—C1—C11—C16	−178.66 (18)	N1—N1—C21—C26	0.0 (7)
N1—C1—C11—C12	1.9 (3)	C1—N1—C21—C26	−10.4 (3)
C16—C11—C12—O1	−179.24 (18)	C1—N1—C21—N1	0E1 (10)
C1—C11—C12—O1	0.2 (3)	C26—C21—C22—C23	1.7 (3)
C16—C11—C12—C13	1.1 (3)	N1—C21—C22—C23	−179.74 (17)
C1—C11—C12—C13	−179.45 (19)	N1—C21—C22—C23	−179.74 (17)
O1—C12—C13—C14	179.49 (19)	C21—C22—C23—C24	−1.3 (3)
C11—C12—C13—C14	−0.8 (3)	C21—C22—C23—C231	179.38 (19)
C12—C13—C14—C15	−0.2 (3)	C22—C23—C24—C25	0.0 (3)

C13—C14—C15—F1	−178.87 (18)	C231—C23—C24—C25	179.33 (19)
C13—C14—C15—C16	1.0 (3)	C23—C24—C25—C26	0.9 (3)
F1—C15—C16—C11	179.14 (17)	C24—C25—C26—C21	−0.5 (3)
C14—C15—C16—C11	−0.8 (3)	C22—C21—C26—C25	−0.7 (3)
C12—C11—C16—C15	−0.3 (3)	N1—C21—C26—C25	−179.19 (19)
C1—C11—C16—C15	−179.79 (18)	N1—C21—C26—C25	−179.19 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···N1	0.84	1.85	2.601 (2)	147
C1—H1*A*···O1[i]	0.95	2.6	3.467 (3)	151
C16—H16···O1[i]	0.95	2.65	3.495 (3)	149
C13—H13···F1[ii]	0.95	2.6	3.472 (3)	153
C231—H23*A*···F1[iii]	0.98	2.73	3.321 (3)	119
C231—H23*C*···F1[iv]	0.98	2.67	3.193 (2)	114

Symmetry codes: (i) x, $-y+1$, $z-1/2$; (ii) x, $-y$, $z+1/2$; (iii) $x-1$, $y+1$, z; (iv) $x-1$, $y+2$, z.