IUCrData

ISSN 2414-3146

Diethyl 3,3′-[(4-fluorophenyl)methylidene]bis(1*H*-indole-2-carboxylate)

Yu-Long Li,[a] Jin Zhou,[a,b] Kai-Long Zhong,[a] Xing-Hao Shi,[a] Zhi-Yuan Zhang,[a] Hong Jiang[a] and Hong-Shun Sun[a]*

[a]Targeted MRI Contrast Agents Laboratory of Jiangsu Province, Nanjing Polytechnic Institute, Nanjing 210048, People's Republic of China, and [b]College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, People's Republic of China. *Correspondence e-mail: njutshs@126.com

Received 3 January 2019
Accepted 24 January 2019

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

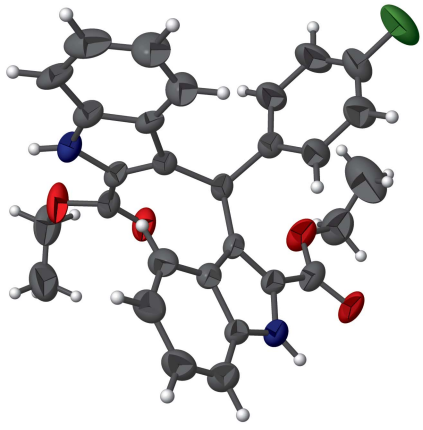
Keywords: crystal structure; bisindole; MRI; contrast agents; hydrogen bonding; C—H···π interactions.

CCDC reference: 1893147

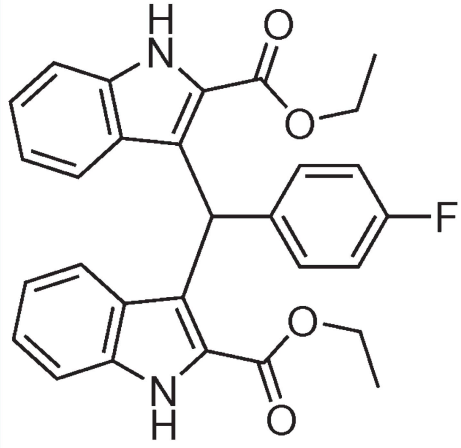
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{29}H_{25}FN_2O_4$, the mean planes of the indole ring systems (r.m.s. deviations = 0.0107 and 0.0158 Å) are approximately perpendicular to each other, subtending a dihedral angle of 87.43 (16)°. The 4-fluorophenyl ring is twisted by 77.6 (2) and 83.0 (2)° with respect to the two indole ring systems. In the crystal, molecules are linked by N—H···O hydrogen bonds, forming layers parallel to the (001) plane. The layers are linked by C—H···π interactions, forming a supramolecular three-dimensional network.

3D view



Chemical scheme



Structure description

There are abundant bis(indolyl)methane derivatives in various terrestrial and marine natural resources (Porter *et al.*, 1977; Sundberg, 1996). They are important antibiotics in the field of pharmaceuticals with diverse activities, such as anticancer, antileishmanial and antihyperlipidemic (Chang *et al.*, 1999; Ge *et al.*, 1999). On the other hand, they can also be used as precursors for MRI necrosis avid contrast agents (Ni, 2008). In recent years, we have reported the synthesis and crystal structures of some similar bis(-indolyl)methane compounds (Sun *et al.*, 2012, 2015; Lu *et al.*, 2014, 2017), and herein we report on the crystal structure of the title bis(indolyl)methane compound.

The molecular structure of the title compound is shown in Fig. 1. The indole ring systems are nearly perpendicular to each other, making a dihedral angle of 87.43 (16)°. The 4-fluorophenyl ring (C2–C7) is twisted with respect to the N1/C8–C15 and N2/C19–C26 indole ring systems, with dihedral angles of 77.6 (2) and 83.0 (2)°, respectively. The carboxylate groups are inclined to the indole ring systems to which they are attached; the O1/O2/C15–C17 mean plane is inclined to the indole ring system N1/C8–C15 by 14.2 (2)°,

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

Cg is the centroid of the C20–C25 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O3^{i}	0.86 (5)	2.19 (5)	2.902 (6)	141 (5)
N2—H2*N*···O1^{ii}	0.90 (4)	2.05 (4)	2.891 (5)	156 (4)
C4—H4···*Cg*^{iii}	0.93	2.95	3.696 (17)	138

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

while the O3/O4/C26–C28 mean plane is inclined to the indole ring system N2/C19–C26 by 8.8 (2)°.

In the crystal, molecules are linked by two N—H···O hydrogen bonds, N1—H1*A*···O3^{i} and N2—H2*A*···O1^{ii} (see Table 1 for details), forming layers parallel to the *ab* plane (Fig. 2). There are C—H···π interactions present linking the layers to form a supramolecular three-dimensional network (Table 2 and Fig. 2).

A search of the Cambridge Structural Database (CSD, Version 5.39, last update August 2018; Groom *et al.*, 2016) revealed the presence of ten similar compounds (see supporting information). Five are dimethyl carboxylates and five are diethyl carboxylates. In all of these structures the indole ring systems are almost normal to each other.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{29}H_{25}FN_2O_4$
M_r	484.51
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	293
a, *b*, *c* (Å)	9.959 (2), 10.490 (2), 23.620 (5)
V (Å^3)	2467.6 (9)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.30 × 0.20 × 0.10
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.963, 0.979
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4526, 4526, 2498
R_{int}	0.054
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.057, 0.100, 0.95
No. of reflections	4526
No. of parameters	333
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.17

Computer programs: *CAD-4 EXPRESS* (Enraf–Nonius, 1994), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS* and *SHELXTL* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

Ethyl indole-2-carboxylate (1.88 g, 10 mmol) was dissolved in 20 ml ethanol, commercially available 4-fluorobenzaldehyde (0.62 g, 5 mmol) and concentrated HCl (0.5 ml) were added, and the mixture was heated to reflux temperature for 2 h. On completion of the reaction (monitored by TLC; AcOEt:hexane = 1:3) the reaction mixture was cooled to room temperature. The white product obtained was filtered off and washed thoroughly with ethanol (yield 90%). Colourless block-like crystals of the title compound suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution in ethanol.

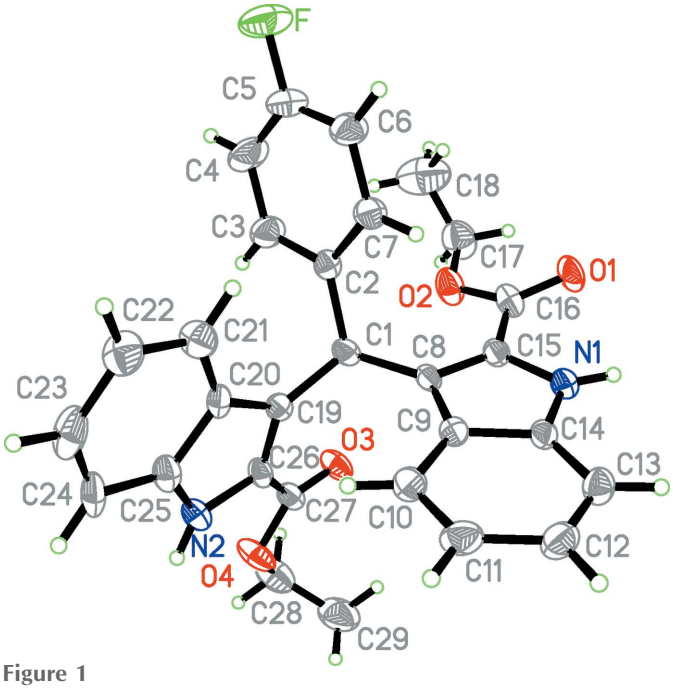


Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

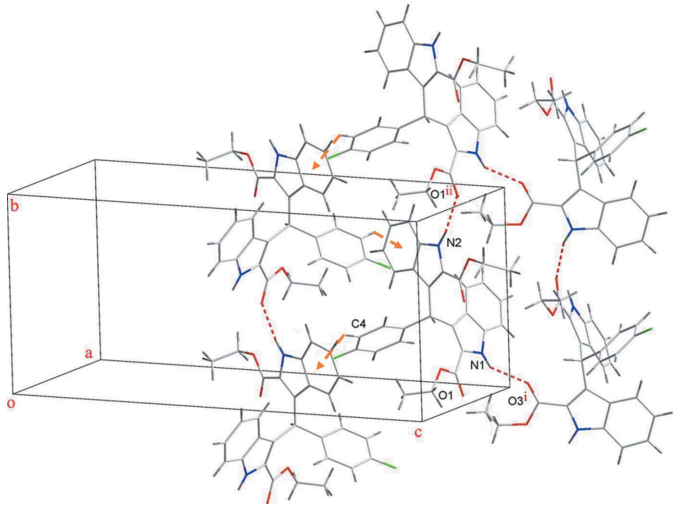


Figure 2
A view along the *a* axis of the crystal packing of the title compound. Hydrogen bonds (red) and C—H···π interactions (orange) are shown as dashed lines and arrows, respectively (see Table 1 for details).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors thank the Center of Testing and Analysis, Nanjing University, for support.

Funding information

Funding for this research was provided by: Natural Science Foundation of Jiangsu Province (grant No. BK20181486); Natural Science Foundation of the Jiangsu Higher Education Institutions (grant No. 17KJB320001); Training program of Students innovation and entrepreneurship in Jiangsu Province (grant No. 201812920002Y); Principals of Jiangsu Province and Qing Lan Project of Jiangsu Province.

References

Chang, Y.-C., Riby, J., Chang, G. H., Peng, G.-F., 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.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.

Lu, X.-H., Sun, H.-S., Cai, Y., Chen, L.-L. & Chen, Y.-F. (2017). *Acta Cryst.* E**73**, 1790–1792.

Lu, X.-H., Sun, H.-S. & Hu, J. (2014). *Acta Cryst.* E**70**, 593–595.

Ni, Y.-C. (2008). *Curr. Med. Imaging Rev.* **4**, 96–112.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 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.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Sun, H.-S., Li, Y., Jiang, H., Xu, N. & Xu, H. (2015). *Acta Cryst.* E**71**, 1140–1142.

Sun, H.-S., Li, Y.-L., Xu, N., Xu, H. & Zhang, J.-D. (2012). *Acta Cryst.* E**68**, o2764.

Sundberg, R. J. (1996). *The Chemistry of Indoles*, p. 113. New York: Academic Press.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2019). **4**, x190134 [https://doi.org/10.1107/S2414314619001342]

Diethyl 3,3′-[(4-fluorophenyl)methylidene]bis(1*H*-indole-2-carboxylate)

Yu-Long Li, Jin Zhou, Kai-Long Zhong, Xing-Hao Shi, Zhi-Yuan Zhang, Hong Jiang and Hong-Shun Sun

Diethyl 3,3′-[(4-fluorophenyl)methylidene]bis(1*H*-indole-2-carboxylate)

Crystal data

$C_{29}H_{25}FN_2O_4$
M_r = 484.51
Orthorhombic, $P2_12_12_1$
a = 9.959 (2) Å
b = 10.490 (2) Å
c = 23.620 (5) Å
V = 2467.6 (9) Å^3
Z = 4
F(000) = 1016
D_x = 1.304 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9–12°
μ = 0.09 mm^{-1}
T = 293 K
Block, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.963, T_{max} = 0.979
4526 measured reflections
4526 independent reflections
2498 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 25.4°, θ_{min} = 1.7°
h = 0→12
k = 0→12
l = −28→28
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.100
S = 0.95
4526 reflections
333 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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.

Refinement. The NH H atoms were located in a difference-Fourier map and freely refined. The C-bound H atom were included in calculated positions and constrained to ride on their parent atoms: C—H = 0.93–0.98 Å with U_{iso}(H) = 1.5U_{eq}(*C*-methyl) and 1.2U_{eq}(C) for other H atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.5636 (4)	0.1711 (4)	0.66324 (15)	0.0980 (14)
O1	0.7624 (4)	−0.0077 (3)	0.93583 (16)	0.0616 (12)
O2	0.6161 (4)	0.1470 (3)	0.91517 (17)	0.0651 (12)
N1	0.9673 (5)	0.1679 (5)	0.94094 (19)	0.0439 (13)
H1N	0.987 (5)	0.095 (5)	0.954 (2)	0.049 (18)*
N2	0.7457 (5)	0.7375 (4)	0.8897 (2)	0.0440 (12)
H2N	0.732 (4)	0.807 (4)	0.9111 (17)	0.035 (14)*
C1	0.7254 (5)	0.3859 (4)	0.8707 (2)	0.0379 (13)
H1	0.649319	0.372414	0.896271	0.045*
C2	0.6851 (5)	0.3247 (5)	0.8145 (2)	0.0381 (13)
O3	0.6074 (4)	0.4948 (3)	0.97917 (15)	0.0553 (11)
C3	0.5596 (6)	0.3537 (6)	0.7911 (2)	0.0624 (18)
H3	0.502862	0.409795	0.809991	0.075*
O4	0.6270 (4)	0.7051 (3)	0.98935 (17)	0.0668 (13)
C4	0.5187 (7)	0.3012 (6)	0.7411 (3)	0.078 (2)
H4	0.434629	0.320404	0.726181	0.094*
C5	0.6028 (7)	0.2204 (6)	0.7134 (3)	0.0608 (17)
C6	0.7254 (6)	0.1904 (6)	0.7342 (2)	0.0598 (17)
H6	0.781467	0.135526	0.714229	0.072*
C7	0.7670 (6)	0.2414 (5)	0.7849 (2)	0.0494 (15)
H7	0.850681	0.219665	0.799467	0.059*
C8	0.8450 (5)	0.3205 (4)	0.8985 (2)	0.0348 (13)
C9	0.9815 (5)	0.3630 (4)	0.9038 (2)	0.0357 (13)
C10	1.0527 (6)	0.4752 (5)	0.8890 (2)	0.0478 (15)
H10	1.009579	0.543523	0.871643	0.057*
C11	1.1868 (6)	0.4796 (5)	0.9009 (2)	0.0574 (17)
H11	1.235035	0.551600	0.890298	0.069*
C12	1.2549 (6)	0.3806 (6)	0.9284 (2)	0.0563 (16)
H12	1.346086	0.388751	0.936085	0.068*
C13	1.1892 (5)	0.2732 (5)	0.9437 (2)	0.0478 (15)
H13A	1.233611	0.207052	0.962106	0.057*
C14	1.0537 (6)	0.2649 (5)	0.9312 (2)	0.0380 (13)
C15	0.8417 (5)	0.2013 (5)	0.9215 (2)	0.0396 (14)
C16	0.7380 (6)	0.1042 (5)	0.9252 (2)	0.0509 (16)
C17	0.5058 (6)	0.0545 (6)	0.9165 (3)	0.083 (2)
H17A	0.537365	−0.026322	0.931406	0.100*
H17B	0.434133	0.085282	0.940774	0.100*
C18	0.4579 (9)	0.0384 (8)	0.8605 (3)	0.131 (3)
H18A	0.385431	−0.021928	0.860357	0.197*
H18B	0.426483	0.118771	0.846183	0.197*
H18C	0.529320	0.007594	0.836852	0.197*

C19	0.7419 (5)	0.5290 (4)	0.8659 (2)	0.0348 (12)
C20	0.7909 (5)	0.6024 (5)	0.8180 (2)	0.0389 (13)
C21	0.8318 (5)	0.5744 (5)	0.7625 (2)	0.0537 (16)
H21	0.831429	0.490806	0.749410	0.064*
C22	0.8716 (6)	0.6706 (6)	0.7285 (2)	0.0622 (18)
H22	0.897897	0.652506	0.691606	0.075*
C23	0.8740 (6)	0.7945 (6)	0.7471 (3)	0.068 (2)
H23A	0.902965	0.857419	0.722241	0.082*
C24	0.8358 (5)	0.8300 (5)	0.8008 (2)	0.0541 (17)
H24	0.838931	0.914251	0.813037	0.065*
C25	0.7920 (6)	0.7313 (5)	0.8355 (2)	0.0460 (15)
C26	0.7135 (5)	0.6151 (4)	0.9070 (2)	0.0374 (13)
C27	0.6450 (5)	0.5951 (5)	0.9619 (2)	0.0435 (14)
C28	0.5525 (7)	0.7020 (6)	1.0417 (3)	0.077 (2)
H28A	0.475881	0.645796	1.037384	0.092*
H28B	0.518857	0.786799	1.049915	0.092*
C29	0.6336 (8)	0.6584 (6)	1.0891 (3)	0.104 (3)
H29A	0.580037	0.657879	1.122901	0.157*
H29B	0.665637	0.573769	1.081584	0.157*
H29C	0.708604	0.714744	1.094113	0.157*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.092 (3)	0.127 (3)	0.076 (3)	−0.010 (3)	−0.026 (2)	−0.042 (3)
O1	0.064 (3)	0.0255 (19)	0.096 (3)	−0.004 (2)	−0.011 (2)	0.011 (2)
O2	0.047 (2)	0.043 (2)	0.105 (4)	−0.002 (2)	−0.006 (3)	0.011 (2)
N1	0.053 (3)	0.032 (3)	0.046 (3)	0.002 (3)	−0.002 (2)	0.001 (2)
N2	0.046 (3)	0.031 (3)	0.055 (3)	−0.002 (3)	0.008 (3)	0.001 (3)
C1	0.037 (3)	0.029 (3)	0.048 (3)	−0.003 (3)	0.000 (3)	−0.002 (3)
C2	0.031 (3)	0.037 (3)	0.046 (3)	0.001 (3)	0.002 (3)	0.001 (3)
O3	0.078 (3)	0.034 (2)	0.055 (3)	−0.011 (2)	0.019 (2)	0.0016 (19)
C3	0.054 (4)	0.071 (4)	0.062 (4)	0.014 (4)	−0.017 (4)	−0.016 (4)
O4	0.100 (3)	0.037 (2)	0.064 (3)	−0.010 (2)	0.034 (3)	−0.015 (2)
C4	0.060 (5)	0.099 (6)	0.076 (5)	0.002 (5)	−0.034 (4)	−0.013 (4)
C5	0.061 (4)	0.071 (4)	0.050 (4)	−0.007 (4)	−0.004 (4)	−0.020 (3)
C6	0.061 (4)	0.071 (4)	0.047 (4)	0.012 (4)	0.002 (3)	−0.012 (3)
C7	0.043 (4)	0.054 (3)	0.051 (4)	0.011 (3)	−0.004 (3)	−0.012 (3)
C8	0.043 (3)	0.026 (3)	0.035 (3)	0.002 (3)	0.003 (3)	−0.001 (2)
C9	0.041 (3)	0.034 (3)	0.032 (3)	0.001 (3)	0.004 (3)	0.001 (2)
C10	0.051 (4)	0.043 (3)	0.049 (4)	−0.013 (3)	−0.006 (3)	0.011 (3)
C11	0.060 (4)	0.055 (4)	0.057 (4)	−0.021 (3)	−0.010 (3)	0.004 (3)
C12	0.045 (4)	0.067 (4)	0.057 (4)	0.001 (4)	−0.013 (3)	−0.005 (3)
C13	0.037 (4)	0.049 (4)	0.058 (4)	0.003 (3)	−0.002 (3)	0.004 (3)
C14	0.047 (3)	0.034 (3)	0.033 (3)	0.007 (3)	−0.001 (3)	−0.002 (2)
C15	0.047 (4)	0.036 (3)	0.036 (3)	0.006 (3)	0.001 (3)	−0.001 (3)
C16	0.058 (4)	0.036 (3)	0.059 (4)	0.004 (4)	0.009 (3)	0.004 (3)
C17	0.069 (5)	0.066 (5)	0.114 (7)	−0.008 (4)	0.002 (5)	0.007 (5)

C18	0.147 (9)	0.150 (8)	0.097 (7)	−0.053 (7)	0.005 (6)	−0.019 (6)
C19	0.029 (3)	0.036 (3)	0.040 (3)	0.001 (3)	−0.001 (3)	0.000 (3)
C20	0.037 (3)	0.038 (3)	0.042 (3)	0.004 (3)	−0.003 (3)	0.012 (3)
C21	0.060 (4)	0.052 (3)	0.049 (4)	−0.006 (3)	0.011 (3)	0.004 (3)
C22	0.068 (5)	0.071 (4)	0.047 (4)	−0.006 (4)	0.014 (3)	0.013 (4)
C23	0.051 (4)	0.085 (5)	0.069 (5)	−0.015 (4)	0.000 (4)	0.047 (4)
C24	0.050 (4)	0.047 (3)	0.065 (4)	0.002 (3)	−0.003 (3)	0.031 (3)
C25	0.042 (4)	0.041 (3)	0.055 (4)	0.001 (3)	0.002 (3)	0.012 (3)
C26	0.036 (3)	0.027 (3)	0.049 (4)	−0.004 (3)	0.003 (3)	0.008 (3)
C27	0.040 (4)	0.033 (3)	0.058 (4)	−0.002 (3)	0.000 (3)	−0.003 (3)
C28	0.094 (6)	0.061 (4)	0.077 (5)	−0.001 (4)	0.039 (5)	−0.017 (4)
C29	0.170 (8)	0.076 (5)	0.068 (5)	−0.010 (6)	0.000 (5)	−0.018 (4)

Geometric parameters (Å, º)

F1—C5	1.350 (6)	C11—C12	1.400 (7)
O1—C16	1.225 (5)	C11—H11	0.9300
O2—C16	1.316 (6)	C12—C13	1.353 (7)
O2—C17	1.466 (7)	C12—H12	0.9300
N1—C14	1.351 (7)	C13—C14	1.384 (7)
N1—C15	1.379 (6)	C13—H13A	0.9300
N1—H1N	0.86 (5)	C15—C16	1.453 (7)
N2—C25	1.362 (6)	C17—C18	1.418 (8)
N2—C26	1.384 (5)	C17—H17A	0.9700
N2—H2N	0.90 (4)	C17—H17B	0.9700
C1—C19	1.514 (6)	C18—H18A	0.9600
C1—C8	1.524 (6)	C18—H18B	0.9600
C1—C2	1.528 (6)	C18—H18C	0.9600
C1—H1	0.9800	C19—C26	1.356 (6)
C2—C7	1.385 (6)	C19—C20	1.453 (6)
C2—C3	1.400 (7)	C20—C21	1.404 (7)
O3—C27	1.190 (5)	C20—C25	1.414 (6)
C3—C4	1.365 (7)	C21—C22	1.350 (7)
C3—H3	0.9300	C21—H21	0.9300
O4—C27	1.336 (5)	C22—C23	1.372 (8)
O4—C28	1.443 (6)	C22—H22	0.9300
C4—C5	1.359 (8)	C23—C24	1.376 (8)
C4—H4	0.9300	C23—H23A	0.9300
C5—C6	1.354 (7)	C24—C25	1.391 (7)
C6—C7	1.376 (7)	C24—H24	0.9300
C6—H6	0.9300	C26—C27	1.479 (7)
C7—H7	0.9300	C28—C29	1.453 (8)
C8—C15	1.363 (6)	C28—H28A	0.9700
C8—C9	1.437 (6)	C28—H28B	0.9700
C9—C14	1.413 (6)	C29—H29A	0.9600
C9—C10	1.419 (6)	C29—H29B	0.9600
C10—C11	1.365 (6)	C29—H29C	0.9600
C10—H10	0.9300		

C16—O2—C17	117.5 (4)	N1—C15—C16	116.5 (5)
C14—N1—C15	109.3 (5)	O1—C16—O2	123.1 (5)
C14—N1—H1N	126 (4)	O1—C16—C15	122.9 (6)
C15—N1—H1N	124 (4)	O2—C16—C15	113.9 (5)
C25—N2—C26	108.2 (4)	C18—C17—O2	108.1 (6)
C25—N2—H2N	128 (3)	C18—C17—H17A	110.1
C26—N2—H2N	124 (3)	O2—C17—H17A	110.1
C19—C1—C8	113.2 (4)	C18—C17—H17B	110.1
C19—C1—C2	112.4 (4)	O2—C17—H17B	110.1
C8—C1—C2	113.0 (4)	H17A—C17—H17B	108.4
C19—C1—H1	105.8	C17—C18—H18A	109.5
C8—C1—H1	105.8	C17—C18—H18B	109.5
C2—C1—H1	105.8	H18A—C18—H18B	109.5
C7—C2—C3	117.6 (5)	C17—C18—H18C	109.5
C7—C2—C1	123.3 (5)	H18A—C18—H18C	109.5
C3—C2—C1	119.1 (5)	H18B—C18—H18C	109.5
C4—C3—C2	121.3 (6)	C26—C19—C20	105.9 (4)
C4—C3—H3	119.3	C26—C19—C1	125.8 (5)
C2—C3—H3	119.3	C20—C19—C1	128.3 (5)
C27—O4—C28	117.8 (4)	C21—C20—C25	118.1 (5)
C5—C4—C3	118.9 (6)	C21—C20—C19	135.5 (5)
C5—C4—H4	120.5	C25—C20—C19	106.4 (5)
C3—C4—H4	120.5	C22—C21—C20	119.0 (5)
F1—C5—C6	119.3 (6)	C22—C21—H21	120.5
F1—C5—C4	118.9 (6)	C20—C21—H21	120.5
C6—C5—C4	121.8 (6)	C21—C22—C23	121.5 (6)
C5—C6—C7	119.8 (6)	C21—C22—H22	119.2
C5—C6—H6	120.1	C23—C22—H22	119.2
C7—C6—H6	120.1	C22—C23—C24	123.2 (6)
C6—C7—C2	120.5 (5)	C22—C23—H23A	118.4
C6—C7—H7	119.8	C24—C23—H23A	118.4
C2—C7—H7	119.8	C23—C24—C25	115.4 (6)
C15—C8—C9	105.8 (4)	C23—C24—H24	122.3
C15—C8—C1	124.5 (5)	C25—C24—H24	122.3
C9—C8—C1	129.6 (4)	N2—C25—C24	128.7 (5)
C14—C9—C10	117.6 (5)	N2—C25—C20	108.5 (5)
C14—C9—C8	107.2 (4)	C24—C25—C20	122.8 (5)
C10—C9—C8	135.2 (5)	C19—C26—N2	111.0 (4)
C11—C10—C9	117.7 (5)	C19—C26—C27	128.9 (5)
C11—C10—H10	121.1	N2—C26—C27	119.8 (5)
C9—C10—H10	121.1	O3—C27—O4	123.7 (5)
C10—C11—C12	123.1 (6)	O3—C27—C26	124.9 (5)
C10—C11—H11	118.5	O4—C27—C26	111.4 (5)
C12—C11—H11	118.5	O4—C28—C29	112.4 (6)
C13—C12—C11	120.5 (5)	O4—C28—H28A	109.1
C13—C12—H12	119.7	C29—C28—H28A	109.1
C11—C12—H12	119.7	O4—C28—H28B	109.1

C12—C13—C14	117.8 (6)	C29—C28—H28B	109.1
C12—C13—H13A	121.1	H28A—C28—H28B	107.8
C14—C13—H13A	121.1	C28—C29—H29A	109.5
N1—C14—C13	129.2 (5)	C28—C29—H29B	109.5
N1—C14—C9	107.6 (5)	H29A—C29—H29B	109.5
C13—C14—C9	123.2 (5)	C28—C29—H29C	109.5
C8—C15—N1	110.1 (5)	H29A—C29—H29C	109.5
C8—C15—C16	133.2 (5)	H29B—C29—H29C	109.5

C19—C1—C2—C7	114.2 (5)	C17—O2—C16—O1	−0.6 (9)
C8—C1—C2—C7	−15.5 (7)	C17—O2—C16—C15	178.4 (5)
C19—C1—C2—C3	−65.7 (6)	C8—C15—C16—O1	162.6 (6)
C8—C1—C2—C3	164.7 (5)	N1—C15—C16—O1	−11.9 (8)
C7—C2—C3—C4	0.4 (9)	C8—C15—C16—O2	−16.5 (9)
C1—C2—C3—C4	−179.8 (6)	N1—C15—C16—O2	169.1 (5)
C2—C3—C4—C5	−0.7 (10)	C16—O2—C17—C18	−110.4 (7)
C3—C4—C5—F1	−178.3 (6)	C8—C1—C19—C26	−84.1 (6)
C3—C4—C5—C6	0.2 (11)	C2—C1—C19—C26	146.4 (5)
F1—C5—C6—C7	179.2 (5)	C8—C1—C19—C20	95.4 (6)
C4—C5—C6—C7	0.6 (10)	C2—C1—C19—C20	−34.1 (8)
C5—C6—C7—C2	−1.0 (9)	C26—C19—C20—C21	−177.0 (6)
C3—C2—C7—C6	0.5 (8)	C1—C19—C20—C21	3.5 (10)
C1—C2—C7—C6	−179.3 (5)	C26—C19—C20—C25	1.8 (6)
C19—C1—C8—C15	161.4 (5)	C1—C19—C20—C25	−177.8 (5)
C2—C1—C8—C15	−69.4 (6)	C25—C20—C21—C22	0.7 (9)
C19—C1—C8—C9	−22.3 (7)	C19—C20—C21—C22	179.4 (6)
C2—C1—C8—C9	106.9 (5)	C20—C21—C22—C23	0.6 (10)
C15—C8—C9—C14	−0.9 (5)	C21—C22—C23—C24	−0.6 (10)
C1—C8—C9—C14	−177.7 (5)	C22—C23—C24—C25	−0.8 (9)
C15—C8—C9—C10	179.9 (5)	C26—N2—C25—C24	179.9 (6)
C1—C8—C9—C10	3.1 (9)	C26—N2—C25—C20	−0.7 (6)
C14—C9—C10—C11	1.5 (7)	C23—C24—C25—N2	−178.5 (5)
C8—C9—C10—C11	−179.4 (5)	C23—C24—C25—C20	2.2 (8)
C9—C10—C11—C12	−1.9 (8)	C21—C20—C25—N2	178.3 (5)
C10—C11—C12—C13	1.1 (9)	C19—C20—C25—N2	−0.7 (6)
C11—C12—C13—C14	0.2 (8)	C21—C20—C25—C24	−2.2 (9)
C15—N1—C14—C13	180.0 (5)	C19—C20—C25—C24	178.8 (5)
C15—N1—C14—C9	−0.9 (6)	C20—C19—C26—N2	−2.3 (6)
C12—C13—C14—N1	178.5 (5)	C1—C19—C26—N2	177.3 (5)
C12—C13—C14—C9	−0.5 (8)	C20—C19—C26—C27	171.5 (5)
C10—C9—C14—N1	−179.5 (4)	C1—C19—C26—C27	−8.9 (9)
C8—C9—C14—N1	1.1 (6)	C25—N2—C26—C19	1.9 (6)
C10—C9—C14—C13	−0.3 (7)	C25—N2—C26—C27	−172.5 (5)
C8—C9—C14—C13	−179.7 (5)	C28—O4—C27—O3	−2.8 (9)
C9—C8—C15—N1	0.4 (6)	C28—O4—C27—C26	175.6 (5)
C1—C8—C15—N1	177.4 (4)	C19—C26—C27—O3	2.8 (9)
C9—C8—C15—C16	−174.3 (5)	N2—C26—C27—O3	176.1 (5)
C1—C8—C15—C16	2.6 (9)	C19—C26—C27—O4	−175.6 (5)

C14—N1—C15—C8	0.3 (6)	N2—C26—C27—O4	−2.2 (7)
C14—N1—C15—C16	176.0 (4)	C27—O4—C28—C29	79.4 (7)

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C20–C25 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O3^{i}	0.86 (5)	2.19 (5)	2.902 (6)	141 (5)
N2—H2*N*···O1^{ii}	0.90 (4)	2.05 (4)	2.891 (5)	156 (4)
C4—H4···*Cg*^{iii}	0.93	2.95	3.696 (17)	138

Symmetry codes: (i) *x*+1/2, −*y*+1/2, −*z*+2; (ii) *x*, *y*+1, *z*; (iii) −*x*+1, *y*−1/2, −*z*+3/2.