Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

5-Methylspiro[indoline-3,7′-[6*H*,7*H*,8*H*]-pyrano[3,2-c:5,6-c′]di[1]benzopyran]-2,6′,8′-trione chloroform hemisolvate

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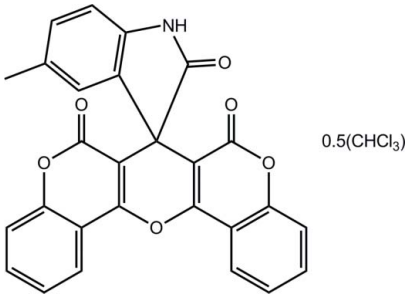
Received 16 March 2012; accepted 20 March 2012

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.067; wR factor = 0.174; data-to-parameter ratio = 24.5.

In the title compound, $C_{27}H_{15}NO_6\cdot0.5CHCl_3$, the central pyran ring and both the benzopyran systems are planar, with the dihedral angle between the outer rings being 3.24 (6)°. The indolin-2-one system is in a perpendicular configuration with respect to the pyran ring [dihedral angle = 87.58 (2)°]. Supramolecular layers in the *ac* plane are formed in the crystal structure whereby inversion-related molecules are connected by N—H···O hydrogen bonds. These are further linked by C—H···O interactions, forming a supramolecular layer in the *ac* plane. Disordered $CHCl_3$ solvent in the structure was modelled with the SQUEEZE routine in *PLATON* [Spek (2009). *Acta Cryst.* D**65**, 148–155].

Related literature

For hydrogen-bonding motifs, see: Bernstein *et al.* (1995). For the biological relevance of benzopyrans, see: Martin & Critchlow (1999); Teague & Davis (1999). For the importance of spiro[indole-pyran] systems, see: Ninamiya (1980); Kobayashi & Matsuda (1970).



Experimental

Crystal data

$C_{27}H_{15}NO_6\cdot0.5CHCl_3$
M_r = 509.08
Monoclinic, $P2_1/c$
a = 9.9341 (2) Å
b = 19.1498 (4) Å
c = 12.8279 (2) Å
β = 95.078 (1)°
V = 2430.75 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 293 K
0.21 × 0.17 × 0.12 mm

Data collection

Bruker Kappa APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.973, T_{max} = 0.978
30555 measured reflections
7646 independent reflections
5443 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.174
S = 1.05
7646 reflections
312 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5^{i}	0.89 (3)	2.25 (3)	2.965 (2)	138 (2)
C45—H45···O5^{i}	0.93	2.51	3.212 (2)	133
C63—H63···O3^{ii}	0.93	2.51	3.347 (3)	150
C65—H65···O4^{iii}	0.93	2.59	3.363 (2)	141

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

This project was supported by the Research Center, College of Science, King Saud University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5070).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Kobayashi, G. & Matsuda, Y. (1970). Jpn Patent No. 7025894.
Martin, E. J. & Critchlow, R. E. (1999). *J. Combin. Chem.* **1**, 32–45.
Ninamiya, K. (1980). Jpn Patent No. 7025894.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Teague, S. J. & Davis, A. M. (1999). *Angew. Chem. Int. Ed.* **38**, 3743–3748.

supporting information

Acta Cryst. (2012). E**68**, o1194 [https://doi.org/10.1107/S1600536812012020]

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S1. Comment

Benzopyran is a structural motif observed in many biologically active natural products and it plays an important role in binding with various biopolymers (Martin *et al.*, 1999; Teague *et al.*, 1999). Of the various spiro indoles, the spiro[indole-pyran] system has attracted attention due to its interesting pharmacological properties (Ninamiya *et al.*, 1980; Kobayashi *et al.*, 1970). The biological importance of these heterocycles in conjunction with our research interests prompted us to synthesize and report the X-ray structure of the title compound.

In the title compound, Fig 1, the central pyrano ring and both the benzopyran rings are planar. In the indolin-2-one system, the benzene and pyrrole rings are individually planar and make a dihedral angle of 1.42 (1)°. The indoline-2-one system is in a perpendicular configuration with respect to the pyrano ring, as can be seen from the dihedral angle of 87.58 (2)°. The sum of the angles at atom N1 of the indolin-2-one moiety is in accordance with sp^2-hybridization [359.85 (2)°].

The N1—H1···O5 hydrogen bond connects two centrosymmetrically related molecules and generate the graph set motif $R_2^2(14)$ (Bernstein *et al.*, 1995). These centrosymmetric dimers are interrelated by zigzag linear chains of C—H···O hydrogen bonds to form a layered structure (Fig. 2).

S2. Experimental

A mixture of 5-methylindoline-2,3-dione (0.100 g, 0.62 mmol), 4-hydroxy-2*H*-chromen-2-one (0.201 g, 1.24 mmol) and paratoluene sulfonic acid (0.118 g, 0.62 mmol) were dissolved in 5 ml of ethanol:water (1:1 *v*/*v*) and refluxed for 2 h. After completion of the reaction, as evidenced from TLC, the precipitated solid was filtered and washed with water to afford the product which was recrystallized from $CHCl_3$ to produce the title compound as colourless crystals. Yield 76%. *M*. pt: 540–541 K.

S3. Refinement

Initial structural solution showed a disordered co-crystallized solvent chloroform molecule for which a suitable model could not be found. Therefore, the data set was treated with SQUEEZE routine of *PLATON* (Spek, 2009) to model the electron density in the void regions. There are two cavities of 277 Å^3 per unit cell. Each cavity contains approximately 125 electrons which were assigned to two solvent chloroform molecules. The N-bound H atom was located in a difference map and refined freely. The C-bound H atoms were placed at calculated positions and allowed to ride on their carrier atoms with C—H = 0.93–0.96 Å, and with U_{iso} = 1.2 to 1.5U_{eq}(C).

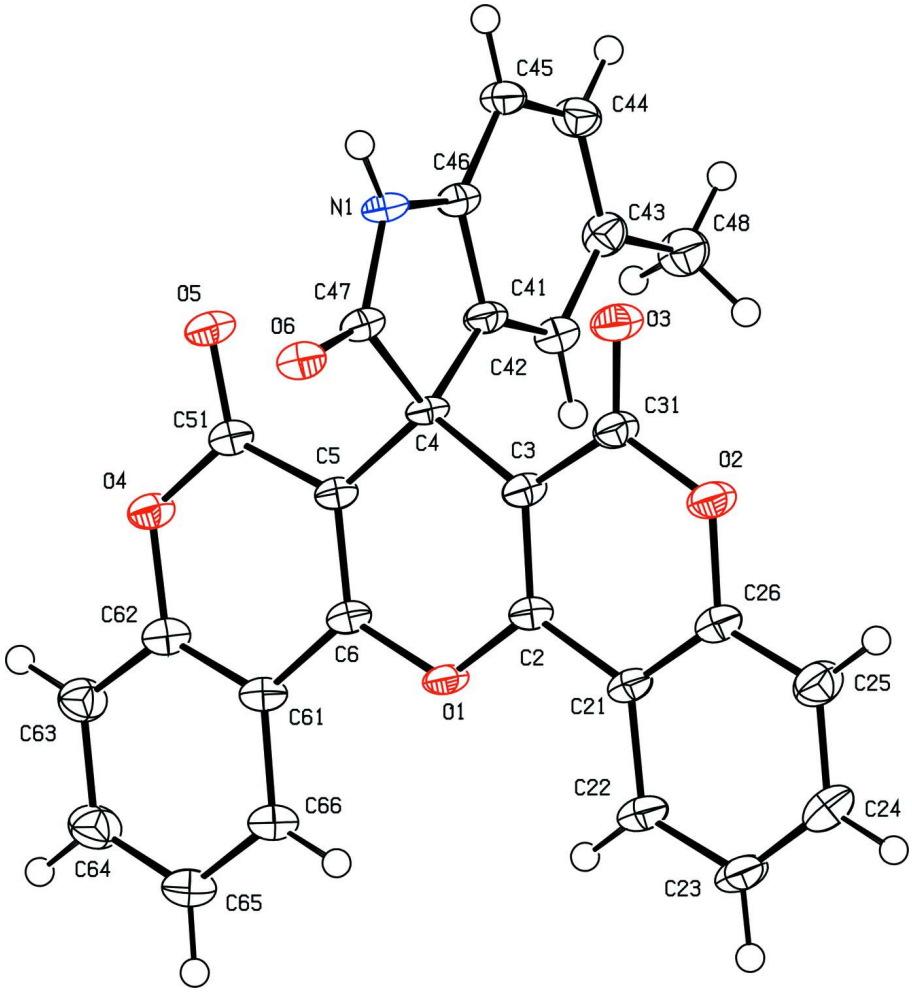

Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

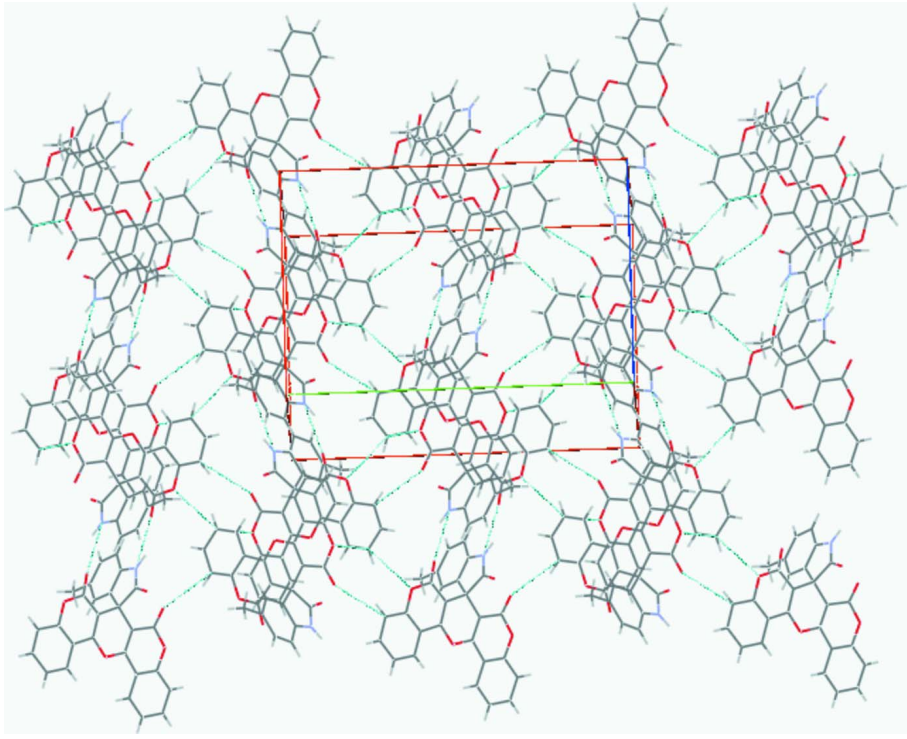

Figure 2

A packing diagram for (I).

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$c = 12.8279$ (2) Å
$\beta = 95.078$ (1)°
$V = 2430.75$ (8) Å^3
$Z = 4$
$F(000) = 1044$
$D_x = 1.391$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2000 reflections
$\theta = 2$–31°
$\mu = 0.26$ mm^{-1}
$T = 293$ K
Block, colourless
0.21 × 0.17 × 0.12 mm

Data collection

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.973$, $T_{max} = 0.978$
30555 measured reflections
7646 independent reflections
5443 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 31.0°$, $\theta_{min} = 1.9°$
$h = -14 \rightarrow 13$
$k = -25 \rightarrow 27$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.174$
$S = 1.05$
7646 reflections
312 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 2.2541P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
H1	0.457 (3)	−0.0749 (15)	0.036 (2)	0.039 (7)*
O1	0.36729 (14)	0.05045 (7)	0.45866 (9)	0.0208 (3)
O4	0.61175 (14)	0.16085 (7)	0.27455 (10)	0.0218 (3)
O2	0.13685 (15)	−0.11955 (8)	0.35920 (10)	0.0260 (3)
O5	0.55602 (15)	0.09408 (7)	0.13736 (10)	0.0237 (3)
C5	0.45433 (18)	0.06556 (9)	0.29103 (13)	0.0173 (3)
C4	0.37191 (18)	0.00753 (9)	0.23811 (12)	0.0169 (3)
O3	0.21718 (16)	−0.11890 (8)	0.20426 (11)	0.0274 (3)
C61	0.5243 (2)	0.14056 (10)	0.44128 (13)	0.0206 (3)
O6	0.55858 (14)	−0.07739 (7)	0.22758 (10)	0.0227 (3)
N1	0.42069 (17)	−0.04625 (8)	0.08013 (11)	0.0194 (3)
C51	0.54180 (19)	0.10595 (9)	0.22880 (13)	0.0191 (3)
C62	0.6029 (2)	0.17960 (10)	0.37751 (14)	0.0224 (4)
C21	0.20946 (19)	−0.03669 (10)	0.49302 (13)	0.0201 (3)
C26	0.1330 (2)	−0.09402 (10)	0.45856 (14)	0.0232 (4)
C6	0.44858 (19)	0.08330 (9)	0.39331 (13)	0.0187 (3)
C66	0.5210 (2)	0.16042 (10)	0.54660 (14)	0.0242 (4)
H66	0.4702	0.1348	0.5907	0.029*
C31	0.2182 (2)	−0.09080 (10)	0.28832 (14)	0.0223 (4)
C2	0.29255 (19)	−0.00495 (9)	0.41954 (13)	0.0189 (3)
C3	0.29520 (19)	−0.02882 (10)	0.31997 (13)	0.0201 (3)
C22	0.2006 (2)	−0.01261 (11)	0.59664 (14)	0.0255 (4)
H22	0.2501	0.0261	0.6213	0.031*
C47	0.46395 (19)	−0.04504 (9)	0.18295 (13)	0.0194 (3)

C41	0.27664 (19)	0.03172 (10)	0.14649 (13)	0.0199 (3)
C23	0.1178 (2)	−0.04734 (12)	0.66075 (15)	0.0297 (4)
H23	0.1116	−0.0318	0.7289	0.036*
C65	0.5931 (2)	0.21793 (11)	0.58413 (16)	0.0285 (4)
H65	0.5922	0.2307	0.6540	0.034*
C42	0.17032 (19)	0.07831 (10)	0.14353 (14)	0.0214 (4)
H42	0.1506	0.1013	0.2042	0.026*
C63	0.6734 (2)	0.23846 (10)	0.41314 (16)	0.0262 (4)
H63	0.7229	0.2647	0.3689	0.031*
C44	0.1267 (2)	0.05638 (11)	−0.04015 (15)	0.0260 (4)
H44	0.0752	0.0646	−0.1031	0.031*
C25	0.0495 (2)	−0.12924 (12)	0.52263 (16)	0.0298 (4)
H25	−0.0008	−0.1677	0.4979	0.036*
C45	0.2353 (2)	0.00990 (10)	−0.03905 (14)	0.0230 (4)
H45	0.2569	−0.0123	−0.0999	0.028*
C46	0.30960 (19)	−0.00194 (10)	0.05576 (13)	0.0196 (3)
C43	0.0926 (2)	0.09085 (10)	0.04953 (15)	0.0244 (4)
C24	0.0432 (2)	−0.10568 (13)	0.62359 (17)	0.0332 (5)
H24	−0.0114	−0.1288	0.6677	0.040*
C48	−0.0246 (2)	0.14117 (12)	0.04545 (17)	0.0301 (4)
H48A	−0.0772	0.1368	−0.0207	0.045*
H48B	0.0090	0.1880	0.0535	0.045*
H48C	−0.0802	0.1307	0.1010	0.045*
C64	0.6678 (2)	0.25713 (11)	0.51757 (17)	0.0306 (4)
H64	0.7145	0.2964	0.5435	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0288 (7)	0.0230 (6)	0.0110 (5)	−0.0020 (5)	0.0047 (5)	−0.0020 (5)
O4	0.0298 (7)	0.0208 (6)	0.0154 (6)	−0.0013 (5)	0.0046 (5)	0.0001 (5)
O2	0.0354 (8)	0.0263 (7)	0.0173 (6)	−0.0067 (6)	0.0078 (5)	−0.0023 (5)
O5	0.0338 (8)	0.0235 (7)	0.0147 (6)	−0.0001 (6)	0.0070 (5)	−0.0009 (5)
C5	0.0231 (8)	0.0167 (7)	0.0124 (7)	0.0018 (6)	0.0026 (6)	0.0006 (6)
C4	0.0244 (8)	0.0167 (7)	0.0098 (6)	0.0006 (6)	0.0039 (6)	−0.0007 (5)
O3	0.0395 (8)	0.0252 (7)	0.0183 (6)	−0.0056 (6)	0.0074 (6)	−0.0041 (5)
C61	0.0277 (9)	0.0198 (8)	0.0140 (7)	0.0028 (7)	0.0011 (7)	−0.0004 (6)
O6	0.0288 (7)	0.0223 (6)	0.0172 (6)	0.0041 (5)	0.0034 (5)	0.0003 (5)
N1	0.0274 (8)	0.0203 (7)	0.0110 (6)	0.0028 (6)	0.0046 (5)	−0.0018 (5)
C51	0.0243 (9)	0.0181 (8)	0.0152 (7)	0.0025 (7)	0.0031 (6)	0.0004 (6)
C62	0.0289 (10)	0.0215 (8)	0.0170 (8)	0.0018 (7)	0.0028 (7)	−0.0007 (6)
C21	0.0245 (9)	0.0233 (8)	0.0132 (7)	0.0034 (7)	0.0048 (6)	0.0015 (6)
C26	0.0273 (9)	0.0262 (9)	0.0168 (8)	0.0021 (7)	0.0057 (7)	0.0006 (7)
C6	0.0247 (9)	0.0186 (8)	0.0129 (7)	0.0022 (7)	0.0031 (6)	0.0009 (6)
C66	0.0315 (10)	0.0254 (9)	0.0158 (8)	0.0011 (8)	0.0019 (7)	−0.0023 (7)
C31	0.0278 (9)	0.0231 (9)	0.0165 (8)	−0.0016 (7)	0.0052 (7)	0.0001 (6)
C2	0.0242 (9)	0.0195 (8)	0.0132 (7)	0.0013 (7)	0.0023 (6)	0.0001 (6)
C3	0.0257 (9)	0.0205 (8)	0.0145 (7)	0.0001 (7)	0.0049 (6)	−0.0006 (6)

C22	0.0318 (10)	0.0304 (10)	0.0148 (8)	0.0033 (8)	0.0058 (7)	−0.0001 (7)
C47	0.0263 (9)	0.0185 (8)	0.0143 (7)	0.0005 (7)	0.0059 (6)	−0.0009 (6)
C41	0.0257 (9)	0.0222 (8)	0.0123 (7)	−0.0013 (7)	0.0038 (6)	−0.0002 (6)
C23	0.0351 (11)	0.0391 (11)	0.0162 (8)	0.0029 (9)	0.0091 (7)	−0.0001 (8)
C65	0.0365 (11)	0.0289 (10)	0.0198 (8)	0.0008 (9)	0.0015 (8)	−0.0059 (7)
C42	0.0255 (9)	0.0227 (8)	0.0165 (8)	0.0011 (7)	0.0046 (7)	−0.0007 (6)
C63	0.0314 (10)	0.0232 (9)	0.0240 (9)	−0.0021 (8)	0.0021 (8)	−0.0008 (7)
C44	0.0295 (10)	0.0300 (10)	0.0181 (8)	−0.0010 (8)	−0.0003 (7)	0.0008 (7)
C25	0.0347 (11)	0.0304 (10)	0.0254 (9)	−0.0035 (9)	0.0091 (8)	0.0007 (8)
C45	0.0277 (9)	0.0275 (9)	0.0139 (7)	−0.0019 (8)	0.0024 (7)	−0.0023 (6)
C46	0.0253 (9)	0.0199 (8)	0.0141 (7)	−0.0004 (7)	0.0044 (6)	−0.0016 (6)
C43	0.0249 (9)	0.0254 (9)	0.0230 (9)	0.0009 (7)	0.0039 (7)	0.0020 (7)
C24	0.0362 (12)	0.0407 (12)	0.0248 (10)	−0.0017 (10)	0.0138 (8)	0.0036 (9)
C48	0.0289 (10)	0.0342 (11)	0.0272 (10)	0.0065 (9)	0.0031 (8)	0.0020 (8)
C64	0.0372 (12)	0.0273 (10)	0.0271 (10)	−0.0036 (9)	0.0013 (9)	−0.0068 (8)

Geometric parameters (Å, º)

O1—C2	1.365 (2)	C31—C3	1.451 (3)
O1—C6	1.368 (2)	C2—C3	1.359 (2)
O4—C51	1.364 (2)	C22—C23	1.384 (3)
O4—C62	1.379 (2)	C22—H22	0.9300
O2—C26	1.369 (2)	C41—C42	1.381 (3)
O2—C31	1.383 (2)	C41—C46	1.395 (2)
O5—C51	1.215 (2)	C23—C24	1.401 (3)
C5—C6	1.361 (2)	C23—H23	0.9300
C5—C51	1.454 (2)	C65—C64	1.398 (3)
C5—C4	1.506 (2)	C65—H65	0.9300
C4—C41	1.515 (2)	C42—C43	1.394 (3)
C4—C3	1.520 (2)	C42—H42	0.9300
C4—C47	1.570 (2)	C63—C64	1.392 (3)
O3—C31	1.204 (2)	C63—H63	0.9300
C61—C62	1.396 (3)	C44—C43	1.394 (3)
C61—C66	1.407 (2)	C44—C45	1.398 (3)
C61—C6	1.437 (3)	C44—H44	0.9300
O6—C47	1.225 (2)	C25—C24	1.378 (3)
N1—C47	1.351 (2)	C25—H25	0.9300
N1—C46	1.405 (2)	C45—C46	1.384 (3)
N1—H1	0.88 (3)	C45—H45	0.9300
C62—C63	1.384 (3)	C43—C48	1.509 (3)
C21—C26	1.385 (3)	C24—H24	0.9300
C21—C22	1.417 (2)	C48—H48A	0.9600
C21—C2	1.441 (2)	C48—H48B	0.9600
C26—C25	1.393 (3)	C48—H48C	0.9600
C66—C65	1.378 (3)	C64—H64	0.9300
C66—H66	0.9300		
C2—O1—C6	117.62 (13)	C21—C22—H22	120.3

C51—O4—C62	122.64 (15)	O6—C47—N1	127.77 (17)
C26—O2—C31	122.42 (16)	O6—C47—C4	124.55 (15)
C6—C5—C51	118.32 (16)	N1—C47—C4	107.67 (15)
C6—C5—C4	123.45 (16)	C42—C41—C46	120.75 (17)
C51—C5—C4	118.21 (14)	C42—C41—C4	130.01 (16)
C5—C4—C41	113.67 (14)	C46—C41—C4	109.24 (16)
C5—C4—C3	108.20 (13)	C22—C23—C24	120.37 (18)
C41—C4—C3	111.05 (15)	C22—C23—H23	119.8
C5—C4—C47	111.18 (15)	C24—C23—H23	119.8
C41—C4—C47	101.25 (13)	C66—C65—C64	120.24 (18)
C3—C4—C47	111.43 (14)	C66—C65—H65	119.9
C62—C61—C66	118.68 (17)	C64—C65—H65	119.9
C62—C61—C6	117.14 (16)	C41—C42—C43	119.94 (17)
C66—C61—C6	124.15 (17)	C41—C42—H42	120.0
C47—N1—C46	112.50 (15)	C43—C42—H42	120.0
C47—N1—H1	121.3 (18)	C62—C63—C64	117.69 (19)
C46—N1—H1	126.0 (18)	C62—C63—H63	121.2
O5—C51—O4	117.46 (16)	C64—C63—H63	121.2
O5—C51—C5	123.83 (17)	C43—C44—C45	122.47 (18)
O4—C51—C5	118.71 (15)	C43—C44—H44	118.8
O4—C62—C63	117.07 (17)	C45—C44—H44	118.8
O4—C62—C61	120.54 (17)	C24—C25—C26	118.4 (2)
C63—C62—C61	122.39 (17)	C24—C25—H25	120.8
C26—C21—C22	118.67 (17)	C26—C25—H25	120.8
C26—C21—C2	117.08 (16)	C46—C45—C44	117.67 (17)
C22—C21—C2	124.25 (18)	C46—C45—H45	121.2
O2—C26—C21	121.37 (16)	C44—C45—H45	121.2
O2—C26—C25	116.34 (18)	C45—C46—C41	120.74 (18)
C21—C26—C25	122.28 (17)	C45—C46—N1	129.92 (16)
C5—C6—O1	123.59 (16)	C41—C46—N1	109.34 (15)
C5—C6—C61	122.55 (17)	C44—C43—C42	118.42 (18)
O1—C6—C61	113.81 (15)	C44—C43—C48	121.13 (18)
C65—C66—C61	119.73 (19)	C42—C43—C48	120.45 (18)
C65—C66—H66	120.1	C25—C24—C23	120.9 (2)
C61—C66—H66	120.1	C25—C24—H24	119.5
O3—C31—O2	116.87 (17)	C23—C24—H24	119.5
O3—C31—C3	125.33 (17)	C43—C48—H48A	109.5
O2—C31—C3	117.78 (15)	C43—C48—H48B	109.5
C3—C2—O1	123.50 (16)	H48A—C48—H48B	109.5
C3—C2—C21	122.19 (17)	C43—C48—H48C	109.5
O1—C2—C21	114.31 (15)	H48A—C48—H48C	109.5
C2—C3—C31	118.98 (16)	H48B—C48—H48C	109.5
C2—C3—C4	123.23 (17)	C63—C64—C65	121.23 (19)
C31—C3—C4	117.76 (15)	C63—C64—H64	119.4
C23—C22—C21	119.4 (2)	C65—C64—H64	119.4
C23—C22—H22	120.3		

C6—C5—C4—C41	119.26 (19)	O3—C31—C3—C4	5.5 (3)

C51—C5—C4—C41	−59.0 (2)	O2—C31—C3—C4	−173.18 (16)
C6—C5—C4—C3	−4.6 (2)	C5—C4—C3—C2	7.4 (2)
C51—C5—C4—C3	177.16 (15)	C41—C4—C3—C2	−118.02 (19)
C6—C5—C4—C47	−127.26 (18)	C47—C4—C3—C2	129.91 (19)
C51—C5—C4—C47	54.5 (2)	C5—C4—C3—C31	−174.52 (16)
C62—O4—C51—O5	179.51 (17)	C41—C4—C3—C31	60.1 (2)
C62—O4—C51—C5	0.0 (3)	C47—C4—C3—C31	−52.0 (2)
C6—C5—C51—O5	178.95 (18)	C26—C21—C22—C23	0.8 (3)
C4—C5—C51—O5	−2.7 (3)	C2—C21—C22—C23	−179.77 (19)
C6—C5—C51—O4	−1.6 (3)	C46—N1—C47—O6	−179.44 (19)
C4—C5—C51—O4	176.77 (15)	C46—N1—C47—C4	−0.5 (2)
C51—O4—C62—C63	−176.75 (17)	C5—C4—C47—O6	58.0 (2)
C51—O4—C62—C61	2.6 (3)	C41—C4—C47—O6	179.11 (18)
C66—C61—C62—O4	178.32 (17)	C3—C4—C47—O6	−62.8 (2)
C6—C61—C62—O4	−3.4 (3)	C5—C4—C47—N1	−120.92 (16)
C66—C61—C62—C63	−2.4 (3)	C41—C4—C47—N1	0.15 (19)
C6—C61—C62—C63	175.88 (18)	C3—C4—C47—N1	118.29 (16)
C31—O2—C26—C21	1.1 (3)	C5—C4—C41—C42	−61.1 (3)
C31—O2—C26—C25	−178.23 (18)	C3—C4—C41—C42	61.1 (3)
C22—C21—C26—O2	179.75 (18)	C47—C4—C41—C42	179.55 (19)
C2—C21—C26—O2	0.3 (3)	C5—C4—C41—C46	119.56 (17)
C22—C21—C26—C25	−0.9 (3)	C3—C4—C41—C46	−118.15 (17)
C2—C21—C26—C25	179.66 (19)	C47—C4—C41—C46	0.26 (19)
C51—C5—C6—O1	178.11 (16)	C21—C22—C23—C24	−0.1 (3)
C4—C5—C6—O1	−0.1 (3)	C61—C66—C65—C64	1.0 (3)
C51—C5—C6—C61	0.6 (3)	C46—C41—C42—C43	1.6 (3)
C4—C5—C6—C61	−177.62 (17)	C4—C41—C42—C43	−177.67 (18)
C2—O1—C6—C5	2.8 (3)	O4—C62—C63—C64	−178.62 (19)
C2—O1—C6—C61	−179.47 (15)	C61—C62—C63—C64	2.1 (3)
C62—C61—C6—C5	1.8 (3)	O2—C26—C25—C24	179.55 (19)
C66—C61—C6—C5	179.99 (18)	C21—C26—C25—C24	0.2 (3)
C62—C61—C6—O1	−175.87 (16)	C43—C44—C45—C46	0.6 (3)
C66—C61—C6—O1	2.3 (3)	C44—C45—C46—C41	−0.2 (3)
C62—C61—C66—C65	0.8 (3)	C44—C45—C46—N1	178.69 (19)
C6—C61—C66—C65	−177.36 (19)	C42—C41—C46—C45	−0.9 (3)
C26—O2—C31—O3	177.49 (18)	C4—C41—C46—C45	178.49 (17)
C26—O2—C31—C3	−3.8 (3)	C42—C41—C46—N1	−179.95 (17)
C6—O1—C2—C3	0.1 (3)	C4—C41—C46—N1	−0.6 (2)
C6—O1—C2—C21	−179.93 (16)	C47—N1—C46—C45	−178.25 (19)
C26—C21—C2—C3	1.1 (3)	C47—N1—C46—C41	0.7 (2)
C22—C21—C2—C3	−178.30 (18)	C45—C44—C43—C42	0.1 (3)
C26—C21—C2—O1	−178.86 (16)	C45—C44—C43—C48	179.5 (2)
C22—C21—C2—O1	1.7 (3)	C41—C42—C43—C44	−1.1 (3)
O1—C2—C3—C31	176.20 (17)	C41—C42—C43—C48	179.48 (19)
C21—C2—C3—C31	−3.8 (3)	C26—C25—C24—C23	0.6 (3)
O1—C2—C3—C4	−5.7 (3)	C22—C23—C24—C25	−0.7 (4)
C21—C2—C3—C4	174.32 (17)	C62—C63—C64—C65	−0.2 (3)
O3—C31—C3—C2	−176.4 (2)	C66—C65—C64—C63	−1.3 (3)

O2—C31—C3—C2	5.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5^{i}	0.89 (3)	2.25 (3)	2.965 (2)	138 (2)
C45—H45···O5^{i}	0.93	2.51	3.212 (2)	133
C63—H63···O3^{ii}	0.93	2.51	3.347 (3)	150
C65—H65···O4^{iii}	0.93	2.59	3.363 (2)	141

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