

3-(2,4-Difluoroanilino)-9-nitrodibenzo-
[b,e]oxepin-11(6H)-oneBenjamin Baur,^a Dieter Schollmeyer^b and Stefan Laufer^{a*}^aInstitute of Pharmacy, Department of Pharmaceutical Chemistry, Eberhard Karls University Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany, and^bDepartment of Organic Chemistry, Johannes Gutenberg-University Mainz, Duessbergweg 10-14, 55099 Mainz, Germany

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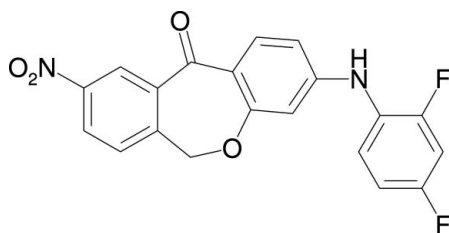
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Key indicators: single-crystal X-ray study; $T = 193$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.047; wR factor = 0.127; data-to-parameter ratio = 11.9.

In the title compound, $\text{C}_{20}\text{H}_{12}\text{F}_2\text{N}_2\text{O}_4$, the two benzene rings of the tricyclic unit are oriented at a dihedral angle of $30.6(1)^\circ$. The 2,4-difluoroanilino residue is oriented at a dihedral angle of $68.2(1)^\circ$ with respect to the phenoxy ring. In the crystal, $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between the amino group and the carbonyl O atom of the oxepinone ring link the molecules into infinite chains along the c axis.

Related literature

For palladium-catalysed amination reactions of aryl halides with anilines, see: Jensen *et al.* (2004). For p38 MAP kinase inhibitors based on dibenzo[*b,e*]oxepin-11(6H)-one, see: Laufer *et al.* (2006).



Experimental

Crystal data

 $\text{C}_{20}\text{H}_{12}\text{F}_2\text{N}_2\text{O}_4$ $M_r = 382.32$

Orthorhombic, $Pna2_1$
 $a = 27.0813(15)$ Å
 $b = 13.0411(8)$ Å
 $c = 4.5998(2)$ Å
 $V = 1624.51(15)$ Å³

$Z = 4$
 $\text{Cu } K\alpha$ radiation
 $\mu = 1.08 \text{ mm}^{-1}$
 $T = 193 \text{ K}$
 $0.47 \times 0.24 \times 0.12 \text{ mm}$

Data collection

Enraf-Nonius CAD-4
 diffractometer
 Absorption correction: numerical
 (CORINC; Dräger & Gattow,
 1971)
 $T_{\min} = 0.721$, $T_{\max} = 0.882$

3417 measured reflections
 3010 independent reflections
 2924 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 3 standard reflections every 60 min
 intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.127$
 $S = 1.03$
 3010 reflections
 253 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack, (1983),
 1270 Friedel pairs
 Flack parameter: $-0.22(18)$

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| $\text{N16}-\text{H16}\cdots\text{O25}^i$ | 0.95 | 2.32 | 3.236 (3) | 162 |

Symmetry code: (i) $-x + 1, -y + 1, z + \frac{1}{2}$.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2261).

References

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supplementary materials

Acta Cryst. (2011). E67, o555 [doi:10.1107/S1600536811002881]

3-(2,4-Difluoroanilino)-9-nitrodibenzo[*b,e*]oxepin-11(6*H*)-one

B. Baur, D. Schollmeyer and S. Laufer

Comment

Based on dibenzo[*b,e*]oxepin-11(6*H*)-one (Laufer *et al.* 2006) as p38 MAP kinase inhibitors, our intent was to synthesize disubstituted oxepin derivatives. The title compound was synthesized in the course of an ongoing study to increase the solubility of the molecules. The structure of the title compound, at 193 K shows orthorhombic symmetry. The two phenyl rings of the tricyclic unit are oriented at a dihedral angle of 30.6 (1°). The 2,4-difluoroanilino residue is oriented at a dihedral angle of 68.2 (1°) towards the phenoxy ring. The crystal structure is characterized by an intermolecular hydrogen bond N16–H···O25 (2.32 Å).

Experimental

For the preparation of the title compound a mixture of 200 mg (0.69 mmol) 3-chloro-9-nitrodibenzo[*b,e*]oxepin-11(6*H*)-one, 100 mg (0.77 mmol) 2,4-difluoroaniline, 1.00 g (3.07 mmol) Cs₂CO₃, 45 mg (0.10 mmol) 2-(dicyclohexylphosphino)-2',4'-6'-triisopropylbiphenyl and 20 mg (0.09 mmol) Pd(OAc)₂ in 2 ml absolute *tert*-butanol and 10 ml absolute 2,4-dioxane was stirred for 1 h at 284 K under an argon atmosphere. The mixture was then filtered and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO₂ n-hexane/ethyl acetate 2:1) to get 103 mg (0.27 mmol) of the product as a yellow solid (yield 39 %). Crystals of the title compound were obtained by slow evaporation of diethyl ether and hexane (1:1) at room temperature.

Refinement

Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (aromatic) or 0.98–0.99 Å (*sp*³ C-atom). Hydrogen atom attached to nitrogen was located in diff. Fourier maps. All H atoms were refined in the riding-model approximation with isotropic displacement parameters (set at 1.2–1.5 times of the *U*_{eq} of the parent atom). The absolute structure was determined on the basis of 1270 Friedel pairs.

Figures

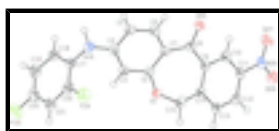


Fig. 1. View of compound **I**. Displacement ellipsoids are drawn at the 50% probability level.

3-(2,4-Difluoroanilino)-9-nitrodibenzo[*b,e*]oxepin- 11(6*H*)-one

Crystal data

C₂₀H₁₂F₂N₂O₄

F(000) = 784

supplementary materials

$$M_r = 382.32$$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$$a = 27.0813 (15) \text{ \AA}$$

$$b = 13.0411 (8) \text{ \AA}$$

$$c = 4.5998 (2) \text{ \AA}$$

$$V = 1624.51 (15) \text{ \AA}^3$$

$$Z = 4$$

$$D_x = 1.563 \text{ Mg m}^{-3}$$

Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$

Cell parameters from 25 reflections

$$\theta = 65\text{--}69^\circ$$

$$\mu = 1.08 \text{ mm}^{-1}$$

$$T = 193 \text{ K}$$

Needle, yellow

$$0.47 \times 0.24 \times 0.12 \text{ mm}$$

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: rotating anode

graphite

$\omega/2\theta$ scans

Absorption correction: numerical
(CORINC; Dräger & Gattow, 1971)

$$T_{\min} = 0.721, T_{\max} = 0.882$$

3417 measured reflections

3010 independent reflections

2924 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.051$$

$$\theta_{\max} = 69.8^\circ, \theta_{\min} = 3.3^\circ$$

$$h = -33 \rightarrow 33$$

$$k = -15 \rightarrow 15$$

$$l = -5 \rightarrow 5$$

3 standard reflections every 60 min

intensity decay: 3%

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.047$$

$$wR(F^2) = 0.127$$

$$S = 1.03$$

3010 reflections

253 parameters

1 restraint

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0989P)^2 + 0.3414P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.023$$

$$\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$$

Absolute structure: Flack, (1983), 1270 Friedel pairs

$$\text{Flack parameter: } -0.22 (18)$$

Special details

Experimental. ^1H NMR (200 MHz, DMSO- d_6) δ in p.p.m. 5.32 (s, 2 H), 6.26 (m, 1 H), 6.65 (dd, $J=8.65, 1.96$ Hz, 1 H), 7.11 (m, 1 H), 7.39 (m, 2 H), 7.82 (m, 1 H), 8.02 (d, $J=8.97$ Hz, 1 H), 8.41 (dd, $J=8.21, 2.53$ Hz, 1 H), 8.52 (d, $J=2.40$ Hz, 1 H), 8.85 (s, NH, 1 H).

^{13}C NMR (50 MHz, DMSO- d_6) δ in p.p.m. 72.5, 102.1, 110.5, 116.5, 124.3, 127.0, 130.4, 134.1, 141.1, 142.9, 148.3, 152.9, 163.4, 185.1, C—F not detected.

GC/MS, m/z (%) 382 (100, M^+), 308 (12), 152 (9), 98 (7), 63 (1).

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)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|------------|----------------------------------|
| O1 | 0.58864 (5) | 0.24963 (11) | 0.3890 (3) | 0.0240 (3) |
| C2 | 0.56177 (7) | 0.30020 (15) | 0.5965 (4) | 0.0215 (4) |
| C3 | 0.51656 (8) | 0.25513 (16) | 0.6587 (5) | 0.0242 (4) |
| H3 | 0.5068 | 0.1947 | 0.5587 | 0.029* |
| C4 | 0.48548 (8) | 0.29789 (17) | 0.8665 (5) | 0.0245 (4) |
| C5 | 0.50161 (8) | 0.38484 (16) | 1.0212 (5) | 0.0242 (4) |
| H5 | 0.4818 | 0.4123 | 1.1728 | 0.029* |
| C6 | 0.54556 (8) | 0.42947 (15) | 0.9536 (5) | 0.0234 (4) |
| H6 | 0.5556 | 0.4882 | 1.0605 | 0.028* |
| C7 | 0.57698 (7) | 0.39218 (15) | 0.7306 (4) | 0.0216 (4) |
| C8 | 0.61655 (7) | 0.46277 (15) | 0.6377 (4) | 0.0222 (4) |
| C9 | 0.65513 (7) | 0.43587 (15) | 0.4150 (5) | 0.0215 (4) |
| C10 | 0.68194 (8) | 0.51865 (17) | 0.3032 (5) | 0.0248 (4) |
| H10 | 0.6752 | 0.5865 | 0.3670 | 0.030* |
| C11 | 0.71823 (7) | 0.50081 (16) | 0.0997 (5) | 0.0262 (5) |
| C12 | 0.73012 (8) | 0.40368 (18) | 0.0000 (5) | 0.0275 (5) |
| H12 | 0.7551 | 0.3936 | −0.1423 | 0.033* |
| C13 | 0.70420 (7) | 0.32175 (17) | 0.1161 (5) | 0.0253 (5) |
| H13 | 0.7120 | 0.2541 | 0.0550 | 0.030* |
| C14 | 0.66696 (7) | 0.33663 (16) | 0.3204 (5) | 0.0223 (4) |
| C15 | 0.64067 (7) | 0.24498 (15) | 0.4420 (5) | 0.0253 (5) |
| H15A | 0.6542 | 0.1820 | 0.3525 | 0.030* |
| H15B | 0.6466 | 0.2412 | 0.6541 | 0.030* |
| N16 | 0.43947 (7) | 0.25975 (16) | 0.9317 (5) | 0.0341 (5) |
| H16 | 0.4191 | 0.3040 | 1.0435 | 0.041* |
| C17 | 0.41597 (8) | 0.18098 (18) | 0.7713 (5) | 0.0287 (5) |
| C18 | 0.37502 (8) | 0.20134 (19) | 0.5998 (6) | 0.0352 (5) |
| H18 | 0.3631 | 0.2697 | 0.5860 | 0.042* |
| C19 | 0.35112 (10) | 0.1240 (2) | 0.4481 (7) | 0.0434 (6) |
| H19 | 0.3226 | 0.1381 | 0.3345 | 0.052* |
| C20 | 0.36991 (10) | 0.0266 (2) | 0.4670 (6) | 0.0407 (6) |
| C21 | 0.41046 (10) | 0.00166 (19) | 0.6308 (7) | 0.0409 (6) |
| H21 | 0.4229 | −0.0664 | 0.6384 | 0.049* |
| C22 | 0.43238 (9) | 0.0805 (2) | 0.7842 (6) | 0.0355 (6) |
| F23 | 0.34769 (7) | −0.04940 (15) | 0.3148 (5) | 0.0629 (6) |

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| | | | | |
|-----|-------------|--------------|-------------|------------|
| F24 | 0.47133 (6) | 0.05902 (13) | 0.9539 (5) | 0.0558 (5) |
| O25 | 0.61751 (6) | 0.55042 (11) | 0.7364 (4) | 0.0302 (4) |
| N26 | 0.74461 (7) | 0.58919 (15) | −0.0221 (5) | 0.0315 (4) |
| O27 | 0.73855 (7) | 0.67347 (14) | 0.0898 (5) | 0.0476 (5) |
| O28 | 0.77170 (7) | 0.57374 (15) | −0.2321 (5) | 0.0434 (5) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0251 (7) | 0.0263 (7) | 0.0205 (8) | −0.0019 (5) | 0.0021 (6) | −0.0047 (6) |
| C2 | 0.0275 (9) | 0.0227 (10) | 0.0143 (9) | 0.0030 (7) | −0.0011 (8) | 0.0020 (8) |
| C3 | 0.0306 (10) | 0.0249 (10) | 0.0171 (10) | −0.0024 (8) | −0.0015 (9) | −0.0011 (8) |
| C4 | 0.0270 (10) | 0.0287 (10) | 0.0179 (11) | −0.0006 (8) | 0.0009 (8) | 0.0029 (8) |
| C5 | 0.0303 (10) | 0.0286 (11) | 0.0137 (10) | 0.0044 (8) | 0.0011 (8) | 0.0012 (8) |
| C6 | 0.0327 (10) | 0.0243 (9) | 0.0132 (10) | 0.0013 (8) | −0.0043 (8) | 0.0005 (8) |
| C7 | 0.0253 (9) | 0.0251 (10) | 0.0142 (10) | 0.0013 (8) | −0.0036 (8) | 0.0021 (8) |
| C8 | 0.0271 (9) | 0.0210 (9) | 0.0184 (10) | 0.0019 (7) | −0.0060 (8) | 0.0015 (8) |
| C9 | 0.0230 (9) | 0.0245 (9) | 0.0170 (10) | −0.0001 (8) | −0.0063 (8) | 0.0033 (8) |
| C10 | 0.0283 (10) | 0.0227 (9) | 0.0234 (11) | −0.0015 (8) | −0.0083 (9) | 0.0037 (8) |
| C11 | 0.0246 (9) | 0.0300 (11) | 0.0239 (11) | −0.0059 (8) | −0.0052 (8) | 0.0067 (9) |
| C12 | 0.0252 (9) | 0.0333 (11) | 0.0239 (11) | −0.0003 (8) | −0.0023 (9) | 0.0038 (9) |
| C13 | 0.0256 (9) | 0.0261 (10) | 0.0241 (11) | 0.0017 (8) | −0.0032 (9) | 0.0014 (8) |
| C14 | 0.0218 (9) | 0.0249 (10) | 0.0201 (10) | 0.0013 (7) | −0.0055 (8) | 0.0019 (8) |
| C15 | 0.0266 (10) | 0.0220 (10) | 0.0275 (11) | 0.0005 (7) | 0.0022 (9) | 0.0028 (9) |
| N16 | 0.0318 (9) | 0.0404 (11) | 0.0301 (11) | −0.0050 (8) | 0.0088 (9) | −0.0101 (9) |
| C17 | 0.0274 (10) | 0.0336 (11) | 0.0250 (12) | −0.0039 (8) | 0.0078 (9) | −0.0015 (9) |
| C18 | 0.0338 (11) | 0.0355 (13) | 0.0363 (14) | 0.0036 (9) | 0.0046 (10) | −0.0016 (11) |
| C19 | 0.0371 (12) | 0.0532 (15) | 0.0400 (16) | −0.0028 (11) | −0.0025 (12) | −0.0075 (13) |
| C20 | 0.0447 (14) | 0.0424 (13) | 0.0349 (15) | −0.0147 (11) | 0.0132 (11) | −0.0110 (11) |
| C21 | 0.0444 (12) | 0.0287 (12) | 0.0495 (16) | −0.0035 (10) | 0.0142 (12) | 0.0015 (12) |
| C22 | 0.0309 (11) | 0.0381 (12) | 0.0373 (14) | −0.0009 (9) | 0.0052 (11) | 0.0077 (11) |
| F23 | 0.0677 (11) | 0.0604 (11) | 0.0606 (12) | −0.0257 (9) | 0.0120 (10) | −0.0305 (10) |
| F24 | 0.0483 (9) | 0.0541 (10) | 0.0649 (12) | 0.0051 (7) | −0.0134 (9) | 0.0171 (9) |
| O25 | 0.0352 (8) | 0.0244 (8) | 0.0311 (9) | −0.0034 (6) | 0.0017 (7) | −0.0047 (7) |
| N26 | 0.0312 (9) | 0.0318 (10) | 0.0314 (11) | −0.0070 (8) | −0.0010 (9) | 0.0060 (9) |
| O27 | 0.0584 (11) | 0.0300 (9) | 0.0545 (13) | −0.0103 (8) | 0.0147 (10) | 0.0022 (8) |
| O28 | 0.0460 (9) | 0.0441 (10) | 0.0402 (11) | −0.0120 (8) | 0.0137 (9) | 0.0031 (9) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-----------|----------|-----------|
| O1—C2 | 1.370 (2) | C12—H12 | 0.9500 |
| O1—C15 | 1.431 (3) | C13—C14 | 1.392 (3) |
| C2—C3 | 1.388 (3) | C13—H13 | 0.9500 |
| C2—C7 | 1.410 (3) | C14—C15 | 1.499 (3) |
| C3—C4 | 1.390 (3) | C15—H15A | 0.9900 |
| C3—H3 | 0.9500 | C15—H15B | 0.9900 |
| C4—N16 | 1.375 (3) | N16—C17 | 1.416 (3) |
| C4—C5 | 1.408 (3) | N16—H16 | 0.9504 |
| C5—C6 | 1.361 (3) | C17—C18 | 1.387 (3) |

| | | | |
|-------------|-------------|---------------|-------------|
| C5—H5 | 0.9500 | C17—C22 | 1.385 (3) |
| C6—C7 | 1.419 (3) | C18—C19 | 1.387 (4) |
| C6—H6 | 0.9500 | C18—H18 | 0.9500 |
| C7—C8 | 1.476 (3) | C19—C20 | 1.371 (4) |
| C8—O25 | 1.230 (3) | C19—H19 | 0.9500 |
| C8—C9 | 1.504 (3) | C20—F23 | 1.355 (3) |
| C9—C10 | 1.399 (3) | C20—C21 | 1.371 (4) |
| C9—C14 | 1.403 (3) | C21—C22 | 1.381 (4) |
| C10—C11 | 1.377 (3) | C21—H21 | 0.9500 |
| C10—H10 | 0.9500 | C22—F24 | 1.341 (3) |
| C11—C12 | 1.385 (3) | N26—O27 | 1.225 (3) |
| C11—N26 | 1.467 (3) | N26—O28 | 1.230 (3) |
| C12—C13 | 1.385 (3) | | |
| C2—O1—C15 | 115.13 (16) | C12—C13—H13 | 119.3 |
| O1—C2—C3 | 114.11 (19) | C14—C13—H13 | 119.3 |
| O1—C2—C7 | 123.99 (18) | C13—C14—C9 | 120.24 (19) |
| C3—C2—C7 | 121.85 (19) | C13—C14—C15 | 119.00 (19) |
| C2—C3—C4 | 120.4 (2) | C9—C14—C15 | 120.75 (19) |
| C2—C3—H3 | 119.8 | O1—C15—C14 | 111.72 (16) |
| C4—C3—H3 | 119.8 | O1—C15—H15A | 109.3 |
| N16—C4—C3 | 123.6 (2) | C14—C15—H15A | 109.3 |
| N16—C4—C5 | 117.53 (19) | O1—C15—H15B | 109.3 |
| C3—C4—C5 | 118.85 (19) | C14—C15—H15B | 109.3 |
| C6—C5—C4 | 120.02 (19) | H15A—C15—H15B | 107.9 |
| C6—C5—H5 | 120.0 | C4—N16—C17 | 123.8 (2) |
| C4—C5—H5 | 120.0 | C4—N16—H16 | 115.2 |
| C5—C6—C7 | 122.89 (19) | C17—N16—H16 | 117.5 |
| C5—C6—H6 | 118.6 | C18—C17—C22 | 117.5 (2) |
| C7—C6—H6 | 118.6 | C18—C17—N16 | 121.1 (2) |
| C2—C7—C6 | 115.63 (18) | C22—C17—N16 | 121.3 (2) |
| C2—C7—C8 | 128.01 (18) | C17—C18—C19 | 121.4 (2) |
| C6—C7—C8 | 115.54 (18) | C17—C18—H18 | 119.3 |
| O25—C8—C7 | 119.20 (19) | C19—C18—H18 | 119.3 |
| O25—C8—C9 | 116.95 (18) | C20—C19—C18 | 117.9 (2) |
| C7—C8—C9 | 123.78 (18) | C20—C19—H19 | 121.0 |
| C10—C9—C14 | 118.6 (2) | C18—C19—H19 | 121.0 |
| C10—C9—C8 | 115.52 (18) | F23—C20—C19 | 118.7 (3) |
| C14—C9—C8 | 125.81 (18) | F23—C20—C21 | 117.8 (3) |
| C11—C10—C9 | 119.3 (2) | C19—C20—C21 | 123.5 (2) |
| C11—C10—H10 | 120.3 | C20—C21—C22 | 116.6 (2) |
| C9—C10—H10 | 120.3 | C20—C21—H21 | 121.7 |
| C10—C11—C12 | 123.1 (2) | C22—C21—H21 | 121.7 |
| C10—C11—N26 | 118.3 (2) | F24—C22—C21 | 118.7 (2) |
| C12—C11—N26 | 118.6 (2) | F24—C22—C17 | 118.3 (2) |
| C11—C12—C13 | 117.4 (2) | C21—C22—C17 | 123.0 (2) |
| C11—C12—H12 | 121.3 | O27—N26—O28 | 123.8 (2) |
| C13—C12—H12 | 121.3 | O27—N26—C11 | 118.7 (2) |
| C12—C13—C14 | 121.3 (2) | O28—N26—C11 | 117.5 (2) |

supplementary materials

| | | | |
|-----------------|--------------|-----------------|--------------|
| C15—O1—C2—C3 | −140.97 (18) | C12—C13—C14—C9 | −0.5 (3) |
| C15—O1—C2—C7 | 41.3 (3) | C12—C13—C14—C15 | −179.1 (2) |
| O1—C2—C3—C4 | 179.62 (18) | C10—C9—C14—C13 | −0.9 (3) |
| C7—C2—C3—C4 | −2.6 (3) | C8—C9—C14—C13 | −178.83 (19) |
| C2—C3—C4—N16 | 177.5 (2) | C10—C9—C14—C15 | 177.64 (19) |
| C2—C3—C4—C5 | −2.8 (3) | C8—C9—C14—C15 | −0.3 (3) |
| N16—C4—C5—C6 | −176.1 (2) | C2—O1—C15—C14 | −88.1 (2) |
| C3—C4—C5—C6 | 4.2 (3) | C13—C14—C15—O1 | −121.5 (2) |
| C4—C5—C6—C7 | −0.2 (3) | C9—C14—C15—O1 | 59.9 (3) |
| O1—C2—C7—C6 | −176.19 (18) | C3—C4—N16—C17 | −8.2 (4) |
| C3—C2—C7—C6 | 6.3 (3) | C5—C4—N16—C17 | 172.1 (2) |
| O1—C2—C7—C8 | 14.7 (3) | C4—N16—C17—C18 | −110.1 (3) |
| C3—C2—C7—C8 | −162.8 (2) | C4—N16—C17—C22 | 71.2 (3) |
| C5—C6—C7—C2 | −4.9 (3) | C22—C17—C18—C19 | 0.4 (4) |
| C5—C6—C7—C8 | 165.57 (19) | N16—C17—C18—C19 | −178.4 (2) |
| C2—C7—C8—O25 | 162.9 (2) | C17—C18—C19—C20 | −1.5 (4) |
| C6—C7—C8—O25 | −6.2 (3) | C18—C19—C20—F23 | −178.5 (2) |
| C2—C7—C8—C9 | −14.0 (3) | C18—C19—C20—C21 | 1.0 (4) |
| C6—C7—C8—C9 | 176.95 (17) | F23—C20—C21—C22 | −179.9 (2) |
| O25—C8—C9—C10 | −11.8 (3) | C19—C20—C21—C22 | 0.6 (4) |
| C7—C8—C9—C10 | 165.16 (18) | C20—C21—C22—F24 | 178.1 (2) |
| O25—C8—C9—C14 | 166.2 (2) | C20—C21—C22—C17 | −1.8 (4) |
| C7—C8—C9—C14 | −16.9 (3) | C18—C17—C22—F24 | −178.6 (2) |
| C14—C9—C10—C11 | 1.4 (3) | N16—C17—C22—F24 | 0.1 (3) |
| C8—C9—C10—C11 | 179.54 (17) | C18—C17—C22—C21 | 1.3 (4) |
| C9—C10—C11—C12 | −0.6 (3) | N16—C17—C22—C21 | −179.9 (2) |
| C9—C10—C11—N26 | 177.82 (18) | C10—C11—N26—O27 | 10.3 (3) |
| C10—C11—C12—C13 | −0.8 (3) | C12—C11—N26—O27 | −171.3 (2) |
| N26—C11—C12—C13 | −179.2 (2) | C10—C11—N26—O28 | −169.8 (2) |
| C11—C12—C13—C14 | 1.3 (3) | C12—C11—N26—O28 | 8.7 (3) |

Hydrogen-bond geometry (Å, °)

| <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> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N16—H16 \cdots O25 ⁱ | 0.95 | 2.32 | 3.236 (3) | 162 |

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

Fig. 1

