Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-Methyl-3-(4-chlorobenzoyl)imidazo-[1,2-*a*]pyridin-1-ium-2-olate

Victor B. Rybakov* and Eugene V. Babaev

Departament of Chemistry, Moscow State University, 119992 Moscow, Russian Federation
Correspondence e-mail: rybakov20021@yandex.ru

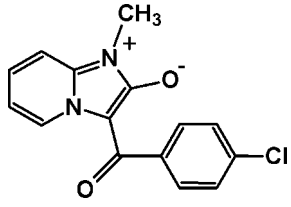
Received 12 September 2011; accepted 27 September 2011

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.044; wR factor = 0.107; data-to-parameter ratio = 14.0.

In the molecule of the title compound, $C_{15}H_{11}ClN_2O_2$, the nine-membered heterobicycle is approximately planar [largest deviation from least-squares plane = 0.012 (2) Å] and forms a dihedral angle of 51.14 (8)° with the plane of the 4-chlorophenyl group. There is a non-classical intramolecular hydrogen bond between the pyridine α-H atom and the O atom of the benzoyl group. The crystal structure is stabilized by weak C—H···O and C—H···Cl interactions involving the 'olate' O atom and the Cl atom attached to the benzoyl group as acceptors.

Related literature

For related structures, see: Friedman *et al.* (1978); Rybakov *et al.* (1999, 2000*a*,*b*, 2001, 2002). For the synthesis of 1-methyl-2-oxo-2,3-dihydroimidazopyridinium perchlorate, see: Sych & Gorb (1976). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$C_{15}H_{11}ClN_2O_2$
M_r = 286.71
Monoclinic, $P2_1/c$
a = 8.190 (8) Å
b = 13.914 (3) Å
c = 11.675 (4) Å
β = 102.38 (2)°
V = 1299.5 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 295 K
0.30 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
2675 measured reflections
2546 independent reflections
1486 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
1 standard reflections every 200 reflections
intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.107
S = 0.94
2546 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 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
C5—H5···O30	0.93	2.30	2.863 (3)	119
C8—H8···O2^{i}	0.93	2.47	3.291 (4)	148
C32—H32···Cl34^{ii}	0.93	2.93	3.794 (3)	155

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are indebted to I. V. Dlinnykh for the preparation of title compound. The authors wish to thank Russian Foundation for Basic Research for covering the licence fee for use of the Cambridge Structural Database ver. 5.32 (Allen, 2002).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YK2022).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Enraf–Nonius (1994). *CAD–4 Software*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Friedman, A. E., Anderson, W. K. & Shefter, E. (1978). *Cryst. Struct. Commun.* **7**, 723–726.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Rybakov, V. B., Babaev, E. V., Pasichnichenko, K. Yu. & Sonneveld, E. J. (2002). *Crystallogr. Rep.* **47**, 69–74.
Rybakov, V. B., Zhukov, S. G., Babaev, E. V., Mazina, O. S. & Aslanov, L. A. (1999). *Crystallogr. Rep.* **44**, 997–999.
Rybakov, V. B., Zhukov, S. G., Babaev, E. V., Mazina, O. S. & Aslanov, L. A. (2000*a*). *Crystallogr. Rep.* **45**, 103–104.
Rybakov, V. B., Zhukov, S. G., Babaev, E. V., Mazina, O. S. & Aslanov, L. A. (2000*b*). *Crystallogr. Rep.* **45**, 261–263.
Rybakov, V. B., Zhukov, S. G., Babaev, E. V. & Sonneveld, E. J. (2001). *Crystallogr. Rep.* **46**, 385–388.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sych, E. D. & Gorb, L. T. (1976). *Ukr. Khim. Zh. (Russ. Ed.)*, **9**, 961–963.

supporting information

Acta Cryst. (2011). E**67**, o2814 [https://doi.org/10.1107/S1600536811039614]

1-Methyl-3-(4-chlorobenzoyl)imidazo[1,2-*a*]pyridin-1-ium-2-olate

Victor B. Rybakov and Eugene V. Babaev

S1. Comment

Early we described crystal structures of "pyridylglycine" **I** (Rybakov *et al.*, 1999) (Fig. 1) and the product of its cyclo-condensation – 2-oxoimidazo[1,2-*a*]pyridine **II** (Rybakov *et al.*, 2000*a*) (Fig. 1). According to Sych & Gorb (1976), we have also performed selective *N*–methylation of **II** and investigated the molecular and crystal structures of the resulting salt **III** (Rybakov *et al.*, 2000*b*) (Fig. 1). In the present paper we continue the sequence **I**-**II**-**III** and report the molecular structure of the acylated derivative of the compound **III** - the mesoionic 1-methyl-3-(*p*–chlorobenzoyl)imidazo[1,2-*a*] pyridinium-2-olate **IV** (Fig. 1). The acylation of **III** was performed by using of 4-chlorobenzoyl chloride in the presence of triethylamine leading to green crystals of the derivative **IV** with the 60% yield.

The molecular structure of the mesoionic compound **IV** (Fig. 2) displays some remarkable features early observed for analogous fused imidazopyridines (Friedman *et al.*, 1978) and oxazolopyridines (Rybakov *et al.*, 2001; Rybakov *et al.*, 2002). In particular, in the moiety O10═ C30—C3—C2═O2 the bonds length C3—C30 and C2—C3 correspond to single bonds (~1.43 Å), whereas the bonds length C30═O30 and C2═ O2 (~1.23 Å) correspond to double bonds, thus displaying the unusual ylide-like pattern of the imidazolone fragment. On the other hand, the sequence C5═C6–C7═C8 displays alternation of the bonds length, thus corresponding to quasi-diene fragment of the pyridine ring. These facts seem to be common to the entire class of azolopyridinium-2-olates. The intramolecular interaction C5—H5···O30 with parameters H5···O30 = 2.296 Å, C5···O30 = 2.863 (3)Å and angle C5—H5···O30 = 118.83° (Table 1) is found. The molecules in crystal are linked by weak intermolecular interactions: C8—H8···O2^{i} with parameters H8···O2^{i} = 2.466 Å, C8···O2^{i} = 3.291 (4)Å and angle C8—H8···O2^{i} = 147.86°; C32—H32···Cl34^{ii} with parameters H32···Cl34^{ii} = 2.931 Å, C32···Cl34 = 3.794 (3)Å and angle C32—H32···Cl34^{ii} = 154.93°. Symmetry codes: (i) -*x*, *y* + 1/2, -*z* + 1/2; (ii) -*x* + 1, *y* + 1/2, -*z* + 1/2.

S2. Experimental

1-Methyl-2-oxo-2,3-dihydroimidazopyridinium perchlorate **III** was obtained as described by Sych & Gorb (1976) (Fig. 2). In order to obtain 1-methyl-3-(4-chlorobenzoyl)imidazo[1,2-*a*]pyridinium-2-olate **IV**, triethylamine (2.24 ml, 0.016 mol) was added slowly to the solution of 2.0 g (8 mmol) **III** in 10 ml of acetonitrile, and 1.4 g (8 mmol) of 4-chloro-benzoil chloride was added to the obtained mixture. The reaction flask was stirred at room temperature for 1 h and then kept overnight. The precipitate was filtered and recrystallized from isopropyl alcohol. The yield was 1.3 g (60%). *M*.p. 479–481 K. ^{1}H NMR spectra (*DMSO*-d$_6$, p.p.m.): 9.96 (d, 1H, 9-H), 7.85 (dd, 1H, 8-H), 7.68 (m, 2H, *p*-Cl*Ph*), 7.61 (d, 1H, 6-H), 7.44 (m, 2H, *p*-Cl*Ph*), 7.34 (dd, 1H, 7-H), 3.38 (s, 3H, 4-*Me*). The numbering of protons is given according to the atoms numbering on Fig. 1.

S3. Refinement

All the hydrogen atoms in the molecule were placed geometrically and allowed to ride on their parent atoms with C—H distance in the range 0.93Å and 0.96Å and with U_{iso}(H) = 1.5U_{eq}(C) for CH_3 group and U_{iso}(H) = 1.2U_{eq}(C) for the aryl groups.

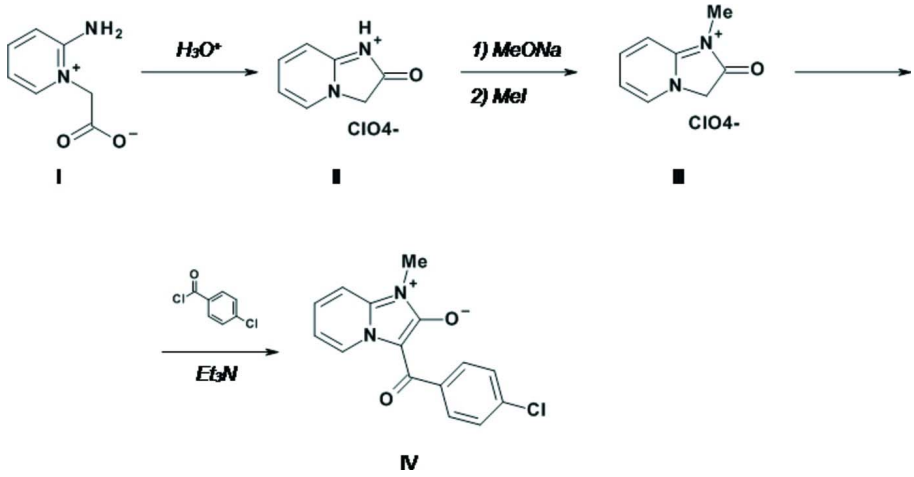


Figure 1

Synthesis path for **IV**.

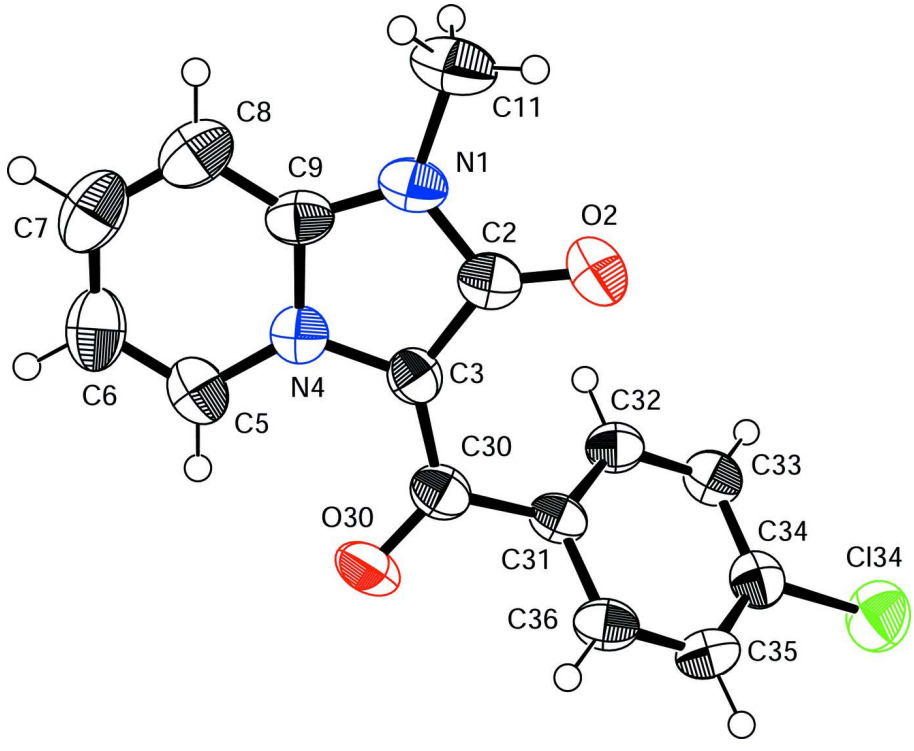


Figure 2

ORTEP-3 (Farrugia, 1997) plot of the molecule **IV** with the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

1-Methyl-3-(4-chlorobenzoyl)imidazo[1,2-*a*]pyridin-1-ium-2-olate

Crystal data

$C_{15}H_{11}ClN_2O_2$
$M_r = 286.71$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.190$ (8) Å
$b = 13.914$ (3) Å
$c = 11.675$ (4) Å
$\beta = 102.38$ (2)°
$V = 1299.5$ (14) Å^3
$Z = 4$
$F(000) = 592$
$D_x = 1.465$ Mg m^{-3}
Melting point = 479–481 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.0$–14.8°
$\mu = 0.30$ mm^{-1}
$T = 295$ K
Prism, green
0.30 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
non–profiled ω scans
2675 measured reflections
2546 independent reflections
1486 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.3°$
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 14$
1 standard reflections every 200 reflections
intensity decay: 2%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.107$
$S = 0.94$
2546 reflections
182 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
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
N1	0.0863 (3)	0.54749 (15)	0.22101 (19)	0.0505 (6)
C2	0.1226 (3)	0.45544 (18)	0.1820 (2)	0.0449 (6)
O2	0.0815 (2)	0.38150 (13)	0.22548 (16)	0.0594 (5)
C3	0.2076 (3)	0.47398 (16)	0.0895 (2)	0.0424 (6)

N4	0.2102 (2)	0.57470 (13)	0.07555 (17)	0.0416 (5)
C5	0.2755 (3)	0.62878 (19)	−0.0013 (2)	0.0521 (7)
H5	0.3244	0.5997	−0.0574	0.063*
C6	0.2675 (4)	0.7264 (2)	0.0060 (3)	0.0646 (9)
H6	0.3118	0.7641	−0.0457	0.078*
C7	0.1947 (4)	0.7704 (2)	0.0887 (3)	0.0690 (9)
H7	0.1903	0.8371	0.0920	0.083*
C8	0.1292 (4)	0.71635 (19)	0.1653 (3)	0.0609 (8)
H8	0.0801	0.7453	0.2213	0.073*
C9	0.1377 (3)	0.61773 (18)	0.1577 (2)	0.0469 (6)
C11	−0.0063 (4)	0.5623 (2)	0.3124 (3)	0.0725 (9)
H11A	0.0696	0.5797	0.3840	0.109*
H11B	−0.0636	0.5041	0.3240	0.109*
H11C	−0.0863	0.6129	0.2895	0.109*
C30	0.2748 (3)	0.40950 (17)	0.0162 (2)	0.0459 (6)
O30	0.3115 (3)	0.43543 (13)	−0.07607 (15)	0.0659 (6)
C31	0.3064 (3)	0.30759 (17)	0.0552 (2)	0.0390 (6)
C32	0.3762 (3)	0.28280 (17)	0.1699 (2)	0.0451 (6)
H32	0.3955	0.3304	0.2271	0.054*
C33	0.4177 (3)	0.18918 (18)	0.2012 (2)	0.0463 (6)
H33	0.4654	0.1733	0.2785	0.056*
C34	0.3869 (3)	0.11962 (17)	0.1154 (2)	0.0450 (6)
Cl34	0.43791 (11)	0.00078 (5)	0.15427 (8)	0.0725 (3)
C35	0.3144 (3)	0.14142 (17)	0.0010 (2)	0.0478 (7)
H35	0.2914	0.0931	−0.0552	0.057*
C36	0.2766 (3)	0.23515 (18)	−0.0291 (2)	0.0460 (7)
H36	0.2305	0.2507	−0.1068	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0450 (14)	0.0641 (14)	0.0448 (14)	0.0060 (11)	0.0150 (12)	−0.0039 (12)
C2	0.0378 (16)	0.0555 (15)	0.0389 (15)	0.0004 (12)	0.0023 (13)	−0.0033 (13)
O2	0.0603 (13)	0.0647 (12)	0.0568 (13)	−0.0035 (10)	0.0208 (11)	0.0127 (10)
C3	0.0415 (15)	0.0452 (13)	0.0396 (15)	0.0000 (11)	0.0071 (13)	0.0030 (11)
N4	0.0339 (12)	0.0468 (11)	0.0409 (12)	0.0017 (9)	0.0012 (10)	0.0011 (10)
C5	0.0418 (17)	0.0627 (17)	0.0506 (17)	0.0017 (13)	0.0071 (14)	0.0112 (14)
C6	0.050 (2)	0.0561 (17)	0.082 (2)	−0.0012 (14)	0.0015 (18)	0.0165 (16)
C7	0.056 (2)	0.0515 (17)	0.089 (3)	0.0079 (15)	−0.0079 (19)	−0.0010 (18)
C8	0.0476 (19)	0.0582 (17)	0.072 (2)	0.0084 (14)	0.0022 (17)	−0.0111 (16)
C9	0.0372 (16)	0.0568 (15)	0.0460 (17)	0.0101 (12)	0.0071 (13)	−0.0063 (13)
C11	0.069 (2)	0.098 (2)	0.057 (2)	0.0132 (18)	0.0286 (18)	−0.0073 (18)
C30	0.0430 (16)	0.0554 (16)	0.0382 (16)	−0.0002 (12)	0.0060 (13)	0.0004 (12)
O30	0.0985 (17)	0.0675 (12)	0.0383 (11)	0.0132 (11)	0.0289 (12)	0.0086 (10)
C31	0.0336 (14)	0.0519 (14)	0.0291 (14)	0.0011 (11)	0.0012 (11)	−0.0001 (11)
C32	0.0471 (17)	0.0500 (14)	0.0359 (15)	−0.0021 (12)	0.0037 (13)	−0.0056 (12)
C33	0.0409 (16)	0.0557 (15)	0.0392 (15)	0.0044 (12)	0.0019 (12)	0.0035 (13)
C34	0.0362 (15)	0.0475 (14)	0.0536 (17)	0.0070 (11)	0.0149 (14)	0.0050 (13)

Cl34	0.0791 (6)	0.0543 (4)	0.0870 (7)	0.0176 (4)	0.0246 (5)	0.0101 (4)
C35	0.0469 (17)	0.0510 (15)	0.0434 (16)	0.0013 (12)	0.0055 (13)	−0.0132 (13)
C36	0.0412 (16)	0.0596 (16)	0.0343 (15)	0.0038 (12)	0.0016 (13)	−0.0043 (12)

Geometric parameters (Å, º)

Cl34—C34	1.742 (2)	C5—H5	0.9300
N4—C5	1.365 (3)	C30—O30	1.233 (3)
N4—C9	1.370 (3)	C30—C31	1.495 (3)
N4—C3	1.412 (3)	C31—C32	1.382 (3)
C2—C3	1.428 (3)	C31—C36	1.393 (3)
C3—C30	1.429 (3)	C32—C33	1.376 (3)
C2—O2	1.226 (3)	C32—H32	0.9300
C2—N1	1.412 (3)	C33—C34	1.377 (3)
N1—C9	1.346 (3)	C33—H33	0.9300
N1—C11	1.450 (3)	C34—C35	1.374 (3)
C9—C8	1.378 (3)	C35—C36	1.369 (3)
C8—C7	1.364 (4)	C35—H35	0.9300
C8—H8	0.9300	C36—H36	0.9300
C7—C6	1.382 (4)	C11—H11A	0.9600
C7—H7	0.9300	C11—H11B	0.9600
C6—C5	1.364 (4)	C11—H11C	0.9600
C6—H6	0.9300		

C5—N4—C9	120.6 (2)	O30—C30—C3	122.5 (2)
C5—N4—C3	129.8 (2)	O30—C30—C31	119.0 (2)
C9—N4—C3	109.5 (2)	C3—C30—C31	118.5 (2)
N4—C3—C2	106.7 (2)	C32—C31—C36	118.5 (2)
N4—C3—C30	122.5 (2)	C32—C31—C30	122.7 (2)
C2—C3—C30	130.7 (2)	C36—C31—C30	118.6 (2)
O2—C2—N1	122.1 (2)	C33—C32—C31	121.4 (2)
O2—C2—C3	133.4 (2)	C33—C32—H32	119.3
N1—C2—C3	104.5 (2)	C31—C32—H32	119.3
C9—N1—C2	111.7 (2)	C32—C33—C34	118.4 (2)
C9—N1—C11	125.1 (2)	C32—C33—H33	120.8
C2—N1—C11	123.1 (2)	C34—C33—H33	120.8
N1—C9—N4	107.5 (2)	C35—C34—C33	121.7 (2)
N1—C9—C8	131.5 (3)	C35—C34—Cl34	119.5 (2)
N4—C9—C8	121.0 (3)	C33—C34—Cl34	118.8 (2)
C7—C8—C9	118.4 (3)	C36—C35—C34	119.1 (2)
C7—C8—H8	120.8	C36—C35—H35	120.4
C9—C8—H8	120.8	C34—C35—H35	120.4
C8—C7—C6	120.2 (3)	C35—C36—C31	120.8 (2)
C8—C7—H7	119.9	C35—C36—H36	119.6
C6—C7—H7	119.9	C31—C36—H36	119.6
C5—C6—C7	121.3 (3)	N1—C11—H11A	109.5
C5—C6—H6	119.4	N1—C11—H11B	109.5
C7—C6—H6	119.4	N1—C11—H11C	109.5

C6—C5—N4	118.5 (3)	H11A—C11—H11B	109.5
C6—C5—H5	120.7	H11A—C11—H11C	109.5
N4—C5—H5	120.7	H11B—C11—H11C	109.5
C5—N4—C3—C2	−179.6 (2)	C8—C7—C6—C5	0.1 (5)
C9—N4—C3—C2	2.5 (3)	C7—C6—C5—N4	−0.2 (4)
C5—N4—C3—C30	−2.0 (4)	C9—N4—C5—C6	0.3 (4)
C9—N4—C3—C30	−179.9 (2)	C3—N4—C5—C6	−177.5 (2)
N4—C3—C2—O2	176.9 (3)	N4—C3—C30—O30	−13.5 (4)
C30—C3—C2—O2	−0.5 (5)	C2—C3—C30—O30	163.5 (3)
N4—C3—C2—N1	−2.5 (3)	N4—C3—C30—C31	164.6 (2)
C30—C3—C2—N1	−179.8 (3)	C2—C3—C30—C31	−18.4 (4)
O2—C2—N1—C9	−177.7 (2)	O30—C30—C31—C32	136.1 (3)
C3—C2—N1—C9	1.8 (3)	C3—C30—C31—C32	−42.1 (4)
O2—C2—N1—C11	−2.0 (4)	O30—C30—C31—C36	−38.7 (4)
C3—C2—N1—C11	177.5 (2)	C3—C30—C31—C36	143.1 (2)
C2—N1—C9—N4	−0.3 (3)	C36—C31—C32—C33	0.7 (4)
C11—N1—C9—N4	−175.9 (2)	C30—C31—C32—C33	−174.1 (2)
C2—N1—C9—C8	−179.5 (3)	C31—C32—C33—C34	−0.5 (4)
C11—N1—C9—C8	4.9 (5)	C32—C33—C34—C35	−0.9 (4)
C5—N4—C9—N1	−179.5 (2)	C32—C33—C34—Cl34	−179.66 (19)
C3—N4—C9—N1	−1.4 (3)	C33—C34—C35—C36	2.0 (4)
C5—N4—C9—C8	−0.2 (4)	Cl34—C34—C35—C36	−179.18 (19)
C3—N4—C9—C8	177.9 (3)	C34—C35—C36—C31	−1.8 (4)
N1—C9—C8—C7	179.3 (3)	C32—C31—C36—C35	0.5 (4)
N4—C9—C8—C7	0.1 (4)	C30—C31—C36—C35	175.5 (2)
C9—C8—C7—C6	−0.1 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O30	0.93	2.30	2.863 (3)	119
C8—H8···O2^{i}	0.93	2.47	3.291 (4)	148
C32—H32···Cl34^{ii}	0.93	2.93	3.794 (3)	155

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