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(*R*)-2-[1-(2,6-Dichloro-3,4,5-trimethoxybenzoyl)pyrrolidin-2-yl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide

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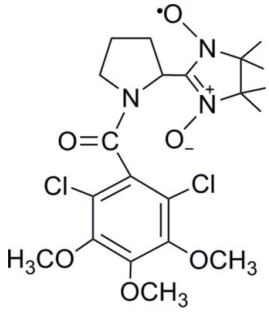
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; R factor = 0.053; wR factor = 0.131; data-to-parameter ratio = 14.3.

In the title compound, $C_{21}H_{28}Cl_2N_3O_6$, the nitronyl nitroxide ring displays a half-chair conformation, whereas the pyrrolidine ring has an envelope conformation. These two rings are twisted to each other with N—C—C—N torsion angles around the connecting C—C bond of 48.9 (6) and −127.0 (5)°. The benzene ring is nearly perpendicular to the pyrrolidine ring, with torsion angles around the connecting C—C bond of 86.3 (6) and −97.7 (6)°. The crystal structure is stabilized by C—H···O and C—H···π hydrogen bonds, which build up a three-dimensional network.

Related literature

For the chemical and physical properties of nitronyl nitroxides, see: Minguet *et al.* (2001); Osiecki & Ullman (1968); Shemsi *et al.* (2007); Wu *et al.* (2006). For related structures, see: Shimono *et al.* (2004); Minguet *et al.* (2001); Tian *et al.* (2011). For puckering parameters, see Cremer & Pople (1975). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$C_{21}H_{28}Cl_2N_3O_6$
M_r = 489.36
Orthorhombic, $P2_12_12_1$
a = 10.975 (2) Å
b = 12.255 (3) Å
c = 17.741 (4) Å
V = 2386.2 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 296 K
0.38 × 0.27 × 0.16 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.892, T_{max} = 0.952
12018 measured reflections
4252 independent reflections
2217 reflections with $I > 2\sigma(I)$
R_{int} = 0.067

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.131
S = 1.02
4252 reflections
297 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Absolute structure: Flack (1983), 1834 Friedel pairs
Flack parameter: 0.01 (10)

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

*Cg*3 is the centroid of the C13–C18 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6B···O3^{i}	0.96	2.54	3.498 (8)	173
C11—H11A···O1^{ii}	0.97	2.36	3.281 (6)	159
C21—H21B···O2^{iii}	0.96	2.44	3.403 (6)	178
C4—H4A···*Cg*3^{i}	0.96	2.86	3.619 (7)	136

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2666).

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supporting information

Acta Cryst. (2011). E**67**, o985–o986 [doi:10.1107/S1600536811010270]

(*R*)-2-[1-(2,6-Dichloro-3,4,5-trimethoxybenzoyl)pyrrolidin-2-yl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide

Hai-Bo Wang, Zhuo Xiang, Lin-Lin Jing, Min Tian and Xiao-Li Sun

S1. Comment

Nitronyl nitroxides, stable organic radicals, synthesized more than 30 years ago (Osiecki *et al.*, 1968), have received considerable attention recently because of their capability of magnetism, anticancer, antiradiation and antioxidation in biological chemistry and magnetic material fields (Shemsi *et al.*, 2007; Wu *et al.*, 2006). Chiral nitroxides are well chosen as potential precursors of chiralmolecule-based magnets. However, chiral nitronyl nitroxide radicals with the chiral centers sitting very close to the oxyl group are relatively few in the literature (Minguet *et al.*, 2001; Shimono *et al.*, 2004; Tian *et al.*, 2011).

In the title compound, the nitronyl nitroxide ring displays half-chair conformation with puckering parameters, Q2 = 0.096 (5)Å and φ = 272 (3)° (Cremer & Pople, 1975) whereas the pyrrolidine ring has an envelope conformation with puckering parameters Q(2)= 0.393 (6) Å and φ = 104.3 (7)°. The N3—C12—C13—C14, -97.7 (6)°, and N3—C12—C13—C18, 86.3 (6)°, torsion angles the involving the ketone bridging group show that the phenyl and the pyrrolidine rings are nearly perpendicular (Fig. 1). The bond distances and bond angles within the molecule agree with values reported in the Cambridge Structural Database (Allen, 2002).

Intermolecular C—H···O and C—H···π hydrogen bonds stabilize the packing building up a three dimensionnal network (Table 1).

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S2. Experimental

2,6-dichloro-3,4,5-trimethoxybenzoylchloride (2.98 g, 10.0 mmol), Et_3N (3.1 ml) were added to in dry CH_2Cl_2 with vigorous stirring in an ice bath. To this mixture, a solution of prolinol (1.0 g, 10 mmol) in dry $CH_2Cl_2$was added dropwise over a period of 20 min. The mixture was warmed to room temperature and stirred for 2 h. Then the reaction mixture was treated with water and extracted with CH_2Cl_2. The organic layer wasdried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (3:1) as eluant, giving a colorless oil product (3.1 g, 83.8%). To a reaction mixture of this product (3.61 g, 10 mmol), TEMPO (0.025 g, 0.16 mmol) and trichloroisocyanuric acid (TCCA, 3.7 g, 16 mmol), CH_2Cl_2 was added. Then the mixture was stirred for 20 min and filtered on Celite. The precipitate was purified by column chromatography on silica gel using ethyl acetate/petroleumether/triethylamine (2:1:0.1) as eluant, giving the product 1-(2,6-dichloro-3,4,5-trimethoxybenzoyl)-pyrrolidine-2-carbaldehyde (3.10 g, 85.0%). 2,3-Dimethyl-2,3-bis(hydroxylamino) butane (0.74 g, 10.0 mmol) and 1-(2,6-dichloro-3,4,5- trime thoxybenzoyl) pyrrolidine-2-carbaldehyde (1.81 g, 5.0 mmol) were dissolved in methanol. The reaction was stirred for 10 h at reflux temperature, then cooled to room temperature and filtered. The cake was suspended in CH_2Cl_2 (150.0 ml) and cooled at ice bath for 10 min. Then the reaction mixture was added to an aqueous solution of $NaIO_4$ stirring for 15 min. The aqueous phase was extracted with CH_2Cl_2 and the organic layer was combined

and dried over $MgSO_4$. Then the solvent wasremoved to give a amaranthine residue which was purified by a flash columnchromatography with the elution of n-hexane/ethyl acetate (1:1) to yield thetitle compound (I) as a dark amaranthine powder. Single crystals of compound (I) were obtained from the 1/1 mixed solution of *n*-heptane and di-chloromethane.

S3. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.96 Å (methyl), 0.97 Å (methylene) and 0.93 Å (aromatic) with U_{iso}(H) = 1.2U_{eq}(C) or U_{iso}(H) = 1.5U_{eq}(Cmethyl).

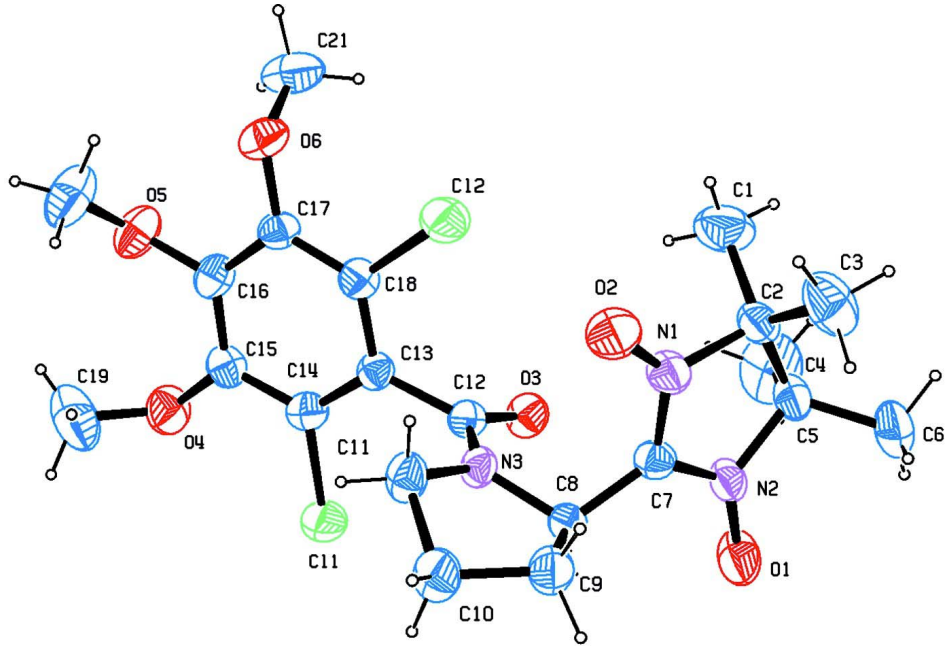

Figure 1

Molecular structure of the title compound (I), showing the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

(*R*)-2-[1-(2,6-Dichloro-3,4,5-trimethoxybenzoyl)pyrrolidin-2-yl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide

Crystal data

$C_{21}H_{28}Cl_2N_3O_6$
M_r = 489.36
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 10.975 (2) Å
b = 12.255 (3) Å
c = 17.741 (4) Å
V = 2386.2 (8) Å^3
Z = 4
$F(000)$ = 1028
D_x = 1.362 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1127 reflections
θ = 2.3–16.9°
μ = 0.31 mm^{-1}
T = 296 K
Block, blue
0.38 × 0.27 × 0.16 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.892, T_{max} = 0.952
12018 measured reflections
4252 independent reflections
2217 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
θ_{max} = 25.1°, θ_{min} = 2.0°
h = −13→12
k = −12→14
l = −18→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.131
S = 1.02
4252 reflections
297 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.1713P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0025 (7)
Absolute structure: Flack (1983), 1834 Friedel pairs
Absolute structure parameter: 0.01 (10)

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}
Cl1	0.54734 (13)	0.50531 (12)	−0.00306 (8)	0.0831 (5)
Cl2	0.85841 (13)	0.71203 (11)	0.18279 (8)	0.0843 (5)
N1	0.6828 (4)	0.9676 (3)	0.1322 (2)	0.0620 (11)
N2	0.4878 (4)	0.9819 (3)	0.1078 (2)	0.0610 (11)
N3	0.6736 (3)	0.7723 (3)	0.03080 (19)	0.0511 (10)
O1	0.3875 (3)	0.9782 (3)	0.0717 (2)	0.0963 (13)
O2	0.7966 (3)	0.9505 (3)	0.1213 (2)	0.0897 (12)
O3	0.5442 (3)	0.7190 (3)	0.12213 (17)	0.0648 (9)
O4	0.6903 (4)	0.3135 (3)	0.0339 (2)	0.0835 (11)
O5	0.8841 (4)	0.3034 (3)	0.1329 (2)	0.0840 (11)
O6	0.9682 (3)	0.4954 (3)	0.2006 (2)	0.0741 (10)
C1	0.6747 (6)	0.9565 (5)	0.2688 (3)	0.106 (2)
H1A	0.6584	0.8809	0.2591	0.160*

H1B	0.6307	0.9794	0.3128	0.160*
H1C	0.7605	0.9666	0.2769	0.160*
C2	0.6345 (5)	1.0242 (4)	0.2016 (2)	0.0634 (13)
C3	0.6941 (6)	1.1358 (4)	0.2038 (3)	0.104 (2)
H3A	0.7810	1.1274	0.2056	0.157*
H3B	0.6670	1.1745	0.2477	0.157*
H3C	0.6719	1.1760	0.1594	0.157*
C4	0.4234 (6)	0.9421 (6)	0.2350 (4)	0.137 (3)
H4A	0.4187	0.9680	0.2860	0.205*
H4B	0.4643	0.8728	0.2341	0.205*
H4C	0.3427	0.9339	0.2149	0.205*
C5	0.4950 (5)	1.0246 (4)	0.1868 (3)	0.0706 (15)
C6	0.4332 (7)	1.1325 (5)	0.1905 (4)	0.129 (3)
H6A	0.4699	1.1812	0.1547	0.194*
H6B	0.4416	1.1621	0.2403	0.194*
H6C	0.3484	1.1237	0.1788	0.194*
C7	0.5945 (5)	0.9425 (4)	0.0838 (3)	0.0547 (12)
C8	0.6088 (4)	0.8744 (3)	0.0148 (2)	0.0523 (12)
H8	0.5279	0.8571	−0.0053	0.063*
C9	0.6861 (5)	0.9281 (4)	−0.0482 (3)	0.0736 (15)
H9A	0.6349	0.9666	−0.0840	0.088*
H9B	0.7451	0.9786	−0.0273	0.088*
C10	0.7487 (5)	0.8315 (5)	−0.0850 (3)	0.0785 (17)
H10A	0.6946	0.7946	−0.1199	0.094*
H10B	0.8218	0.8540	−0.1116	0.094*
C11	0.7795 (4)	0.7592 (4)	−0.0183 (3)	0.0674 (15)
H11A	0.7893	0.6838	−0.0338	0.081*
H11B	0.8534	0.7835	0.0065	0.081*
C12	0.6345 (4)	0.7020 (4)	0.0830 (3)	0.0527 (12)
C13	0.7062 (4)	0.5988 (4)	0.0917 (3)	0.0496 (11)
C14	0.6708 (4)	0.5020 (4)	0.0577 (2)	0.0594 (12)
C15	0.7333 (5)	0.4047 (4)	0.0686 (3)	0.0593 (14)
C16	0.8309 (5)	0.4042 (4)	0.1181 (3)	0.0604 (13)
C17	0.8696 (4)	0.4979 (4)	0.1537 (2)	0.0546 (11)
C18	0.8091 (5)	0.5945 (4)	0.1389 (3)	0.0565 (12)
C19	0.7769 (6)	0.2553 (6)	−0.0120 (5)	0.133 (3)
H19A	0.8400	0.3044	−0.0280	0.199*
H19B	0.7363	0.2259	−0.0554	0.199*
H19C	0.8121	0.1970	0.0168	0.199*
C20	1.0077 (5)	0.2909 (5)	0.1148 (4)	0.115 (2)
H20A	1.0224	0.3193	0.0652	0.172*
H20B	1.0287	0.2149	0.1160	0.172*
H20C	1.0565	0.3299	0.1507	0.172*
C21	0.9414 (5)	0.4668 (5)	0.2767 (3)	0.106 (2)
H21A	0.8876	0.5202	0.2981	0.159*
H21B	1.0156	0.4644	0.3053	0.159*
H21C	0.9030	0.3964	0.2779	0.159*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0821 (9)	0.0807 (9)	0.0865 (10)	0.0042 (8)	−0.0286 (8)	−0.0133 (8)
Cl2	0.0864 (11)	0.0714 (9)	0.0951 (10)	−0.0046 (8)	−0.0274 (9)	−0.0111 (7)
N1	0.049 (3)	0.071 (3)	0.066 (3)	−0.003 (2)	−0.003 (2)	−0.011 (2)
N2	0.049 (3)	0.062 (3)	0.072 (3)	0.003 (2)	−0.006 (2)	−0.024 (2)
N3	0.047 (2)	0.055 (2)	0.052 (2)	0.009 (2)	0.0078 (19)	0.0005 (19)
O1	0.056 (2)	0.103 (3)	0.130 (3)	0.015 (2)	−0.017 (2)	−0.052 (2)
O2	0.054 (2)	0.110 (3)	0.105 (3)	0.001 (2)	−0.014 (2)	−0.015 (2)
O3	0.056 (2)	0.074 (2)	0.065 (2)	0.0052 (19)	0.0137 (19)	0.0060 (18)
O4	0.088 (3)	0.059 (2)	0.103 (3)	−0.005 (2)	−0.010 (2)	−0.013 (2)
O5	0.073 (3)	0.061 (2)	0.118 (3)	0.007 (2)	0.001 (2)	0.018 (2)
O6	0.053 (2)	0.090 (2)	0.079 (3)	0.006 (2)	−0.0084 (19)	0.012 (2)
C1	0.141 (6)	0.108 (5)	0.070 (4)	−0.009 (4)	−0.021 (4)	0.014 (3)
C2	0.085 (4)	0.053 (3)	0.053 (3)	−0.005 (3)	−0.006 (3)	−0.007 (2)
C3	0.145 (6)	0.073 (4)	0.095 (5)	−0.035 (4)	0.014 (4)	−0.013 (3)
C4	0.110 (6)	0.158 (7)	0.142 (6)	−0.001 (5)	0.067 (5)	0.019 (5)
C5	0.089 (4)	0.061 (4)	0.062 (3)	0.010 (3)	0.003 (3)	−0.015 (3)
C6	0.146 (6)	0.113 (5)	0.129 (6)	0.061 (5)	−0.032 (5)	−0.064 (5)
C7	0.050 (3)	0.060 (3)	0.054 (3)	−0.002 (3)	−0.004 (3)	−0.001 (2)
C8	0.051 (3)	0.058 (3)	0.048 (3)	0.004 (2)	−0.004 (2)	−0.006 (2)
C9	0.092 (4)	0.067 (4)	0.062 (3)	0.013 (3)	0.009 (3)	0.006 (3)
C10	0.083 (4)	0.087 (4)	0.065 (4)	0.014 (3)	0.029 (3)	0.011 (3)
C11	0.071 (4)	0.065 (4)	0.066 (4)	0.011 (3)	0.021 (3)	0.007 (3)
C12	0.053 (3)	0.055 (3)	0.050 (3)	0.001 (3)	−0.002 (3)	0.000 (2)
C13	0.045 (3)	0.053 (3)	0.051 (3)	0.002 (2)	0.003 (2)	0.001 (2)
C14	0.056 (3)	0.067 (4)	0.056 (3)	−0.002 (3)	−0.002 (2)	0.003 (3)
C15	0.059 (4)	0.054 (3)	0.065 (3)	−0.010 (3)	0.002 (3)	−0.005 (3)
C16	0.062 (4)	0.049 (3)	0.071 (3)	0.001 (3)	0.005 (3)	0.011 (3)
C17	0.050 (3)	0.055 (3)	0.059 (3)	−0.004 (3)	−0.008 (2)	0.004 (3)
C18	0.061 (3)	0.051 (3)	0.057 (3)	−0.004 (3)	0.001 (3)	0.002 (2)
C19	0.142 (6)	0.124 (6)	0.132 (6)	−0.007 (5)	0.017 (5)	−0.062 (5)
C20	0.070 (4)	0.094 (5)	0.180 (7)	0.017 (4)	−0.001 (4)	0.004 (5)
C21	0.083 (4)	0.157 (6)	0.078 (4)	0.005 (4)	−0.019 (4)	0.026 (4)

Geometric parameters (Å, º)

Cl1—C14	1.731 (5)	C5—C6	1.487 (7)
Cl2—C18	1.724 (5)	C6—H6A	0.9600
N1—O2	1.281 (5)	C6—H6B	0.9600
N1—C7	1.331 (5)	C6—H6C	0.9600
N1—C2	1.510 (6)	C7—C8	1.490 (6)
N2—O1	1.274 (4)	C8—C9	1.550 (6)
N2—C7	1.336 (5)	C8—H8	0.9800
N2—C5	1.499 (6)	C9—C10	1.516 (6)
N3—C12	1.335 (5)	C9—H9A	0.9700
N3—C11	1.461 (5)	C9—H9B	0.9700

N3—C8	1.468 (5)	C10—C11	1.516 (6)
O3—C12	1.228 (5)	C10—H10A	0.9700
O4—C15	1.359 (5)	C10—H10B	0.9700
O4—C19	1.441 (7)	C11—H11A	0.9700
O5—C16	1.391 (5)	C11—H11B	0.9700
O5—C20	1.403 (6)	C12—C13	1.497 (6)
O6—C17	1.366 (5)	C13—C14	1.387 (6)
O6—C21	1.425 (6)	C13—C18	1.407 (6)
C1—C2	1.517 (6)	C14—C15	1.390 (6)
C1—H1A	0.9600	C15—C16	1.386 (6)
C1—H1B	0.9600	C16—C17	1.377 (6)
C1—H1C	0.9600	C17—C18	1.383 (6)
C2—C3	1.516 (6)	C19—H19A	0.9600
C2—C5	1.554 (7)	C19—H19B	0.9600
C3—H3A	0.9600	C19—H19C	0.9600
C3—H3B	0.9600	C20—H20A	0.9600
C3—H3C	0.9600	C20—H20B	0.9600
C4—C5	1.539 (7)	C20—H20C	0.9600
C4—H4A	0.9600	C21—H21A	0.9600
C4—H4B	0.9600	C21—H21B	0.9600
C4—H4C	0.9600	C21—H21C	0.9600

O2—N1—C7	125.1 (4)	C10—C9—C8	103.1 (4)
O2—N1—C2	122.7 (4)	C10—C9—H9A	111.1
C7—N1—C2	112.1 (4)	C8—C9—H9A	111.1
O1—N2—C7	125.7 (4)	C10—C9—H9B	111.1
O1—N2—C5	121.9 (4)	C8—C9—H9B	111.1
C7—N2—C5	112.2 (4)	H9A—C9—H9B	109.1
C12—N3—C11	126.8 (4)	C11—C10—C9	102.8 (4)
C12—N3—C8	121.9 (4)	C11—C10—H10A	111.2
C11—N3—C8	111.3 (3)	C9—C10—H10A	111.2
C15—O4—C19	115.7 (5)	C11—C10—H10B	111.2
C16—O5—C20	117.4 (4)	C9—C10—H10B	111.2
C17—O6—C21	114.8 (4)	H10A—C10—H10B	109.1
C2—C1—H1A	109.5	N3—C11—C10	103.0 (4)
C2—C1—H1B	109.5	N3—C11—H11A	111.2
H1A—C1—H1B	109.5	C10—C11—H11A	111.2
C2—C1—H1C	109.5	N3—C11—H11B	111.2
H1A—C1—H1C	109.5	C10—C11—H11B	111.2
H1B—C1—H1C	109.5	H11A—C11—H11B	109.1
N1—C2—C1	106.7 (4)	O3—C12—N3	122.9 (4)
N1—C2—C3	106.5 (4)	O3—C12—C13	120.6 (4)
C1—C2—C3	110.3 (4)	N3—C12—C13	116.6 (4)
N1—C2—C5	102.1 (4)	C14—C13—C18	116.9 (4)
C1—C2—C5	114.9 (4)	C14—C13—C12	122.0 (4)
C3—C2—C5	115.3 (4)	C18—C13—C12	121.0 (4)
C2—C3—H3A	109.5	C13—C14—C15	122.4 (4)
C2—C3—H3B	109.5	C13—C14—Cl1	118.0 (4)

H3A—C3—H3B	109.5	C15—C14—Cl1	119.6 (4)
C2—C3—H3C	109.5	O4—C15—C16	123.5 (5)
H3A—C3—H3C	109.5	O4—C15—C14	118.1 (5)
H3B—C3—H3C	109.5	C16—C15—C14	118.3 (4)
C5—C4—H4A	109.5	C17—C16—C15	121.7 (5)
C5—C4—H4B	109.5	C17—C16—O5	121.6 (5)
H4A—C4—H4B	109.5	C15—C16—O5	116.6 (4)
C5—C4—H4C	109.5	O6—C17—C16	120.3 (5)
H4A—C4—H4C	109.5	O6—C17—C18	121.0 (4)
H4B—C4—H4C	109.5	C16—C17—C18	118.6 (4)
C6—C5—N2	109.1 (4)	C17—C18—C13	122.0 (4)
C6—C5—C4	109.1 (5)	C17—C18—Cl2	118.6 (4)
N2—C5—C4	105.3 (5)	C13—C18—Cl2	119.3 (4)
C6—C5—C2	116.4 (5)	O4—C19—H19A	109.5
N2—C5—C2	102.1 (4)	O4—C19—H19B	109.5
C4—C5—C2	114.0 (5)	H19A—C19—H19B	109.5
C5—C6—H6A	109.5	O4—C19—H19C	109.5
C5—C6—H6B	109.5	H19A—C19—H19C	109.5
H6A—C6—H6B	109.5	H19B—C19—H19C	109.5
C5—C6—H6C	109.5	O5—C20—H20A	109.5
H6A—C6—H6C	109.5	O5—C20—H20B	109.5
H6B—C6—H6C	109.5	H20A—C20—H20B	109.5
N1—C7—N2	110.5 (4)	O5—C20—H20C	109.5
N1—C7—C8	125.6 (4)	H20A—C20—H20C	109.5
N2—C7—C8	123.8 (4)	H20B—C20—H20C	109.5
N3—C8—C7	111.7 (4)	O6—C21—H21A	109.5
N3—C8—C9	103.6 (4)	O6—C21—H21B	109.5
C7—C8—C9	114.4 (4)	H21A—C21—H21B	109.5
N3—C8—H8	109.0	O6—C21—H21C	109.5
C7—C8—H8	109.0	H21A—C21—H21C	109.5
C9—C8—H8	109.0	H21B—C21—H21C	109.5

O2—N1—C2—C1	−59.4 (5)	C8—N3—C11—C10	−22.5 (5)
C7—N1—C2—C1	123.1 (5)	C9—C10—C11—N3	37.7 (5)
O2—N1—C2—C3	58.4 (6)	C11—N3—C12—O3	−179.9 (4)
C7—N1—C2—C3	−119.1 (5)	C8—N3—C12—O3	−1.8 (7)
O2—N1—C2—C5	179.6 (4)	C11—N3—C12—C13	−0.4 (6)
C7—N1—C2—C5	2.2 (5)	C8—N3—C12—C13	177.7 (4)
O1—N2—C5—C6	−50.3 (7)	O3—C12—C13—C14	81.7 (6)
C7—N2—C5—C6	134.2 (5)	N3—C12—C13—C14	−97.8 (5)
O1—N2—C5—C4	66.7 (6)	O3—C12—C13—C18	−94.3 (6)
C7—N2—C5—C4	−108.8 (5)	N3—C12—C13—C18	86.2 (5)
O1—N2—C5—C2	−173.9 (4)	C18—C13—C14—C15	−0.5 (7)
C7—N2—C5—C2	10.5 (5)	C12—C13—C14—C15	−176.7 (4)
N1—C2—C5—C6	−125.7 (5)	C18—C13—C14—Cl1	−178.0 (3)
C1—C2—C5—C6	119.3 (5)	C12—C13—C14—Cl1	5.8 (6)
C3—C2—C5—C6	−10.7 (7)	C19—O4—C15—C16	−58.5 (7)
N1—C2—C5—N2	−7.0 (5)	C19—O4—C15—C14	126.1 (6)

C1—C2—C5—N2	−122.1 (4)	C13—C14—C15—O4	178.9 (4)
C3—C2—C5—N2	107.9 (5)	Cl1—C14—C15—O4	−3.6 (6)
N1—C2—C5—C4	105.9 (5)	C13—C14—C15—C16	3.1 (7)
C1—C2—C5—C4	−9.2 (6)	Cl1—C14—C15—C16	−179.3 (4)
C3—C2—C5—C4	−139.1 (5)	O4—C15—C16—C17	−178.3 (4)
O2—N1—C7—N2	−172.9 (5)	C14—C15—C16—C17	−2.8 (7)
C2—N1—C7—N2	4.5 (5)	O4—C15—C16—O5	−1.3 (7)
O2—N1—C7—C8	10.8 (7)	C14—C15—C16—O5	174.2 (4)
C2—N1—C7—C8	−171.8 (4)	C20—O5—C16—C17	−63.0 (7)
O1—N2—C7—N1	174.9 (5)	C20—O5—C16—C15	120.0 (5)
C5—N2—C7—N1	−9.8 (5)	C21—O6—C17—C16	−86.5 (6)
O1—N2—C7—C8	−8.7 (8)	C21—O6—C17—C18	95.5 (5)
C5—N2—C7—C8	166.6 (4)	C15—C16—C17—O6	−178.2 (4)
C12—N3—C8—C7	56.3 (5)	O5—C16—C17—O6	4.9 (7)
C11—N3—C8—C7	−125.3 (4)	C15—C16—C17—C18	−0.2 (7)
C12—N3—C8—C9	179.9 (4)	O5—C16—C17—C18	−177.1 (4)
C11—N3—C8—C9	−1.7 (5)	O6—C17—C18—C13	−178.9 (4)
N1—C7—C8—N3	48.9 (6)	C16—C17—C18—C13	3.1 (7)
N2—C7—C8—N3	−127.0 (5)	O6—C17—C18—Cl2	−1.5 (6)
N1—C7—C8—C9	−68.5 (6)	C16—C17—C18—Cl2	−179.5 (4)
N2—C7—C8—C9	115.6 (5)	C14—C13—C18—C17	−2.7 (7)
N3—C8—C9—C10	25.2 (5)	C12—C13—C18—C17	173.5 (4)
C7—C8—C9—C10	147.1 (4)	C14—C13—C18—Cl2	179.8 (3)
C8—C9—C10—C11	−38.9 (5)	C12—C13—C18—Cl2	−3.9 (6)
C12—N3—C11—C10	155.8 (4)		

Hydrogen-bond geometry (Å, º)

Cg3 is the centroid of the C13–C18 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*B*···O3^{i}	0.96	2.54	3.498 (8)	173
C11—H11*A*···O1^{ii}	0.97	2.36	3.281 (6)	159
C21—H21*B*···O2^{iii}	0.96	2.44	3.403 (6)	178
C4—H4*A*···*Cg*3^{i}	0.96	2.86	3.619 (7)	136

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