

# Crystal structure and C—H···F hydrogen bonding in the fluorinated bis-benzoxazine: 3,3'-(ethane-1,2-diyl)bis(6-fluoro-3,4-dihydro-2H-1,3-benzoxazine)

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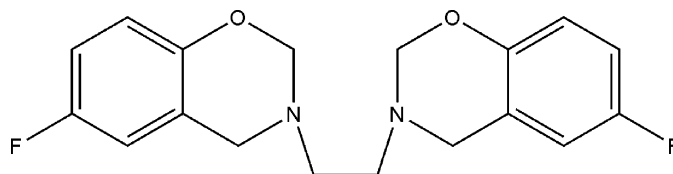
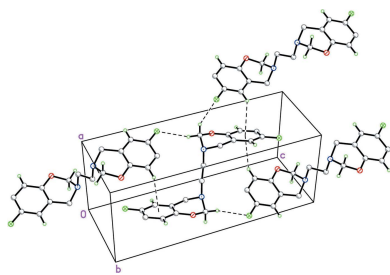
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The title fluorinated bisbenzoxazine, C<sub>18</sub>H<sub>18</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, crystallizes with one half-molecule in the asymmetric unit, which is completed by inversion symmetry. The fused oxazine ring adopts an approximately half-chair conformation. The two benzoxazine rings are oriented *anti* to one another around the central C—C bond. The dominant intermolecular interaction in the crystal structure is a C—H···F hydrogen bond between the F atoms and the axial H atoms of the OCH<sub>2</sub>N methylene group in the oxazine rings of neighbouring molecules. C—H···π contacts further stabilize the crystal packing.

## 1. Chemical context

Even though benzoxazines have been known for more than 60 years, a cursory look at the literature cited in relation to the polybenzoxazines in recent years reveals increasing interest in polybenzoxazine chemistry (Demir *et al.*, 2013). Mannich condensation of a phenol and a primary amine with formaldehyde is perhaps the best synthetic route widely employed for the preparation of a variety of benzoxazine monomers. Mono-functional benzoxazines with one oxazine ring yield linear polymers, while bi- and polyfunctional benzoxazines produce cross-linked polymers. As a result, many kinds of benzoxazine monomers, including both mono-benzoxazines and bis-benzoxazines, have been synthesized. For composite applications, bifunctional benzoxazines are important as they produce fillers with good adhesion properties that in turn give high modulus composite materials (Santhosh-Kumar & Reghunadhan-Nair, 2014).



Much work in our group has been directed at the synthesis of a wide variety of bis-benzoxazines from ethylenediamine, formaldehyde and phenols in the molar ratio of 1:4:2 using a conventional method and solvent-free conditions (Rivera *et al.*, 1989). Recently, we have also investigated the crystal structures of several bis-benzoxazines namely 3,3'-(ethane-1,2-diyl)bis(6-substituted-3,4-dihydro-2H-1,3-benzoxazine)

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

*Cg*2 is the centroid of the C3/C4/C6/C7/C8/C9 ring

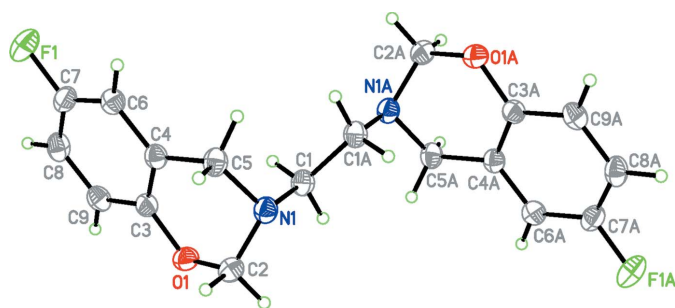
| <i>D</i> —H... <i>A</i>             | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------------|-------------|---------------|-----------------------|-------------------------|
| C2—H2A...F1 <sup>i</sup>            | 0.99        | 2.44          | 3.300 (2)             | 145                     |
| C6—H6... <i>Cg</i> 2 <sup>ii</sup>  | 0.95        | 2.88          | 3.527 (2)             | 126                     |
| C9—H9... <i>Cg</i> 2 <sup>iii</sup> | 0.95        | 2.90          | 3.577 (2)             | 129                     |

Symmetry codes: (i)  $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .

derivatives (Rivera *et al.*, 2010, 2011, 2012*a,b*). These were prepared to determine whether replacement of the substituents at the *para* position of the phenol affects the molecular conformation and possible supramolecular aggregation. In this context, the title compound is a model for studying non-conventional molecular interactions where the halogen atom may act as a hydrogen-bond acceptor. Although debate has surrounded the role of fluorine as a hydrogen-bond (HB) acceptor, the presence of such weak molecular interactions in the solid state has been the subject of both theoretical and spectroscopic studies (Dalvit & Vulpetti, 2016). However, to the best of our knowledge, there are few examples of X-ray studies. On the other hand, polymers containing fluorinated aromatic systems often exhibit exceptional thermal stability and show good water-repellent properties (Su & Chang, 2003). Therefore we report herein the crystal structure of 3,3'-(ethane-1,2-diyl)bis(6-fluoro-3,4-dihydro-2*H*-1,3-benzoxazine) (I), which is a very good candidate as a monomer for the investigation of the polymerization of fluorine-containing bis-benzoxazine monomers.

## 2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The asymmetric unit contains one-half of the formula unit; a centre of inversion located at the mid-point of the central C1—C1<sup>i</sup> bond generates the other half of the bis-benzoxazine compound [symmetry code: (i)  $1 - x, 1 - y, 1 - z$ ]. Bond lengths in the benzoxazine moiety in (I) are within normal ranges and are comparable to those found in related structures (Rivera *et al.*, 2012*a,b*, 2011; Chen & Wu, 2007).



**Figure 1**  
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Atoms labelled with the suffix A are generated using the symmetry operator  $(-x + 1, -y + 1, -z + 1)$ .

The fused six-membered heterocyclic rings exist in an approximately half-chair conformation, characterized by a puckering amplitude  $Q = 0.4913(15)$  Å, and  $\theta = 52.03(17)^\circ$  and  $\varphi = 98.3(2)^\circ$ , with C2 and N1 displaced from the mean plane by  $-0.299(2)$  and  $0.331(1)$  Å, respectively. The C1—C1A bond is in an axial position with a C5—N1—C1—C1A torsion angle of  $75.45(18)^\circ$ . The two benzoxazine rings are oriented *anti* to one another about the central C1—C1A bond, with an N1—C1—C1A—N1A torsion angle of  $180.0(2)^\circ$ .

## 3. Supramolecular features

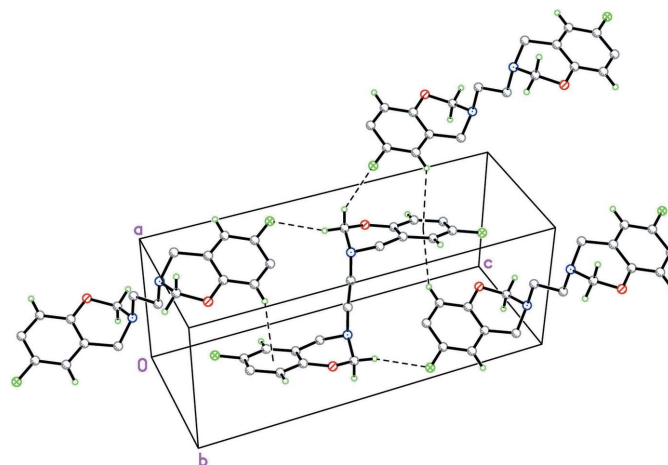
The packing of title compound is dominated by C2—H2A...F1 hydrogen bonds (Table 1), that connect the molecules into a sheet structure, Fig. 2. Symmetry dictates that both F atoms are involved in these hydrogen bonds. The crystal structure also features two weak C—H... $\pi$  interactions (Table 1), as indicated in *PLATON* (Spek, 2009), with C—H...*Cg* distances of  $3.527(2)$  and  $3.577(2)$  Å and with C—H...*Cg* angles of  $126$  and  $129^\circ$ , respectively.

## 4. Database survey

A database search yielded four comparable structures, 3,3'-(ethane-1,2-diyl)bis(6-methyl-3,4-dihydro-2*H*-1,3-benzoxazine) (AXAKAM; Rivera *et al.*, 2011), 3,3'-ethylenebis(3,4-dihydro-6-chloro-2*H*-1,3-benzoxazine) (NUQKAM; Rivera *et al.*, 2010), 3,3'-(ethane-1,2-diyl)-bis(6-methoxy-3,4-dihydro-2*H*-1,3-benzoxazine) monohydrate (QEDDOU; Rivera *et al.*, 2012*b*), and 3,3'-(ethane-1,2-diyl)bis(3,4-dihydro-2*H*-1,3-benzoxazine) (SAGPUN; Rivera *et al.*, 2012*a*).

## 5. Synthesis and crystallization

The title compound was synthesized according to the literature procedure (Rivera *et al.*, 1989), and single crystals were obtained by slow evaporation from an ethyl acetate/benzene 1:3 solvent mixture at room temperature.



**Figure 2**  
Packing diagram for title compound, viewed along the *b* axis. C—H...F and C—F... $\pi$  contacts are drawn as dashed lines.

**Table 2**  
Experimental details.

|  |  |
|--|--|
| Crystal data   |  |
| Chemical formula   | C <sub>18</sub> H <sub>18</sub> F <sub>2</sub> N <sub>2</sub> O <sub>2</sub> |
| <i>M</i> <sub>r</sub>  | 332.34   |
| Crystal system, space group  | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>                               |
| Temperature (K)  | 173  |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)   | 7.0242 (6), 6.2316 (6), 17.1574 (15)   |
| β (°)  | 91.473 (7)   |
| <i>V</i> (Å <sup>3</sup> )   | 750.77 (12)  |
| <i>Z</i>   | 2  |
| Radiation type   | Mo <i>K</i> α  |
| μ (mm <sup>-1</sup> )  | 0.11   |
| Crystal size (mm)  | 0.17 × 0.13 × 0.04   |
| Data collection  |  |
| Diffractometer   | Stoe <i>IPDS</i> II two-circle   |
| Absorption correction  | Multi-scan ( <i>X-AREA</i> ; Stoe & Cie, 2001)                               |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>  | 0.362, 1.000   |
| No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                             | 7746, 1532, 1285   |
| <i>R</i> <sub>int</sub>  | 0.036  |
| (sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )  | 0.625  |
| Refinement   |  |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.041, 0.101, 1.08   |
| No. of reflections   | 1532   |
| No. of parameters  | 109  |
| H-atom treatment   | H-atom parameters constrained  |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )   | 0.18, -0.16  |

Computer programs: *X-AREA* (Stoe & Cie, 2001), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *XP* in *SHELXTL-Plus* (Sheldrick, 2008).

## 6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in difference electron-density maps. C-bound H atoms were fixed geometrically (C–H = 0.95 or 0.99 Å) and refined using a

riding-model approximation, with *U*<sub>iso</sub>(H) set to 1.2*U*<sub>eq</sub> of the parent atom.

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## supporting information

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## Crystal structure and C—H $\cdots$ F hydrogen bonding in the fluorinated bis-benzoxazine: 3,3'-(ethane-1,2-diyl)bis(6-fluoro-3,4-dihydro-2H-1,3-benzoxazine)

Augusto Rivera, Jicli José Rojas, Jaime Ríos-Motta and Michael Bolte

### Computing details

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA* (Stoe & Cie, 2001); data reduction: *X-AREA* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

### 3,3'-(Ethane-1,2-diyl)bis(6-fluoro-3,4-dihydro-2H-1,3-benzoxazine)

#### Crystal data

C<sub>18</sub>H<sub>18</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>

$M_r = 332.34$

Monoclinic, *P2<sub>1</sub>/c*

$a = 7.0242$  (6) Å

$b = 6.2316$  (6) Å

$c = 17.1574$  (15) Å

$\beta = 91.473$  (7)°

$V = 750.77$  (12) Å<sup>3</sup>

$Z = 2$

$F(000) = 348$

$D_x = 1.470$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 7746 reflections

$\theta = 3.5\text{--}27.8^\circ$

$\mu = 0.11$  mm<sup>-1</sup>

$T = 173$  K

Plate, colourless

0.17 × 0.13 × 0.04 mm

#### Data collection

Stoe IPDS II two-circle diffractometer

Radiation source: Genix 3D I $\mu$ S microfocus X-ray source

$\omega$  scans

Absorption correction: multi-scan (X-AREA; Stoe & Cie, 2001)

$T_{\min} = 0.362$ ,  $T_{\max} = 1.000$

7746 measured reflections

1532 independent reflections

1285 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 26.4^\circ$ ,  $\theta_{\min} = 3.5^\circ$

$h = -8 \rightarrow 8$

$k = -7 \rightarrow 7$

$l = -20 \rightarrow 21$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.101$

$S = 1.08$

1532 reflections

109 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.1464P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.18$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.16$  e Å<sup>-3</sup>

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|     | <i>x</i>     | <i>y</i>     | <i>z</i>    | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|-------------|----------------------------------|
| F1  | 0.80087 (14) | 0.60837 (18) | 0.86796 (5) | 0.0408 (3)                       |
| O1  | 0.69940 (16) | 0.06550 (17) | 0.61834 (6) | 0.0293 (3)                       |
| N1  | 0.73058 (17) | 0.3605 (2)   | 0.52754 (7) | 0.0256 (3)                       |
| C1  | 0.5232 (2)   | 0.3961 (2)   | 0.52148 (8) | 0.0260 (3)                       |
| H1A | 0.4706       | 0.4020       | 0.5744      | 0.031*                           |
| H1B | 0.4624       | 0.2743       | 0.4934      | 0.031*                           |
| C2  | 0.7756 (2)   | 0.1410 (3)   | 0.54504 (9) | 0.0294 (4)                       |
| H2A | 0.9158       | 0.1242       | 0.5471      | 0.035*                           |
| H2B | 0.7249       | 0.0493       | 0.5022      | 0.035*                           |
| C3  | 0.72790 (19) | 0.2069 (2)   | 0.67944 (8) | 0.0237 (3)                       |
| C4  | 0.79289 (19) | 0.4168 (2)   | 0.66810 (8) | 0.0228 (3)                       |
| C5  | 0.8283 (2)   | 0.4965 (3)   | 0.58624 (8) | 0.0267 (3)                       |
| H5A | 0.7820       | 0.6459       | 0.5809      | 0.032*                           |
| H5B | 0.9668       | 0.4961       | 0.5770      | 0.032*                           |
| C6  | 0.81932 (19) | 0.5507 (3)   | 0.73252 (8) | 0.0250 (3)                       |
| H6  | 0.8647       | 0.6931       | 0.7263      | 0.030*                           |
| C7  | 0.7786 (2)   | 0.4732 (3)   | 0.80519 (8) | 0.0273 (3)                       |
| C8  | 0.7114 (2)   | 0.2675 (3)   | 0.81752 (9) | 0.0293 (4)                       |
| H8  | 0.6837       | 0.2193       | 0.8685      | 0.035*                           |
| C9  | 0.6854 (2)   | 0.1337 (3)   | 0.75374 (9) | 0.0269 (3)                       |
| H9  | 0.6386       | -0.0079      | 0.7606      | 0.032*                           |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|    | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|----|------------|------------|------------|-------------|-------------|-------------|
| F1 | 0.0442 (6) | 0.0526 (7) | 0.0255 (5) | -0.0053 (5) | 0.0007 (4)  | -0.0122 (4) |
| O1 | 0.0393 (6) | 0.0227 (6) | 0.0258 (6) | -0.0001 (4) | 0.0008 (4)  | -0.0013 (4) |
| N1 | 0.0251 (6) | 0.0299 (7) | 0.0217 (6) | 0.0008 (5)  | 0.0008 (4)  | 0.0007 (5)  |
| C1 | 0.0248 (7) | 0.0289 (8) | 0.0243 (7) | -0.0015 (6) | 0.0006 (5)  | 0.0018 (6)  |
| C2 | 0.0338 (8) | 0.0310 (8) | 0.0233 (7) | 0.0046 (6)  | 0.0025 (6)  | -0.0032 (6) |
| C3 | 0.0227 (7) | 0.0253 (8) | 0.0231 (7) | 0.0034 (6)  | -0.0003 (5) | 0.0000 (6)  |
| C4 | 0.0202 (6) | 0.0264 (8) | 0.0220 (7) | 0.0014 (5)  | 0.0008 (5)  | 0.0018 (6)  |
| C5 | 0.0273 (7) | 0.0296 (8) | 0.0232 (7) | -0.0033 (6) | 0.0000 (5)  | 0.0032 (6)  |
| C6 | 0.0210 (6) | 0.0269 (8) | 0.0271 (7) | -0.0004 (5) | 0.0000 (5)  | 0.0003 (6)  |
| C7 | 0.0245 (7) | 0.0351 (9) | 0.0223 (7) | 0.0020 (6)  | -0.0019 (5) | -0.0057 (6) |
| C8 | 0.0262 (7) | 0.0399 (9) | 0.0218 (7) | 0.0026 (6)  | 0.0036 (6)  | 0.0059 (7)  |
| C9 | 0.0252 (7) | 0.0269 (8) | 0.0287 (8) | 0.0014 (6)  | 0.0024 (6)  | 0.0060 (6)  |

## Geometric parameters (Å, °)

|                          |              |             |              |
|--------------------------|--------------|-------------|--------------|
| F1—C7                    | 1.3731 (17)  | C3—C4       | 1.401 (2)    |
| O1—C3                    | 1.3803 (18)  | C4—C6       | 1.393 (2)    |
| O1—C2                    | 1.4574 (18)  | C4—C5       | 1.5161 (19)  |
| N1—C2                    | 1.434 (2)    | C5—H5A      | 0.9900       |
| N1—C5                    | 1.4721 (19)  | C5—H5B      | 0.9900       |
| N1—C1                    | 1.4746 (18)  | C6—C7       | 1.374 (2)    |
| C1—C1 <sup>i</sup>       | 1.522 (3)    | C6—H6       | 0.9500       |
| C1—H1A                   | 0.9900       | C7—C8       | 1.384 (2)    |
| C1—H1B                   | 0.9900       | C8—C9       | 1.384 (2)    |
| C2—H2A                   | 0.9900       | C8—H8       | 0.9500       |
| C2—H2B                   | 0.9900       | C9—H9       | 0.9500       |
| C3—C9                    | 1.393 (2)    |             |              |
|                          |              |             |              |
| C3—O1—C2                 | 113.57 (12)  | C6—C4—C5    | 121.16 (14)  |
| C2—N1—C5                 | 108.03 (12)  | C3—C4—C5    | 119.75 (13)  |
| C2—N1—C1                 | 111.72 (12)  | N1—C5—C4    | 111.15 (12)  |
| C5—N1—C1                 | 113.84 (12)  | N1—C5—H5A   | 109.4        |
| N1—C1—C1 <sup>i</sup>    | 111.15 (14)  | C4—C5—H5A   | 109.4        |
| N1—C1—H1A                | 109.4        | N1—C5—H5B   | 109.4        |
| C1 <sup>i</sup> —C1—H1A  | 109.4        | C4—C5—H5B   | 109.4        |
| N1—C1—H1B                | 109.4        | H5A—C5—H5B  | 108.0        |
| C1 <sup>i</sup> —C1—H1B  | 109.4        | C7—C6—C4    | 118.88 (15)  |
| H1A—C1—H1B               | 108.0        | C7—C6—H6    | 120.6        |
| N1—C2—O1                 | 113.88 (12)  | C4—C6—H6    | 120.6        |
| N1—C2—H2A                | 108.8        | F1—C7—C6    | 118.28 (15)  |
| O1—C2—H2A                | 108.8        | F1—C7—C8    | 118.74 (13)  |
| N1—C2—H2B                | 108.8        | C6—C7—C8    | 122.95 (14)  |
| O1—C2—H2B                | 108.8        | C7—C8—C9    | 118.40 (13)  |
| H2A—C2—H2B               | 107.7        | C7—C8—H8    | 120.8        |
| O1—C3—C9                 | 117.09 (14)  | C9—C8—H8    | 120.8        |
| O1—C3—C4                 | 122.16 (13)  | C8—C9—C3    | 119.93 (15)  |
| C9—C3—C4                 | 120.75 (14)  | C8—C9—H9    | 120.0        |
| C6—C4—C3                 | 119.07 (13)  | C3—C9—H9    | 120.0        |
|                          |              |             |              |
| C2—N1—C1—C1 <sup>i</sup> | -161.85 (15) | C1—N1—C5—C4 | 75.31 (15)   |
| C5—N1—C1—C1 <sup>i</sup> | 75.45 (18)   | C6—C4—C5—N1 | -160.16 (12) |
| C5—N1—C2—O1              | 65.92 (15)   | C3—C4—C5—N1 | 18.20 (18)   |
| C1—N1—C2—O1              | -60.03 (16)  | C3—C4—C6—C7 | -0.8 (2)     |
| C3—O1—C2—N1              | -45.71 (17)  | C5—C4—C6—C7 | 177.62 (13)  |
| C2—O1—C3—C9              | -170.60 (12) | C4—C6—C7—F1 | -178.47 (12) |
| C2—O1—C3—C4              | 10.67 (19)   | C4—C6—C7—C8 | -0.3 (2)     |
| O1—C3—C4—C6              | -179.71 (12) | F1—C7—C8—C9 | 178.65 (13)  |
| C9—C3—C4—C6              | 1.6 (2)      | C6—C7—C8—C9 | 0.5 (2)      |
| O1—C3—C4—C5              | 1.9 (2)      | C7—C8—C9—C3 | 0.4 (2)      |

|             |              |             |             |
|-------------|--------------|-------------|-------------|
| C9—C3—C4—C5 | -176.79 (13) | O1—C3—C9—C8 | 179.82 (13) |
| C2—N1—C5—C4 | -49.39 (15)  | C4—C3—C9—C8 | -1.4 (2)    |

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

*Hydrogen-bond geometry (Å, °)*

*Cg2* is the centroid of the C3/C4/C6/C7/C8/C9 ring

| <i>D</i> —H $\cdots$ <i>A</i>            | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|--|-------------|---------------------|----------------------------|-------------------------------|
| C2—H2 <i>A</i> $\cdots$ F1 <sup>ii</sup> | 0.99        | 2.44                | 3.300 (2)                  | 145                           |
| C6—H6 $\cdots$ <i>Cg2</i> <sup>iii</sup> | 0.95        | 2.88                | 3.527 (2)                  | 126                           |
| C9—H9 $\cdots$ <i>Cg2</i> <sup>iv</sup>  | 0.95        | 2.90                | 3.577 (2)                  | 129                           |

Symmetry codes: (ii)  $-x+2, y-1/2, -z+3/2$ ; (iii)  $-x+2, y+1/2, -z+3/2$ ; (iv)  $-x+1, y-1/2, -z+3/2$ .