

Crystal structure of dimethyl 3,3'-[(3-fluorophenyl)methylene]bis(1*H*-indole-2-carboxylate)Xin-Hua Lu,^a Hong-Shun Sun^{b*} and Jin Hu^a

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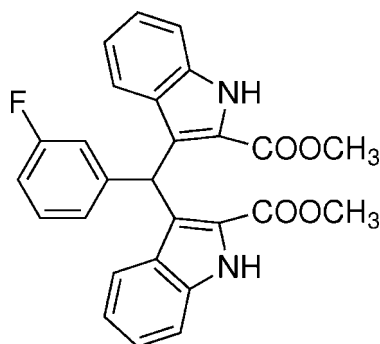
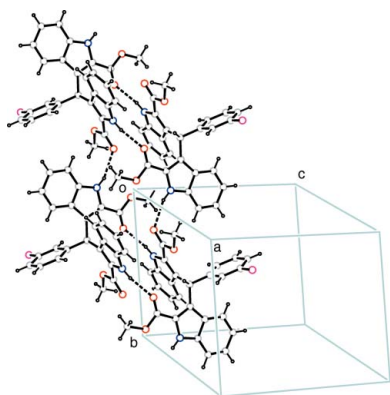
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In the title compound, C₂₇H₂₁FN₂O₄, the mean planes of the two indole ring systems (r.m.s. deviations = 0.0166 and 0.0086 Å) are approximately perpendicular to one another, making a dihedral angle of 87.8 (5)°; the fluorobenzene ring is twisted with respect to the mean planes of the two indole ring systems at 82.7 (5) and 85.5 (3)°. In the crystal, pairs of N—H...O hydrogen bonds link the molecules into the inversion dimers, which are further linked by N—H...O hydrogen bonds into supramolecular chains propagating along the *b*-axis direction. Weak C—H... π interactions are observed between neighbouring chains.

1. Chemical context

The indole unit forms the basis for general bis(indoly)-methanes, which are widely present in bioactive metabolites of numerous compounds isolated from natural sources (Poter *et al.*, 1977; Sundberg, 1996). In addition, bis(indoly)methanes are important antibiotics in the field of pharmaceuticals and the precursor of bioactive metabolites of terrestrial and marine origin (Chang *et al.*, 1999; Ge *et al.*, 1999). The title compound is one of the bis(indoly)methane derivatives used as a precursor for MRI contrast agents (Ni, 2008). In recent years, we have reported the synthesis and crystal structures of some similar compounds (Sun *et al.*, 2012, 2013, 2014; Li *et al.*, 2014). Now we report herein on another bis(indoly)methane compound.



2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The two indole ring systems are nearly perpendicular to each other [dihedral angle = 87.8 (5)°] while the benzene ring (C22–C27) is twisted to the N1/C2–C9 and N2/C12–C19 indole

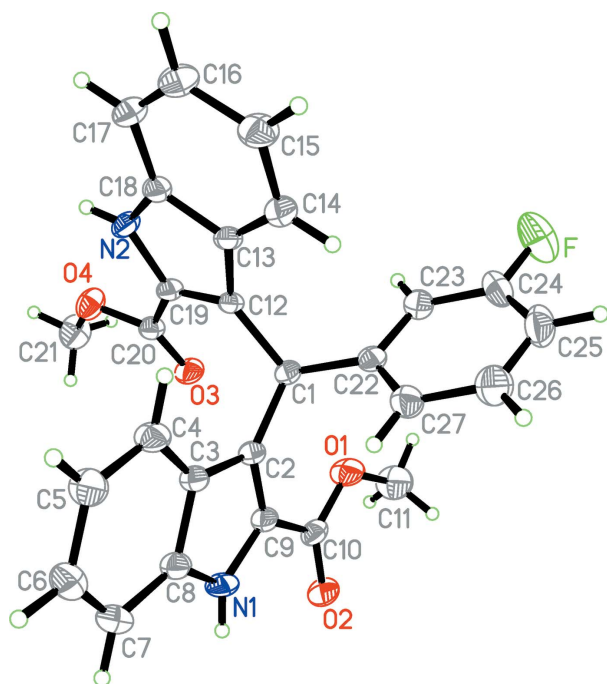


Figure 1
The molecular structure of the title molecule with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

ring systems by dihedral angles of 82.7 (5) and 85.5 (3)°, respectively. The carboxyl groups are approximately co-planar with the attached indole ring systems, the dihedral angles between the carboxyl groups and the mean planes of the attached indole ring systems being 9.6 (3) and 9.6 (4)°.

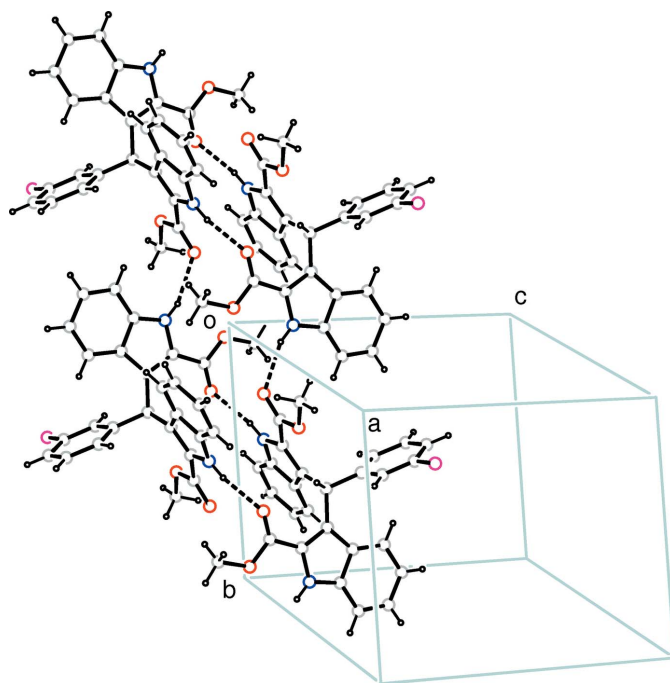


Figure 2
A packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

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

Cg4 is the centroid of the C13–C18 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> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1A...O3 ⁱ | 0.86 | 2.06 | 2.913 (3) | 170 |
| N2—H2A...O2 ⁱⁱ | 0.86 | 2.15 | 2.948 (3) | 155 |
| C6—H6A...Cg4 ⁱⁱⁱ | 0.93 | 2.75 | 3.645 (4) | 162 |

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

3. Supramolecular features

In the crystal, pairs of N1—H1A...O3ⁱ [symmetry code: (i) $-x, 1 - y, -z$] hydrogen bonds link the molecules into inversion dimers, which are further linked by N2—H2A...O2ⁱⁱ [symmetry code: (ii) $x, 1 + y, z$] hydrogen bonds into supramolecular chains propagating along the *b*-axis direction (Table 1 and Fig. 2). Weak C—H... π interactions are also observed between neighbouring chains (Table 1).

4. Database survey

Several similar structures have been reported previously, *viz.* diethyl 3,3'-(phenylmethylene)bis(1*H*-indole-2-carboxylate) (Sun *et al.*, 2012), dimethyl 3,3'-(phenylmethylene)bis(1*H*-indole-2-carboxylate) (Sun *et al.*, 2013), dimethyl 3,3'-[(4-chlorophenyl)methylene]bis(1*H*-indole-2-carboxylate) (Li *et al.*, 2014) and dimethyl 3,3'-[(3-nitrophenyl)methylene]bis(1-

Table 2
Experimental details.

| | |
|---|--|
| Crystal data | |
| Chemical formula | C ₂₇ H ₂₁ FN ₂ O ₄ |
| <i>M_r</i> | 456.46 |
| Crystal system, space group | Triclinic, <i>P</i> $\bar{1}$ |
| Temperature (K) | 293 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 9.6980 (19), 10.119 (2), 12.875 (3) |
| α , β , γ (°) | 89.86 (3), 83.10 (3), 65.45 (3) |
| <i>V</i> (Å ³) | 1139.4 (4) |
| <i>Z</i> | 2 |
| Radiation type | Mo <i>K</i> α |
| μ (mm ⁻¹) | 0.10 |
| Crystal size (mm) | 0.30 × 0.20 × 0.10 |
| Data collection | |
| Diffractionmeter | Enraf–Nonius CAD-4 |
| Absorption correction | ψ scan (North <i>et al.</i> , 1968) |
| <i>T_{min}</i> , <i>T_{max}</i> | 0.972, 0.991 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 4453, 4183, 2587 |
| <i>R_{int}</i> | 0.036 |
| ($\sin \theta/\lambda$) _{max} (Å ⁻¹) | 0.603 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i> | 0.060, 0.163, 1.00 |
| No. of reflections | 4183 |
| No. of parameters | 307 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³) | 0.72, -0.25 |

Computer programs: CAD-4 EXPRESS (Enraf–Nonius, 1994), XCAD4 (Harms & Wocadlo, 1995) and SHELXTL (Sheldrick, 2008).

H-indole-2-carboxylate) ethanol monosolvate (Sun *et al.*, 2014). In those structures, the two indole ring systems are also nearly perpendicular to each other, the dihedral angles being 82.0 (5), 84.5 (5), 79.5 (4) and 89.3 (5)°, respectively.

5. Synthesis and crystallization

Methyl indole-2-carboxylate (17.5 g, 100 mmol) was dissolved in 200 ml methanol; commercially available 3-fluorobenzaldehyde (6.2 g, 50 mmol) was added and the mixture was heated to reflux temperature. Concentrated HCl (3.7 ml) was added and the reaction was left for 1 h. After cooling, the white product was filtered off and washed thoroughly with methanol. The reaction was monitored by TLC (CHCl₃:hexane = 1:1). The yield was 92%. Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of a methanol solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically with N—H = 0.86 and C—H = 0.93–0.98 Å, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C,N})$, where $x = 1.5$ for methyl H atoms and 1.2 for the others.

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References

- Chang, Y.-C., Riby, J., Chang, G. H. F., Peng, B., Firestone, G. & Bjeldanes, L. F. (1999). *Biochem. Pharmacol.* **58**, 825–834.
- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
- Ge, X., Fares, F. A. & Yannai, S. (1999). *Anticancer Res.* **19**, 3199–3203.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Li, Y., Sun, H., Jiang, H., Xu, N. & Xu, H. (2014). *Acta Cryst.* **E70**, 259–261.
- Ni, Y.-C. (2008). *Curr. Med. Imaging Rev.* **4**, 96–112.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Porter, J. K., Bacon, C. W., Robbins, J. D., Himmelsbach, D. S. & Higman, H. C. (1977). *J. Agric. Food Chem.* **25**, 88–93.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sun, H.-S., Li, Y.-L., Jiang, H., Xu, N. & Xu, H. (2014). *Acta Cryst.* **E70**, 370–372.
- Sun, H.-S., Li, Y.-L., Xu, N., Xu, H. & Zhang, J.-D. (2012). *Acta Cryst.* **E68**, o2764.
- Sun, H.-S., Li, Y.-L., Xu, N., Xu, H. & Zhang, J.-D. (2013). *Acta Cryst.* **E69**, o1516.
- Sundberg, R. J. (1996). *The Chemistry of Indoles*, p. 113. New York: Academic Press.

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Acta Cryst. (2014). E70, 593–595 [doi:10.1107/S1600536814025756]

Crystal structure of dimethyl 3,3'-[(3-fluorophenyl)methylene]bis(1*H*-indole-2-carboxylate)

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Computing details

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Dimethyl 3,3'-[(3-fluorophenyl)methylene]bis(1*H*-indole-2-carboxylate)

Crystal data

| | |
|--------------------------------|---|
| $C_{27}H_{21}FN_2O_4$ | $Z = 2$ |
| $M_r = 456.46$ | $F(000) = 476$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.331 \text{ Mg m}^{-3}$ |
| Hall symbol: $-P\ 1$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 9.6980 (19) \text{ \AA}$ | Cell parameters from 25 reflections |
| $b = 10.119 (2) \text{ \AA}$ | $\theta = 9\text{--}13^\circ$ |
| $c = 12.875 (3) \text{ \AA}$ | $\mu = 0.10 \text{ mm}^{-1}$ |
| $\alpha = 89.86 (3)^\circ$ | $T = 293 \text{ K}$ |
| $\beta = 83.10 (3)^\circ$ | Block, colorless |
| $\gamma = 65.45 (3)^\circ$ | $0.30 \times 0.20 \times 0.10 \text{ mm}$ |
| $V = 1139.4 (4) \text{ \AA}^3$ | |

Data collection

| | |
|--|--|
| Enraf–Nonius CAD-4 diffractometer | 4183 independent reflections |
| Radiation source: fine-focus sealed tube | 2587 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{\text{int}} = 0.036$ |
| $\omega/2\theta$ scans | $\theta_{\text{max}} = 25.4^\circ$, $\theta_{\text{min}} = 1.6^\circ$ |
| Absorption correction: ψ scan (North <i>et al.</i> , 1968) | $h = 0 \rightarrow 11$ |
| $T_{\text{min}} = 0.972$, $T_{\text{max}} = 0.991$ | $k = -11 \rightarrow 12$ |
| 4453 measured reflections | $l = -15 \rightarrow 15$ |
| | 3 standard reflections every 200 reflections |
| | intensity decay: 1% |

Refinement

| | |
|---------------------------------|---|
| Refinement on F^2 | 1 restraint |
| Least-squares matrix: full | Primary atom site location: structure-invariant direct methods |
| $R[F^2 > 2\sigma(F^2)] = 0.060$ | Secondary atom site location: difference Fourier map |
| $wR(F^2) = 0.163$ | Hydrogen site location: inferred from neighbouring sites |
| $S = 1.00$ | |
| 4183 reflections | |
| 307 parameters | |

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.085P)^2]$$

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

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

$$\Delta\rho_{\max} = 0.72 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$$

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. 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> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|------------|---------------|----------------------------------|
| N1 | −0.1052 (3) | 0.5029 (2) | 0.13830 (18) | 0.0445 (6) |
| H1A | −0.1408 | 0.4496 | 0.1090 | 0.053* |
| O1 | 0.3009 (2) | 0.3113 (2) | 0.08820 (18) | 0.0586 (6) |
| C1 | 0.2144 (3) | 0.5855 (3) | 0.2059 (2) | 0.0334 (6) |
| H1B | 0.2859 | 0.5329 | 0.1441 | 0.040* |
| O2 | 0.1188 (3) | 0.2409 (2) | 0.05471 (17) | 0.0555 (6) |
| N2 | 0.1837 (3) | 0.9546 (2) | 0.14191 (17) | 0.0396 (6) |
| H2A | 0.1767 | 1.0211 | 0.0985 | 0.048* |
| C2 | 0.0646 (3) | 0.5803 (3) | 0.1908 (2) | 0.0341 (6) |
| O3 | 0.2455 (2) | 0.6468 (2) | −0.02476 (15) | 0.0486 (5) |
| C3 | −0.0884 (3) | 0.6830 (3) | 0.2299 (2) | 0.0359 (6) |
| O4 | 0.1821 (3) | 0.8813 (2) | −0.05567 (15) | 0.0529 (6) |
| C4 | −0.1512 (3) | 0.8120 (3) | 0.2943 (2) | 0.0439 (7) |
| H4A | −0.0880 | 0.8485 | 0.3207 | 0.053* |
| F | 0.6593 (3) | 0.3395 (3) | 0.38335 (19) | 0.1028 (8) |
| C5 | −0.3065 (4) | 0.8827 (3) | 0.3173 (2) | 0.0522 (8) |
| H5B | −0.3483 | 0.9676 | 0.3601 | 0.063* |
| C6 | −0.4039 (4) | 0.8314 (3) | 0.2787 (3) | 0.0545 (8) |
| H6A | −0.5090 | 0.8841 | 0.2951 | 0.065* |
| C7 | −0.3497 (4) | 0.7059 (3) | 0.2175 (3) | 0.0518 (8) |
| H7A | −0.4154 | 0.6715 | 0.1924 | 0.062* |
| C8 | −0.1906 (3) | 0.6313 (3) | 0.1940 (2) | 0.0394 (7) |
| C9 | 0.0469 (3) | 0.4723 (3) | 0.1365 (2) | 0.0368 (6) |
| C10 | 0.1559 (4) | 0.3315 (3) | 0.0883 (2) | 0.0416 (7) |
| C11 | 0.4154 (4) | 0.1713 (4) | 0.0498 (3) | 0.0767 (11) |
| H11A | 0.5149 | 0.1686 | 0.0529 | 0.115* |
| H11B | 0.4049 | 0.1537 | −0.0215 | 0.115* |
| H11C | 0.4031 | 0.0977 | 0.0921 | 0.115* |
| C12 | 0.2062 (3) | 0.7399 (3) | 0.2047 (2) | 0.0312 (6) |
| C13 | 0.1975 (3) | 0.8347 (3) | 0.2903 (2) | 0.0331 (6) |
| C14 | 0.2017 (3) | 0.8230 (3) | 0.3985 (2) | 0.0416 (7) |
| H14A | 0.2120 | 0.7368 | 0.4295 | 0.050* |

| | | | | |
|------|------------|------------|-------------|-------------|
| C15 | 0.1906 (4) | 0.9398 (3) | 0.4581 (2) | 0.0517 (8) |
| H15A | 0.1949 | 0.9317 | 0.5297 | 0.062* |
| C16 | 0.1728 (4) | 1.0709 (3) | 0.4134 (3) | 0.0547 (9) |
| H16A | 0.1632 | 1.1488 | 0.4563 | 0.066* |
| C17 | 0.1692 (4) | 1.0876 (3) | 0.3093 (2) | 0.0489 (8) |
| H17A | 0.1586 | 1.1748 | 0.2799 | 0.059* |
| C18 | 0.1821 (3) | 0.9681 (3) | 0.2474 (2) | 0.0373 (7) |
| C19 | 0.1986 (3) | 0.8161 (3) | 0.1163 (2) | 0.0339 (6) |
| C20 | 0.2100 (3) | 0.7701 (3) | 0.0063 (2) | 0.0376 (7) |
| C21 | 0.1995 (4) | 0.8471 (4) | −0.1662 (2) | 0.0666 (10) |
| H21A | 0.1770 | 0.9343 | −0.2036 | 0.100* |
| H21B | 0.1303 | 0.8053 | −0.1797 | 0.100* |
| H21C | 0.3027 | 0.7788 | −0.1891 | 0.100* |
| C22 | 0.2846 (3) | 0.5040 (3) | 0.2992 (2) | 0.0367 (7) |
| C23 | 0.4402 (3) | 0.4571 (3) | 0.3005 (2) | 0.0449 (7) |
| H23A | 0.5000 | 0.4746 | 0.2449 | 0.054* |
| C24 | 0.5055 (4) | 0.3846 (4) | 0.3845 (3) | 0.0548 (8) |
| C25 | 0.4234 (4) | 0.3559 (4) | 0.4673 (3) | 0.0629 (10) |
| H25A | 0.4706 | 0.3062 | 0.5232 | 0.076* |
| C26 | 0.2694 (4) | 0.4020 (4) | 0.4664 (3) | 0.0639 (10) |
| H26A | 0.2105 | 0.3844 | 0.5226 | 0.077* |
| C27 | 0.2007 (4) | 0.4745 (3) | 0.3822 (2) | 0.0491 (8) |
| H27A | 0.0963 | 0.5036 | 0.3820 | 0.059* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| N1 | 0.0524 (17) | 0.0385 (13) | 0.0546 (15) | −0.0295 (12) | −0.0120 (12) | −0.0062 (11) |
| O1 | 0.0498 (14) | 0.0351 (11) | 0.0876 (17) | −0.0160 (10) | −0.0029 (12) | −0.0176 (11) |
| C1 | 0.0389 (16) | 0.0255 (13) | 0.0378 (15) | −0.0145 (12) | −0.0079 (12) | −0.0016 (11) |
| O2 | 0.0730 (16) | 0.0339 (11) | 0.0677 (14) | −0.0277 (11) | −0.0187 (12) | −0.0071 (10) |
| N2 | 0.0548 (16) | 0.0283 (11) | 0.0403 (14) | −0.0212 (11) | −0.0092 (11) | 0.0015 (10) |
| C2 | 0.0378 (16) | 0.0297 (13) | 0.0389 (15) | −0.0173 (12) | −0.0088 (12) | −0.0001 (11) |
| O3 | 0.0655 (15) | 0.0392 (11) | 0.0468 (12) | −0.0257 (10) | −0.0143 (10) | −0.0053 (9) |
| C3 | 0.0392 (16) | 0.0349 (14) | 0.0392 (15) | −0.0200 (13) | −0.0086 (12) | 0.0029 (12) |
| O4 | 0.0744 (16) | 0.0425 (11) | 0.0401 (12) | −0.0228 (11) | −0.0075 (10) | 0.0044 (9) |
| C4 | 0.0446 (19) | 0.0390 (16) | 0.0507 (18) | −0.0197 (14) | −0.0065 (14) | −0.0108 (14) |
| F | 0.0659 (15) | 0.131 (2) | 0.0963 (18) | −0.0211 (15) | −0.0317 (13) | 0.0148 (15) |
| C5 | 0.0440 (19) | 0.0439 (17) | 0.063 (2) | −0.0142 (15) | 0.0002 (15) | −0.0118 (15) |
| C6 | 0.0383 (19) | 0.055 (2) | 0.067 (2) | −0.0171 (16) | −0.0064 (16) | 0.0020 (17) |
| C7 | 0.0432 (19) | 0.0553 (19) | 0.067 (2) | −0.0292 (16) | −0.0115 (16) | 0.0039 (16) |
| C8 | 0.0422 (17) | 0.0407 (16) | 0.0422 (16) | −0.0233 (14) | −0.0094 (13) | 0.0029 (13) |
| C9 | 0.0433 (17) | 0.0332 (14) | 0.0400 (16) | −0.0205 (13) | −0.0111 (13) | 0.0015 (12) |
| C10 | 0.057 (2) | 0.0320 (14) | 0.0411 (16) | −0.0232 (14) | −0.0096 (14) | 0.0026 (12) |
| C11 | 0.058 (2) | 0.047 (2) | 0.108 (3) | −0.0091 (18) | 0.003 (2) | −0.020 (2) |
| C12 | 0.0289 (14) | 0.0286 (13) | 0.0399 (15) | −0.0149 (11) | −0.0085 (12) | −0.0012 (11) |
| C13 | 0.0305 (15) | 0.0307 (14) | 0.0413 (16) | −0.0156 (12) | −0.0066 (12) | −0.0027 (12) |
| C14 | 0.0461 (18) | 0.0370 (15) | 0.0437 (17) | −0.0187 (14) | −0.0076 (13) | 0.0002 (13) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C15 | 0.064 (2) | 0.0522 (19) | 0.0421 (17) | −0.0270 (17) | −0.0089 (15) | −0.0080 (15) |
| C16 | 0.067 (2) | 0.0413 (17) | 0.055 (2) | −0.0216 (16) | −0.0093 (16) | −0.0156 (15) |
| C17 | 0.056 (2) | 0.0346 (15) | 0.058 (2) | −0.0204 (15) | −0.0095 (15) | −0.0068 (14) |
| C18 | 0.0351 (16) | 0.0317 (14) | 0.0451 (17) | −0.0133 (12) | −0.0080 (13) | −0.0043 (12) |
| C19 | 0.0376 (16) | 0.0297 (13) | 0.0384 (15) | −0.0174 (12) | −0.0070 (12) | −0.0028 (12) |
| C20 | 0.0383 (17) | 0.0363 (15) | 0.0414 (16) | −0.0180 (13) | −0.0078 (13) | −0.0015 (13) |
| C21 | 0.088 (3) | 0.069 (2) | 0.0409 (19) | −0.031 (2) | −0.0089 (18) | 0.0063 (16) |
| C22 | 0.0415 (17) | 0.0274 (13) | 0.0429 (16) | −0.0155 (12) | −0.0075 (13) | −0.0046 (12) |
| C23 | 0.0471 (19) | 0.0438 (16) | 0.0451 (18) | −0.0196 (14) | −0.0083 (14) | 0.0030 (14) |
| C24 | 0.0472 (19) | 0.0567 (19) | 0.054 (2) | −0.0121 (16) | −0.0195 (16) | 0.0022 (16) |
| C25 | 0.078 (3) | 0.062 (2) | 0.048 (2) | −0.023 (2) | −0.0242 (19) | 0.0152 (16) |
| C26 | 0.075 (3) | 0.072 (2) | 0.052 (2) | −0.037 (2) | −0.0126 (18) | 0.0107 (18) |
| C27 | 0.0469 (19) | 0.0564 (19) | 0.0498 (19) | −0.0263 (16) | −0.0105 (15) | 0.0107 (15) |

Geometric parameters (Å, °)

| | | | |
|----------|-----------|------------|-----------|
| N1—C8 | 1.362 (3) | C11—H11A | 0.9600 |
| N1—C9 | 1.373 (4) | C11—H11B | 0.9600 |
| N1—H1A | 0.8600 | C11—H11C | 0.9600 |
| O1—C10 | 1.333 (4) | C12—C19 | 1.365 (4) |
| O1—C11 | 1.431 (4) | C12—C13 | 1.435 (3) |
| C1—C2 | 1.511 (4) | C13—C14 | 1.402 (4) |
| C1—C22 | 1.520 (4) | C13—C18 | 1.413 (4) |
| C1—C12 | 1.532 (3) | C14—C15 | 1.370 (4) |
| C1—H1B | 0.9800 | C14—H14A | 0.9300 |
| O2—C10 | 1.213 (3) | C15—C16 | 1.396 (4) |
| N2—C18 | 1.363 (3) | C15—H15A | 0.9300 |
| N2—C19 | 1.385 (3) | C16—C17 | 1.353 (4) |
| N2—H2A | 0.8600 | C16—H16A | 0.9300 |
| C2—C9 | 1.379 (3) | C17—C18 | 1.403 (4) |
| C2—C3 | 1.440 (4) | C17—H17A | 0.9300 |
| O3—C20 | 1.203 (3) | C19—C20 | 1.469 (4) |
| C3—C4 | 1.409 (4) | C21—H21A | 0.9600 |
| C3—C8 | 1.419 (4) | C21—H21B | 0.9600 |
| O4—C20 | 1.330 (3) | C21—H21C | 0.9600 |
| O4—C21 | 1.439 (3) | C22—C27 | 1.373 (4) |
| C4—C5 | 1.366 (4) | C22—C23 | 1.383 (4) |
| C4—H4A | 0.9300 | C23—C24 | 1.372 (4) |
| F—C24 | 1.364 (4) | C23—H23A | 0.9300 |
| C5—C6 | 1.389 (4) | C24—C25 | 1.357 (5) |
| C5—H5B | 0.9300 | C25—C26 | 1.370 (5) |
| C6—C7 | 1.364 (4) | C25—H25A | 0.9300 |
| C6—H6A | 0.9300 | C26—C27 | 1.385 (4) |
| C7—C8 | 1.401 (4) | C26—H26A | 0.9300 |
| C7—H7A | 0.9300 | C27—H27A | 0.9300 |
| C9—C10 | 1.458 (4) | | |
| C8—N1—C9 | 109.0 (2) | C13—C12—C1 | 129.4 (2) |

| | | | |
|---------------|-----------|---------------|-----------|
| C8—N1—H1A | 125.5 | C14—C13—C18 | 118.0 (2) |
| C9—N1—H1A | 125.5 | C14—C13—C12 | 135.4 (2) |
| C10—O1—C11 | 116.3 (2) | C18—C13—C12 | 106.6 (2) |
| C2—C1—C22 | 113.7 (2) | C15—C14—C13 | 119.3 (3) |
| C2—C1—C12 | 112.9 (2) | C15—C14—H14A | 120.4 |
| C22—C1—C12 | 112.7 (2) | C13—C14—H14A | 120.4 |
| C2—C1—H1B | 105.5 | C14—C15—C16 | 121.3 (3) |
| C22—C1—H1B | 105.5 | C14—C15—H15A | 119.4 |
| C12—C1—H1B | 105.5 | C16—C15—H15A | 119.4 |
| C18—N2—C19 | 108.7 (2) | C17—C16—C15 | 121.8 (3) |
| C18—N2—H2A | 125.7 | C17—C16—H16A | 119.1 |
| C19—N2—H2A | 125.7 | C15—C16—H16A | 119.1 |
| C9—C2—C3 | 105.3 (2) | C16—C17—C18 | 117.3 (3) |
| C9—C2—C1 | 126.3 (2) | C16—C17—H17A | 121.3 |
| C3—C2—C1 | 128.5 (2) | C18—C17—H17A | 121.3 |
| C4—C3—C8 | 117.9 (3) | N2—C18—C17 | 129.5 (3) |
| C4—C3—C2 | 134.8 (3) | N2—C18—C13 | 108.2 (2) |
| C8—C3—C2 | 107.3 (2) | C17—C18—C13 | 122.3 (3) |
| C20—O4—C21 | 116.2 (2) | C12—C19—N2 | 109.8 (2) |
| C5—C4—C3 | 118.9 (3) | C12—C19—C20 | 130.1 (2) |
| C5—C4—H4A | 120.6 | N2—C19—C20 | 120.1 (2) |
| C3—C4—H4A | 120.6 | O3—C20—O4 | 124.0 (2) |
| C4—C5—C6 | 121.9 (3) | O3—C20—C19 | 124.5 (3) |
| C4—C5—H5B | 119.0 | O4—C20—C19 | 111.4 (2) |
| C6—C5—H5B | 119.0 | O4—C21—H21A | 109.5 |
| C7—C6—C5 | 121.8 (3) | O4—C21—H21B | 109.5 |
| C7—C6—H6A | 119.1 | H21A—C21—H21B | 109.5 |
| C5—C6—H6A | 119.1 | O4—C21—H21C | 109.5 |
| C6—C7—C8 | 117.0 (3) | H21A—C21—H21C | 109.5 |
| C6—C7—H7A | 121.5 | H21B—C21—H21C | 109.5 |
| C8—C7—H7A | 121.5 | C27—C22—C23 | 118.4 (3) |
| N1—C8—C7 | 129.8 (3) | C27—C22—C1 | 123.0 (3) |
| N1—C8—C3 | 107.7 (2) | C23—C22—C1 | 118.5 (3) |
| C7—C8—C3 | 122.5 (3) | C24—C23—C22 | 119.4 (3) |
| N1—C9—C2 | 110.7 (2) | C24—C23—H23A | 120.3 |
| N1—C9—C10 | 116.5 (2) | C22—C23—H23A | 120.3 |
| C2—C9—C10 | 132.5 (3) | C25—C24—F | 119.4 (3) |
| O2—C10—O1 | 123.6 (3) | C25—C24—C23 | 122.6 (3) |
| O2—C10—C9 | 123.6 (3) | F—C24—C23 | 118.0 (3) |
| O1—C10—C9 | 112.8 (2) | C24—C25—C26 | 118.2 (3) |
| O1—C11—H11A | 109.5 | C24—C25—H25A | 120.9 |
| O1—C11—H11B | 109.5 | C26—C25—H25A | 120.9 |
| H11A—C11—H11B | 109.5 | C25—C26—C27 | 120.4 (3) |
| O1—C11—H11C | 109.5 | C25—C26—H26A | 119.8 |
| H11A—C11—H11C | 109.5 | C27—C26—H26A | 119.8 |
| H11B—C11—H11C | 109.5 | C22—C27—C26 | 121.0 (3) |
| C19—C12—C13 | 106.8 (2) | C22—C27—H27A | 119.5 |
| C19—C12—C1 | 123.7 (2) | C26—C27—H27A | 119.5 |

| | | | |
|-----------------|------------|-----------------|------------|
| C22—C1—C2—C9 | −86.0 (3) | C1—C12—C13—C18 | −176.2 (3) |
| C12—C1—C2—C9 | 143.9 (3) | C18—C13—C14—C15 | 0.1 (4) |
| C22—C1—C2—C3 | 93.1 (3) | C12—C13—C14—C15 | 179.7 (3) |
| C12—C1—C2—C3 | −37.0 (4) | C13—C14—C15—C16 | 1.0 (5) |
| C9—C2—C3—C4 | 176.4 (3) | C14—C15—C16—C17 | −1.5 (5) |
| C1—C2—C3—C4 | −2.8 (5) | C15—C16—C17—C18 | 0.8 (5) |
| C9—C2—C3—C8 | −1.3 (3) | C19—N2—C18—C17 | 180.0 (3) |
| C1—C2—C3—C8 | 179.4 (2) | C19—N2—C18—C13 | 0.5 (3) |
| C8—C3—C4—C5 | −1.4 (4) | C16—C17—C18—N2 | −179.1 (3) |
| C2—C3—C4—C5 | −178.9 (3) | C16—C17—C18—C13 | 0.3 (4) |
| C3—C4—C5—C6 | −0.3 (5) | C14—C13—C18—N2 | 178.7 (2) |
| C4—C5—C6—C7 | 1.4 (5) | C12—C13—C18—N2 | −0.9 (3) |
| C5—C6—C7—C8 | −0.7 (5) | C14—C13—C18—C17 | −0.8 (4) |
| C9—N1—C8—C7 | −179.6 (3) | C12—C13—C18—C17 | 179.6 (3) |
| C9—N1—C8—C3 | −0.7 (3) | C13—C12—C19—N2 | −0.7 (3) |
| C6—C7—C8—N1 | 177.7 (3) | C1—C12—C19—N2 | 176.7 (2) |
| C6—C7—C8—C3 | −1.1 (4) | C13—C12—C19—C20 | 176.5 (3) |
| C4—C3—C8—N1 | −176.9 (2) | C1—C12—C19—C20 | −6.1 (4) |
| C2—C3—C8—N1 | 1.3 (3) | C18—N2—C19—C12 | 0.1 (3) |
| C4—C3—C8—C7 | 2.1 (4) | C18—N2—C19—C20 | −177.4 (2) |
| C2—C3—C8—C7 | −179.7 (3) | C21—O4—C20—O3 | −1.2 (4) |
| C8—N1—C9—C2 | −0.2 (3) | C21—O4—C20—C19 | 176.3 (3) |
| C8—N1—C9—C10 | 174.5 (2) | C12—C19—C20—O3 | −8.5 (5) |
| C3—C2—C9—N1 | 0.9 (3) | N2—C19—C20—O3 | 168.5 (3) |
| C1—C2—C9—N1 | −179.8 (2) | C12—C19—C20—O4 | 174.0 (3) |
| C3—C2—C9—C10 | −172.5 (3) | N2—C19—C20—O4 | −9.0 (4) |
| C1—C2—C9—C10 | 6.7 (5) | C2—C1—C22—C27 | −22.3 (4) |
| C11—O1—C10—O2 | −2.7 (4) | C12—C1—C22—C27 | 107.9 (3) |
| C11—O1—C10—C9 | 175.3 (3) | C2—C1—C22—C23 | 157.6 (2) |
| N1—C9—C10—O2 | −3.0 (4) | C12—C1—C22—C23 | −72.3 (3) |
| C2—C9—C10—O2 | 170.1 (3) | C27—C22—C23—C24 | −0.8 (4) |
| N1—C9—C10—O1 | 179.0 (2) | C1—C22—C23—C24 | 179.4 (2) |
| C2—C9—C10—O1 | −7.9 (4) | C22—C23—C24—C25 | 0.3 (5) |
| C2—C1—C12—C19 | −72.7 (3) | C22—C23—C24—F | 179.9 (3) |
| C22—C1—C12—C19 | 156.8 (2) | F—C24—C25—C26 | −179.8 (3) |
| C2—C1—C12—C13 | 104.0 (3) | C23—C24—C25—C26 | −0.2 (5) |
| C22—C1—C12—C13 | −26.5 (4) | C24—C25—C26—C27 | 0.7 (5) |
| C19—C12—C13—C14 | −178.6 (3) | C23—C22—C27—C26 | 1.2 (4) |
| C1—C12—C13—C14 | 4.3 (5) | C1—C22—C27—C26 | −178.9 (3) |
| C19—C12—C13—C18 | 1.0 (3) | C25—C26—C27—C22 | −1.2 (5) |

Hydrogen-bond geometry (Å, °)

Cg4 is the centroid of the C13—C18 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> |
|---------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1A \cdots O3 ⁱ | 0.86 | 2.06 | 2.913 (3) | 170 |

| | | | | |
|-----------------------------|------|------|-----------|-----|
| N2—H2A...O2 ⁱⁱ | 0.86 | 2.15 | 2.948 (3) | 155 |
| C6—H6A...Cg4 ⁱⁱⁱ | 0.93 | 2.75 | 3.645 (4) | 162 |

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