Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 6-amino-5-cyano-2,4-bis(4-methylphenyl)-4*H*-pyran-3-carboxylate

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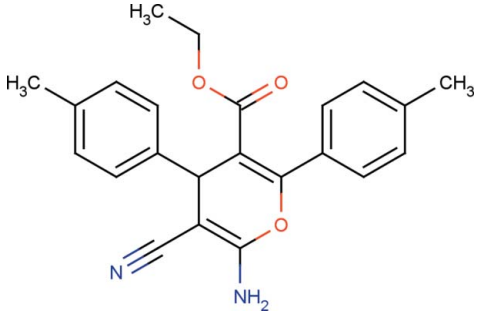
Received 28 August 2010; accepted 4 September 2010

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.066; wR factor = 0.192; data-to-parameter ratio = 14.6.

In the title compound, $C_{23}H_{22}N_2O_3$, the pyran ring adopts a twisted boat conformation. The tolyl rings and carboxylate group are attached to the pyran ring with torsion angles of −77.1 (2), 59.5 (3) and 17.8 (3)°, respectively. The ethyl group is disordered over two orientations with a site-occupancy ratio of 0.508 (5):0.492 (5). In the crystal, molecules are linked by N—H···N and N—H···O hydrogen bonds, generating a chain running the *a* axis. Weak C—H···O, C—H···N and C—H···π interactions are also observed.

Related literature

For the use of related compounds in organic synthesis, see: Liang *et al.* (2009). For the synthesis, see: Vasuki & Kumaravel (2008). For conformational analysis, see: Cremer & Pople (1975). For related structures, see: Athimoolam *et al.* (2007); Kannan *et al.* (2010).



Experimental

Crystal data

$C_{23}H_{22}N_2O_3$
M_r = 374.43
Triclinic, $P\overline{1}$
a = 8.3485 (2) Å
b = 11.4057 (3) Å
c = 11.6689 (3) Å
α = 72.902 (2)°
β = 72.690 (2)°
γ = 89.182 (2)°
V = 1010.64 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 K
0.30 × 0.20 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.981, T_{max} = 0.984
18989 measured reflections
3554 independent reflections
2971 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.192
S = 1.04
3554 reflections
243 parameters
7 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}

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

Cg is the centroid of the C17–C22 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N1^{i}	0.86	2.22	3.081 (3)	177
N2—H2B···O3^{ii}	0.86	2.31	3.088 (3)	150
C6—H6···O3^{iii}	0.93	2.51	3.432 (2)	171
C18—H18···N1^{iv}	0.93	2.60	3.318 (3)	135
C23—H23A···Cg^{v}	0.92	2.85	3.770 (4)	160

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

The authors acknowledge the Centre of Excellence in Bioinformatics, Pondicherry University, for providing facilities and GV thanks the Department of Science and Technology, New Delhi, Government of India, (No. SR/S5/ GC-22/2007) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5024).

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supporting information

Acta Cryst. (2010). E**66**, o2536 [doi:10.1107/S1600536810035592]

Ethyl 6-amino-5-cyano-2,4-bis(4-methylphenyl)-4*H*-pyran-3-carboxylate

M. Kannan, Kandhasamy Kumaravel, Gnanasambandam Vasuki and R. Krishna

S1. Comment

Like the title compounds some of the related compounds are widely used as organic intermediates in organic chemistry (Liang *et al.*, 2009). The title compound was synthesized by using Rapid four-component reactions in water (Vasuki & Kumaravel, 2008) and undertaken this study.

In the title compound (I), the pyran (A) ring adopts screw-boat conformation with the puckering parameters: Amplitude (Q) =0.221 (2) Å, Theta (θ) = 101.3 (5)° and Phi (φ) = 17.6 (7)°(Cremer & Pople, 1975), the puckered C_{11} atom having the maximum deviation of 0.137 (3) Å. The one toluene ring (Fig. 1) deviates significantly from planarity and attached with pyran ring by an (+)-*syn*-clinal conformation with torsion angle (C6—C5—C8—C12) of 59.5 (3)°, whereas the other toluene ring does not deviates from planarity and attached with pyran ring by torsion angle (C10—C11—C17—C22) of -77.1 (2)°, indiacting an (-)-*syn*-clinal conformtion. The carboxylate group is attached to pyran ring at C_{12} with the torsion angle of C_{11}—C_{12}—C_{13}—O_3 = 17.8 (3)°, indicating an (+)-*syn*-periplanar conformation. Moreover the *O*-ethyl group of carboxylate is disordered with the refined site-occupancy ratio of 0.508 (5)/0.492 (5). The two N—H···N and one N—H···O intermolecular interactions with a distance of 3.081 (4) Å and 3.088 (3) Å respectively are observed (Fig 2), in which the N—H···N intermolecular interaction forms R_2^2 (12) ring motifs. The weak C—H···O, C—H···N and C—H···π [C_g: centroid of C_{17}, C_{18}, C_{19}, C_{20}, C_{21} and C_{22}] (Fig. 3) intermolecular interaction also stabilized their three dimensional network of the crystal packing with a distance of 3.432 (3) Å, 3.318 (3) Å and 3.770 (4) Å respectively.

S2. Experimental

The title compound was prepared by the successive addition of 4-methylbenzaldehyde(0.240 g, 2 mmol) and piperidine (5 mol %) to a stirred aqueous mixture of malononitrile(0.132 g, 2 mmol) and ethyl 3-oxo-3-*p*-tolyl propanoate (0.412 g, 2 mmol) at room temperature under an open atmosphere with vigorous stirring for 5–10 min. The precipitated solid was filtered, washed with water and then with a mixture of ethylacetate/hexane (20:80) (Vasuki & Kumaravel, 2008). The product obtained was pure by TLC and ^{1}H NMR spectroscopy. However, the products were further purified by recrystallization from ethanol. Analysis calculated for ethyl6-amino-5-cyano-2, 4-bis (4-methylphenyl)-4*H*-pyran-3-carboxylate showed that it has C_{23} H_{22} N_2 O_3.

S3. Refinement

The non-hydrogen atoms where refined anisotropically whereas hydrogen atoms were refined isotropically. The C—H and amine H atoms were positioned geometrically (C—H= 0.93–0.97 and N—H=0.86 Å) and were refined, using riding model with U_{iso}(H) = xUeq(C), where *x* = 1.5 for methyl and 1.2 for all other atoms. The *O*-ethyl group of carboxylate shows disordered in two postition in the final refinement, the occupancy factors of two possible sites, O_2B/C_{14}B/C_{15}B and O_2A/C_{14}A/C_{15}A, converged to 0.508 (5) and 0.492 (5). For the disordered unit, the distance of C—C and C—O bond restrained to be 1.53 (10) Å and 1.43 (10) Å respectively.

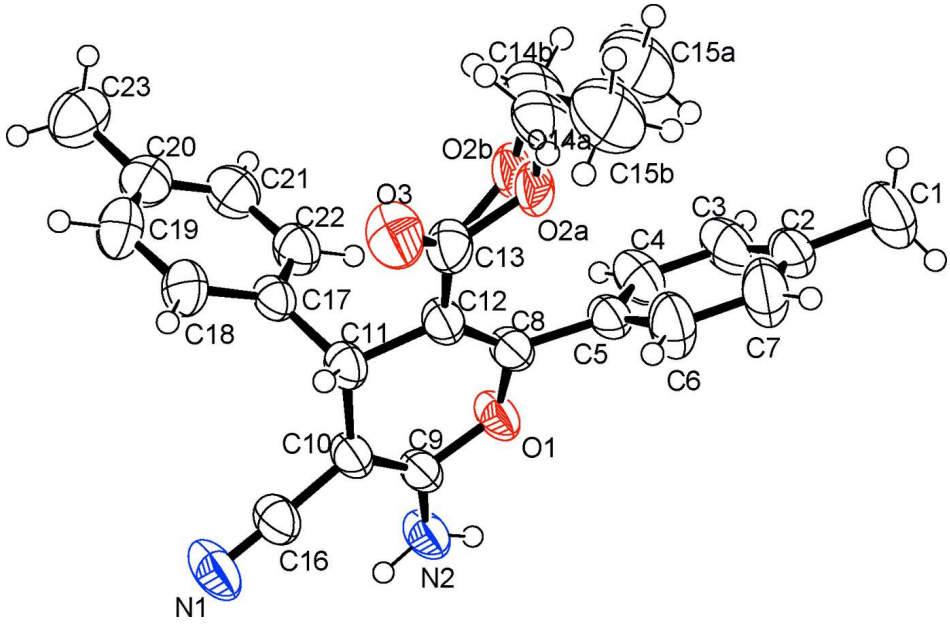

Figure 1

The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. The *O*-ethyl group is disordered over two positions with site-occupancy factor, from refinement of 0.508 (5) and 0.492 (5).

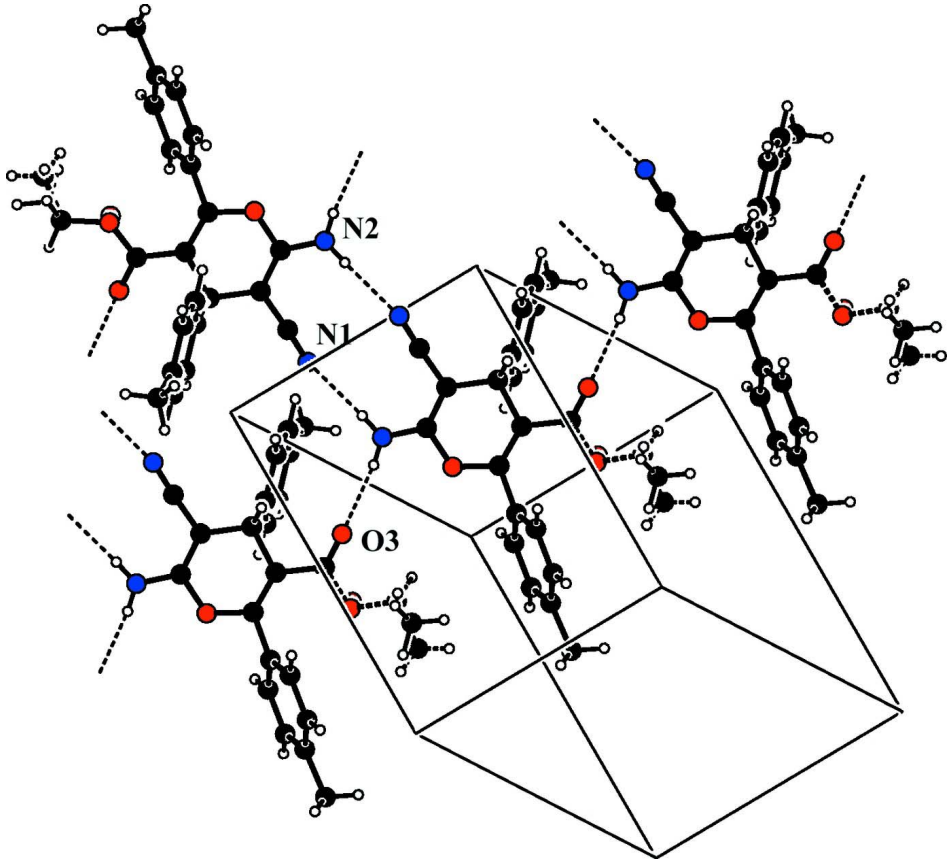

Figure 2

The crystal packing of (I), showing intermolecular hydrogen bonding interactions as dashed lines.

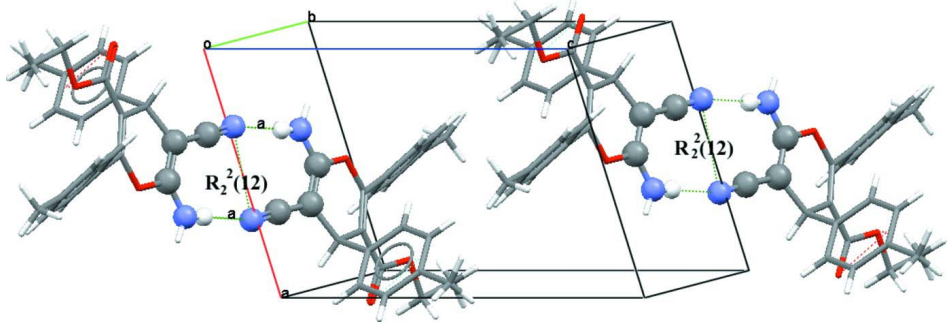

Figure 3

A view of R_2^2 (12) ring motifs formed by N—H···N interaction between to molecules and viewed along b* axis. The ring forming atoms are shown in ball and stick model and the Hydrogen bond are shown in green dashed lines.

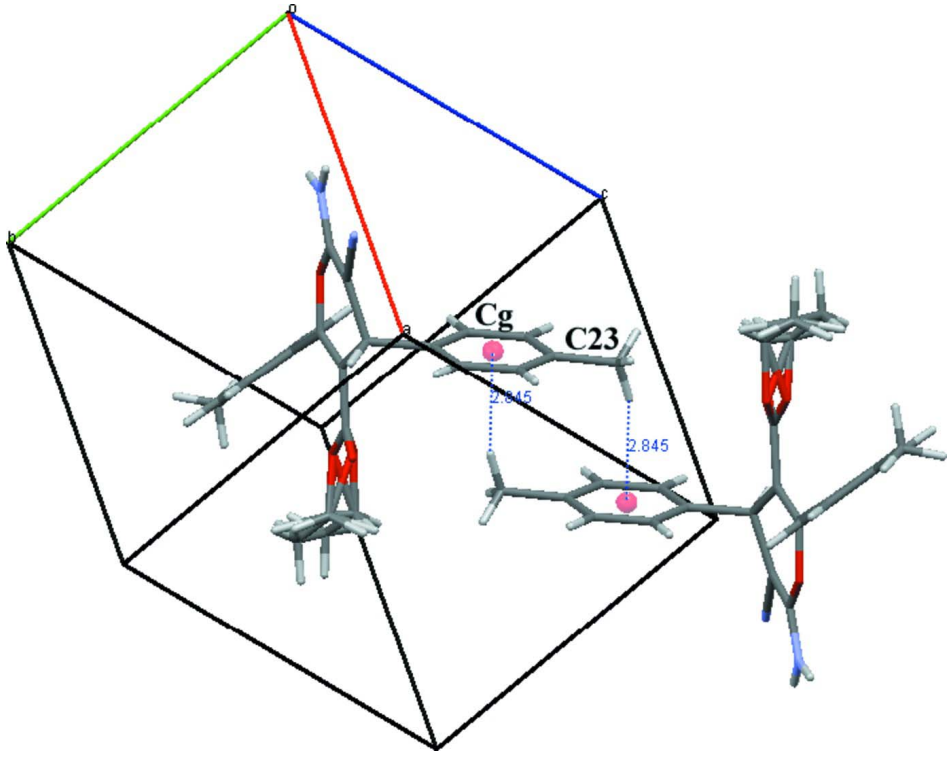

Figure 4

The molecular interaction showing the weak C—H···pi interaction between two molecules (dashed line in blue color), In which the *Cg* is the centriod of C_{17}—C_{22} ring. The disordered B section of the molecules omited for clarity.

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Crystal data

$C_{23}H_{22}N_2O_3$
M_r = 374.43
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.3485 (2) Å
b = 11.4057 (3) Å
c = 11.6689 (3) Å
α = 72.902 (2)°
β = 72.690 (2)°
γ = 89.182 (2)°
V = 1010.64 (4) Å^3
Z = 2
F(000) = 396
D_x = 1.230 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9717 reflections
θ = 2.2–32°
μ = 0.08 mm^{-1}
T = 293 K
Rectangular, colourless
0.30 × 0.20 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0 pixels mm^{-1}
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.981, T_{max} = 0.984
18989 measured reflections
3554 independent reflections
2971 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.0°, θ_{min} = 1.9°
h = −9→9
k = −13→13
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.192$
$S = 1.04$
3554 reflections
243 parameters
7 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0869P)^2 + 0.7661P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.025$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.4425 (5)	0.8123 (3)	0.3388 (4)	0.0986 (13)	
H1A	0.3452	0.7959	0.4120	0.148*	
H1B	0.4206	0.8739	0.2701	0.148*	
H1C	0.5369	0.8412	0.3568	0.148*	
C2	0.4816 (3)	0.69499 (14)	0.30303 (19)	0.0648 (8)	
C3	0.4067 (2)	0.58140 (17)	0.38598 (15)	0.0720 (9)	
H3	0.3282	0.5769	0.4631	0.086*	
C4	0.4491 (2)	0.47452 (13)	0.35366 (15)	0.0618 (7)	
H4	0.3990	0.3985	0.4092	0.074*	
C5	0.5664 (2)	0.48123 (12)	0.23840 (15)	0.0473 (6)	
C6	0.6414 (2)	0.59482 (15)	0.15545 (14)	0.0718 (9)	
H6	0.7199	0.5993	0.0783	0.086*	
C7	0.5990 (3)	0.70170 (12)	0.18776 (18)	0.0803 (10)	
H7	0.6491	0.7777	0.1323	0.096*	
C8	0.6149 (3)	0.3670 (2)	0.2054 (2)	0.0449 (5)	
C9	0.4918 (3)	0.2162 (2)	0.1459 (2)	0.0466 (6)	
C10	0.6432 (3)	0.1734 (2)	0.1069 (2)	0.0472 (6)	
C11	0.7915 (3)	0.2049 (2)	0.1436 (2)	0.0453 (6)	
H11	0.8914	0.2207	0.0695	0.054*	
C12	0.7648 (3)	0.3221 (2)	0.1804 (2)	0.0453 (6)	
C13	0.9216 (3)	0.3763 (2)	0.1813 (2)	0.0532 (6)	
O2A	0.8984 (11)	0.4720 (4)	0.2391 (6)	0.0562 (13)	0.492 (5)
C14A	1.0588 (11)	0.5280 (9)	0.2238 (9)	0.072 (2)	0.492 (5)

H14A	1.1208	0.5657	0.1357	0.086*	0.492 (5)
H14B	1.1262	0.4692	0.2634	0.086*	0.492 (5)
C15A	1.0050 (13)	0.6246 (9)	0.2921 (12)	0.122 (3)	0.492 (5)
H15A	0.9331	0.6782	0.2539	0.184*	0.492 (5)
H15B	1.1029	0.6719	0.2862	0.184*	0.492 (5)
H15C	0.9453	0.5844	0.3791	0.184*	0.492 (5)
O2B	0.8938 (10)	0.4347 (5)	0.2773 (4)	0.0562 (13)	0.508 (5)
C14B	1.0311 (12)	0.5012 (7)	0.2866 (8)	0.072 (2)	0.508 (5)
H14C	1.1260	0.4507	0.2828	0.086*	0.508 (5)
H14D	0.9984	0.5159	0.3679	0.086*	0.508 (5)
C15B	1.0869 (14)	0.6244 (7)	0.1830 (9)	0.122 (3)	0.508 (5)
H15D	1.1080	0.6118	0.1022	0.184*	0.508 (5)
H15E	1.1879	0.6592	0.1877	0.184*	0.508 (5)
H15F	0.9997	0.6796	0.1941	0.184*	0.508 (5)
C16	0.6647 (3)	0.0898 (2)	0.0364 (3)	0.0536 (6)	
C17	0.82337 (19)	0.09928 (12)	0.24806 (13)	0.0442 (5)	
C18	0.95357 (19)	0.02588 (15)	0.21696 (12)	0.0555 (6)	
H18	1.0204	0.0420	0.1337	0.067*	
C19	0.9840 (2)	−0.07159 (15)	0.31037 (16)	0.0649 (7)	
H19	1.0711	−0.1207	0.2896	0.078*	
C20	0.8841 (2)	−0.09565 (14)	0.43487 (14)	0.0596 (7)	
C21	0.7539 (2)	−0.02225 (16)	0.46597 (11)	0.0626 (7)	
H21	0.6871	−0.0383	0.5493	0.075*	
C22	0.72354 (18)	0.07522 (15)	0.37256 (15)	0.0568 (7)	
H22	0.6364	0.1243	0.3934	0.068*	
C23	0.9202 (5)	−0.1997 (3)	0.5378 (3)	0.0826 (10)	
H23A	0.9932	−0.1682	0.5736	0.124*	
H23B	0.9736	−0.2618	0.5026	0.124*	
H23C	0.8165	−0.2349	0.6023	0.124*	
N1	0.6900 (3)	0.0234 (3)	−0.0223 (3)	0.0743 (8)	
N2	0.3450 (3)	0.1811 (2)	0.1388 (2)	0.0598 (6)	
H2A	0.3389	0.1238	0.1058	0.072*	
H2B	0.2560	0.2157	0.1672	0.072*	
O1	0.4731 (2)	0.30688 (16)	0.20301 (18)	0.0545 (5)	
O3	1.0577 (2)	0.35407 (19)	0.1320 (2)	0.0723 (6)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.112 (3)	0.087 (2)	0.135 (3)	0.041 (2)	−0.050 (3)	−0.079 (3)
C2	0.0700 (18)	0.0665 (18)	0.086 (2)	0.0278 (14)	−0.0392 (16)	−0.0500 (16)
C3	0.0619 (17)	0.088 (2)	0.081 (2)	0.0153 (15)	−0.0124 (15)	−0.0570 (19)
C4	0.0554 (16)	0.0655 (17)	0.0693 (17)	0.0027 (13)	−0.0092 (13)	−0.0376 (14)
C5	0.0441 (12)	0.0527 (14)	0.0593 (14)	0.0138 (10)	−0.0217 (11)	−0.0324 (12)
C6	0.093 (2)	0.0535 (16)	0.0626 (17)	0.0186 (15)	−0.0089 (16)	−0.0245 (14)
C7	0.110 (3)	0.0493 (16)	0.080 (2)	0.0200 (16)	−0.0216 (19)	−0.0258 (15)
C8	0.0424 (12)	0.0490 (13)	0.0520 (13)	0.0063 (10)	−0.0163 (10)	−0.0264 (11)
C9	0.0454 (13)	0.0517 (13)	0.0560 (14)	0.0103 (10)	−0.0202 (11)	−0.0318 (11)

C10	0.0441 (13)	0.0514 (13)	0.0591 (14)	0.0115 (10)	−0.0191 (11)	−0.0329 (12)
C11	0.0371 (12)	0.0496 (13)	0.0564 (14)	0.0096 (10)	−0.0132 (10)	−0.0281 (11)
C12	0.0429 (13)	0.0448 (12)	0.0553 (14)	0.0074 (10)	−0.0161 (10)	−0.0249 (11)
C13	0.0471 (14)	0.0437 (13)	0.0726 (17)	0.0051 (10)	−0.0212 (12)	−0.0204 (12)
O2A	0.0596 (13)	0.029 (3)	0.092 (3)	0.007 (2)	−0.037 (3)	−0.022 (3)
C14A	0.067 (3)	0.061 (4)	0.100 (6)	−0.011 (3)	−0.031 (5)	−0.035 (5)
C15A	0.127 (7)	0.093 (4)	0.177 (8)	−0.009 (4)	−0.073 (6)	−0.058 (6)
O2B	0.0596 (13)	0.029 (3)	0.092 (3)	0.007 (2)	−0.037 (3)	−0.022 (3)
C14B	0.067 (3)	0.061 (4)	0.100 (6)	−0.011 (3)	−0.031 (5)	−0.035 (5)
C15B	0.127 (7)	0.093 (4)	0.177 (8)	−0.009 (4)	−0.073 (6)	−0.058 (6)
C16	0.0396 (13)	0.0638 (15)	0.0714 (17)	0.0123 (11)	−0.0192 (12)	−0.0396 (14)
C17	0.0354 (11)	0.0472 (12)	0.0590 (14)	0.0056 (9)	−0.0157 (10)	−0.0283 (11)
C18	0.0460 (14)	0.0573 (15)	0.0624 (16)	0.0134 (11)	−0.0101 (12)	−0.0238 (13)
C19	0.0545 (16)	0.0587 (16)	0.079 (2)	0.0183 (13)	−0.0179 (14)	−0.0213 (14)
C20	0.0549 (15)	0.0535 (15)	0.0720 (18)	−0.0024 (12)	−0.0233 (13)	−0.0170 (13)
C21	0.0607 (17)	0.0669 (17)	0.0587 (16)	0.0007 (13)	−0.0117 (13)	−0.0233 (14)
C22	0.0497 (14)	0.0629 (16)	0.0636 (16)	0.0121 (12)	−0.0136 (12)	−0.0318 (13)
C23	0.083 (2)	0.0685 (19)	0.089 (2)	−0.0005 (16)	−0.0342 (19)	−0.0051 (17)
N1	0.0520 (13)	0.0912 (18)	0.108 (2)	0.0174 (12)	−0.0227 (13)	−0.0750 (17)
N2	0.0434 (11)	0.0730 (15)	0.0879 (16)	0.0170 (10)	−0.0276 (11)	−0.0542 (13)
O1	0.0403 (9)	0.0644 (11)	0.0780 (12)	0.0137 (8)	−0.0196 (8)	−0.0489 (10)
O3	0.0395 (10)	0.0768 (13)	0.1065 (16)	0.0053 (9)	−0.0157 (10)	−0.0432 (12)

Geometric parameters (Å, º)

C1—C2	1.518 (3)	C14A—C15A	1.5295 (10)
C1—H1A	0.9600	C14A—H14A	0.9700
C1—H1B	0.9600	C14A—H14B	0.9700
C1—H1C	0.9600	C15A—H15A	0.9600
C2—C3	1.3900	C15A—H15B	0.9600
C2—C7	1.3900	C15A—H15C	0.9600
C3—C4	1.3900	O2B—C14B	1.4309 (10)
C3—H3	0.9300	C14B—C15B	1.5295 (10)
C4—C5	1.3900	C14B—H14C	0.9700
C4—H4	0.9300	C14B—H14D	0.9700
C5—C6	1.3900	C15B—H15D	0.9600
C5—C8	1.482 (2)	C15B—H15E	0.9600
C6—C7	1.3900	C15B—H15F	0.9600
C6—H6	0.9300	C16—N1	1.140 (3)
C7—H7	0.9300	C17—C18	1.3900
C8—C12	1.329 (3)	C17—C22	1.3900
C8—O1	1.388 (3)	C18—C19	1.3900
C9—N2	1.328 (3)	C18—H18	0.9300
C9—C10	1.347 (3)	C19—C20	1.3900
C9—O1	1.371 (3)	C19—H19	0.9300
C10—C16	1.410 (3)	C20—C21	1.3900
C10—C11	1.505 (3)	C20—C23	1.520 (3)
C11—C12	1.514 (3)	C21—C22	1.3900

C11—C17	1.525 (3)	C21—H21	0.9300
C11—H11	0.9800	C22—H22	0.9300
C12—C13	1.460 (3)	C23—H23A	0.9600
C13—O3	1.172 (3)	C23—H23B	0.9600
C13—O2A	1.4256 (10)	C23—H23C	0.9600
C13—O2B	1.4261 (10)	N2—H2A	0.8600
O2A—C14A	1.4309 (10)	N2—H2B	0.8600

C2—C1—H1A	109.5	O2A—C14A—C15A	100.8 (5)
C2—C1—H1B	109.5	O2A—C14A—H14A	111.6
H1A—C1—H1B	109.5	C15A—C14A—H14A	111.6
C2—C1—H1C	109.5	O2A—C14A—H14B	111.6
H1A—C1—H1C	109.5	C15A—C14A—H14B	111.6
H1B—C1—H1C	109.5	H14A—C14A—H14B	109.4
C3—C2—C7	120.0	C13—O2B—C14B	119.8 (6)
C3—C2—C1	120.8 (2)	O2B—C14B—C15B	113.5 (6)
C7—C2—C1	119.1 (2)	O2B—C14B—H14C	108.9
C4—C3—C2	120.0	C15B—C14B—H14C	108.8
C4—C3—H3	120.0	O2B—C14B—H14D	108.9
C2—C3—H3	120.0	C15B—C14B—H14D	108.9
C3—C4—C5	120.0	H14C—C14B—H14D	107.7
C3—C4—H4	120.0	C14B—C15B—H15D	109.5
C5—C4—H4	120.0	C14B—C15B—H15E	109.5
C6—C5—C4	120.0	H15D—C15B—H15E	109.5
C6—C5—C8	120.01 (14)	C14B—C15B—H15F	109.5
C4—C5—C8	119.97 (14)	H15D—C15B—H15F	109.5
C5—C6—C7	120.0	H15E—C15B—H15F	109.5
C5—C6—H6	120.0	N1—C16—C10	176.8 (3)
C7—C6—H6	120.0	C18—C17—C22	120.0
C6—C7—C2	120.0	C18—C17—C11	118.98 (12)
C6—C7—H7	120.0	C22—C17—C11	121.02 (12)
C2—C7—H7	120.0	C17—C18—C19	120.0
C12—C8—O1	121.7 (2)	C17—C18—H18	120.0
C12—C8—C5	129.4 (2)	C19—C18—H18	120.0
O1—C8—C5	108.85 (17)	C20—C19—C18	120.0
N2—C9—C10	128.6 (2)	C20—C19—H19	120.0
N2—C9—O1	110.53 (19)	C18—C19—H19	120.0
C10—C9—O1	120.9 (2)	C19—C20—C21	120.0
C9—C10—C16	120.4 (2)	C19—C20—C23	120.16 (18)
C9—C10—C11	122.1 (2)	C21—C20—C23	119.81 (18)
C16—C10—C11	117.4 (2)	C20—C21—C22	120.0
C10—C11—C12	109.30 (18)	C20—C21—H21	120.0
C10—C11—C17	111.98 (19)	C22—C21—H21	120.0
C12—C11—C17	111.80 (18)	C21—C22—C17	120.0
C10—C11—H11	107.9	C21—C22—H22	120.0
C12—C11—H11	107.9	C17—C22—H22	120.0
C17—C11—H11	107.9	C20—C23—H23A	109.5
C8—C12—C13	126.6 (2)	C20—C23—H23B	109.5

C8—C12—C11	121.9 (2)	H23A—C23—H23B	109.5
C13—C12—C11	111.49 (18)	C20—C23—H23C	109.5
O3—C13—O2A	120.1 (4)	H23A—C23—H23C	109.5
O3—C13—O2B	120.3 (4)	H23B—C23—H23C	109.5
O2A—C13—O2B	20.6 (4)	C9—N2—H2A	120.0
O3—C13—C12	125.93 (19)	C9—N2—H2B	120.0
O2A—C13—C12	113.7 (4)	H2A—N2—H2B	120.0
O2B—C13—C12	111.8 (4)	C9—O1—C8	119.48 (17)
C13—O2A—C14A	109.7 (5)		

C7—C2—C3—C4	0.0	C8—C12—C13—O2A	13.2 (5)
C1—C2—C3—C4	−177.4 (2)	C11—C12—C13—O2A	−168.1 (3)
C2—C3—C4—C5	0.0	C8—C12—C13—O2B	35.5 (4)
C3—C4—C5—C6	0.0	C11—C12—C13—O2B	−145.8 (3)
C3—C4—C5—C8	178.43 (18)	O3—C13—O2A—C14A	0.6 (7)
C4—C5—C6—C7	0.0	O2B—C13—O2A—C14A	97.0 (19)
C8—C5—C6—C7	−178.43 (18)	C12—C13—O2A—C14A	−174.0 (5)
C5—C6—C7—C2	0.0	C13—O2A—C14A—C15A	−179.6 (8)
C3—C2—C7—C6	0.0	O3—C13—O2B—C14B	20.1 (7)
C1—C2—C7—C6	177.5 (2)	O2A—C13—O2B—C14B	−75.7 (19)
C6—C5—C8—C12	59.5 (3)	C12—C13—O2B—C14B	−175.3 (5)
C4—C5—C8—C12	−118.9 (3)	C13—O2B—C14B—C15B	73.4 (11)
C6—C5—C8—O1	−120.33 (18)	C9—C10—C16—N1	163 (6)
C4—C5—C8—O1	61.2 (2)	C11—C10—C16—N1	−21 (6)
N2—C9—C10—C16	7.7 (5)	C10—C11—C17—C18	102.33 (18)
O1—C9—C10—C16	−173.2 (2)	C12—C11—C17—C18	−134.63 (16)
N2—C9—C10—C11	−167.9 (3)	C10—C11—C17—C22	−77.07 (19)
O1—C9—C10—C11	11.2 (4)	C12—C11—C17—C22	46.0 (2)
C9—C10—C11—C12	−22.1 (3)	C22—C17—C18—C19	0.0
C16—C10—C11—C12	162.2 (2)	C11—C17—C18—C19	−179.41 (16)
C9—C10—C11—C17	102.4 (3)	C17—C18—C19—C20	0.0
C16—C10—C11—C17	−73.3 (3)	C18—C19—C20—C21	0.0
O1—C8—C12—C13	−179.3 (2)	C18—C19—C20—C23	−178.2 (2)
C5—C8—C12—C13	0.8 (4)	C19—C20—C21—C22	0.0
O1—C8—C12—C11	2.1 (4)	C23—C20—C21—C22	178.2 (2)
C5—C8—C12—C11	−177.8 (2)	C20—C21—C22—C17	0.0
C10—C11—C12—C8	15.4 (3)	C18—C17—C22—C21	0.0
C17—C11—C12—C8	−109.1 (3)	C11—C17—C22—C21	179.39 (16)
C10—C11—C12—C13	−163.4 (2)	N2—C9—O1—C8	−171.9 (2)
C17—C11—C12—C13	72.1 (2)	C10—C9—O1—C8	8.8 (4)
C8—C12—C13—O3	−160.9 (3)	C12—C8—O1—C9	−15.7 (4)
C11—C12—C13—O3	17.8 (4)	C5—C8—O1—C9	164.2 (2)

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C17–C22 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···N1^{i}	0.86	2.22	3.081 (3)	177

N2—H2*B*···O3^{ii}	0.86	2.31	3.088 (3)	150
C6—H6···O3^{iii}	0.93	2.51	3.432 (2)	171
C18—H18···N1^{iv}	0.93	2.60	3.318 (3)	135
C23—H23*A*···*Cg*^{v}	0.92	2.85	3.770 (4)	160

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