Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-Methyl-3-(2-oxo-2*H*-chromen-3-yl)-1*H*-imidazol-3-ium picrate

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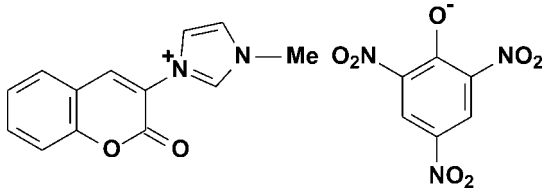
Received 25 April 2013; accepted 29 April 2013

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.005 Å; R factor = 0.063; wR factor = 0.165; data-to-parameter ratio = 14.8.

The title salt, $C_{13}H_{11}N_2O_2^+\cdot C_6H_2N_3O_7^-$, is the unexpected product of a domino reaction of 3-cyanomethyl-1-methylimidazolium chloride with salicylic aldehyde in the presence of picric acid. In the cation, the 1*H*-imidazole ring is twisted by 63.2 (1)° from the 2*H*-chromen plane. In the crystal, cations and anions are alternately stacked along the *a* axis through π–π stacking interactions between the almost parallel aromatic rings [centroid–centroid distances = 3.458 (2) and 3.678 (2) Å]. The stacks are further linked by C—H···O hydrogen bonds into a two-tier layer parallel to (001).

Related literature

For a recent review on coumarin-based drug patents, see: Kontogiorgis *et al.* (2012). For analogous domino reactions, see: Voskressensky *et al.* (2012*a*,*b*). For related compounds, see: Yu *et al.* (2006); Morris *et al.* (2011).



Experimental

Crystal data

$C_{13}H_{11}N_2O_2^+\cdot C_6H_2N_3O_7^-$
M_r = 455.34
Monoclinic, $P2_1$
a = 6.8142 (12) Å
b = 8.1942 (14) Å
c = 16.832 (3) Å
β = 100.081 (4)°
V = 925.3 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 100 K
0.30 × 0.21 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.961, T_{max} = 0.996
10390 measured reflections
4415 independent reflections
3734 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.165
S = 1.00
4415 reflections
299 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O7^{i}	0.95	2.58	3.349 (4)	138
C9—H9···O3	0.95	2.33	3.122 (5)	140
C10—H10···O9^{ii}	0.95	2.51	3.303 (5)	141
C11—H11···O3^{iii}	0.95	2.42	3.196 (5)	139
C11—H11···O5^{iii}	0.95	2.51	3.231 (5)	132
C12—H12*A*···O2^{iv}	0.98	2.58	3.360 (5)	137
C12—H12*B*···O2^{v}	0.98	2.48	3.448 (5)	171
C12—H12*C*···O3^{iv}	0.98	2.39	3.269 (4)	148
C12—H12*C*···O9^{iv}	0.98	2.42	3.160 (5)	132
C17—H17···O5^{vi}	0.95	2.40	3.345 (5)	172

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the Russian Foundation for Basic Research (project No. 12–03-93000-Viet-a) and the Vietnam Academy of Science and Technology (grant VAST·HTQT·NGA. 06/2012–2013) for the financial support of this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5268).

References

Bruker (2001). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Kontogiorgis, C., Detsi, A. & Hadjipavlou-Litina, D. (2012). *Expert Opin. Ther. Pat.* **22**, 437–454.
Morris, J. C., McMurtrie, J. C., Bottle, S. E. & Fairfull-Smith, K. E. (2011). *J. Org. Chem.* **76**, 4964–4972.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Voskressensky, L. G., Festa, A. A., Sokolova, E. A., Khrustalev, V. N. & Varlamov, A. V. (2012*b*). *Eur. J. Org. Chem.* pp. 6124–6126.
Voskressensky, L. G., Festa, A. A., Sokolova, E. A. & Varlamov, A. V. (2012*a*). *Tetrahedron*, **68**, 5498–5504.
Yu, T.-Z., Zhao, Y.-L. & Fan, D.-W. (2006). *J. Mol. Struct.* **791**, 18–22.

supplementary materials

Acta Cryst. (2013). E**69**, o839 [doi:10.1107/S1600536813011690]

1-Methyl-3-(2-oxo-2*H*-chromen-3-yl)-1*H*-imidazol-3-ium picrate

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Comment

Coumarin derivatives are known to possess a range of different biological activities (Kontogiorgis *et al.*, 2012). The title compound, $C_{13}H_{11}N_2O_2^+.C_6H_2N_3O_7^-$ (**I**), is the unexpected product of Knoevenagel condensation of 3-(cyanomethyl)-1-methylimidazolium chloride with salicylic aldehyde followed by the hydrolysis of imino-group and the formation of ammonium salt with picric acid (Fig. 1; Voskressensky *et al.*, 2012*a*,*b*).

The cation and anion of **I** form a tight ionic pair by the C9—H9···O3 hydrogen bond (Table 1) as well as the π–π stacking interactions between the almost parallel aromatic moieties [the dihedral angle between the mean planes of the 2*H*-chromen (cation) and benzene (anion) fragments is 3.55 (7)°; the shortest C8···C17 distance is 3.280 (5) Å; Fig. 2]. The 1*H*-imidazole ring is twisted at 63.2 (1)° from the 2*H*-chromen plane. In the crystal, the tight ionic pairs form stacks along the *a* axis by the π–π stacking interactions (Fig. 3). The stacks are further bound by the C—H···O hydrogen bonds into two-tier layers parallel to (001) (Fig. 4).

Experimental

A solid Na_2CO_3 (67.0 mg, 0.63 mmol) was added to a stirred solution of 3-(cyanomethyl)-1-methylimidazolium chloride (500 mg, 3.2 mmol) and salicylic aldehyde (350 mg, 2.9 mmol) in a mixture of methanol (4 ml) and water (1 ml) at reflux. The reaction mixture was heated at reflux for 1 h. Then picric acid (870 mg, 3.8 mmol) was added to the solution. The formed precipitate was filtered-off and washed with acetone (3x) to give 630 mg of yellow crystals of **I**. The yield is 48%. *M*.p. = 459 K (decomp.). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 4.04 (3*H*, s, Me), 7.54 (1*H*, t, *J* = 7.5 Hz, H6′), 7.63 (1*H*, d, *J* = 8.3 Hz, H5′), 7.79–7.85 (1*H*, m, H7′), 7.87–7.92 (1*H*, m, H8′), 7.98–8.01 (1*H*, m, H5), 8.16–8.19 (1*H*, m, H4), 8.61 (2*H*, s, picric acid CH), 8.70 (1*H*, s, H4′), 9.71 (1*H*, bs, H2); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 36.2, 116.4, 117.6, 121.6, 122.5, 123.7, 124.2, 125.1 (2 C), 125.5, 129.4, 133.5, 137.3, 137.5, 141.8, 152.4 (2 C), 156.1, 160.8. Anal. Calcd for $C_{13}H_{11}N_2O_2.C_6H_2N_3O_7$: C 50.12, H 2.88, N 15.38; found: C 50.34, H 3.01, N 15.53.

Refinement

H atoms were placed in calculated positions with C—H = 0.95 Å (CH) and 0.98 Å (CH_3) and refined in the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the CH_3 group and 1.2U_{eq}(C) for the CH groups].

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

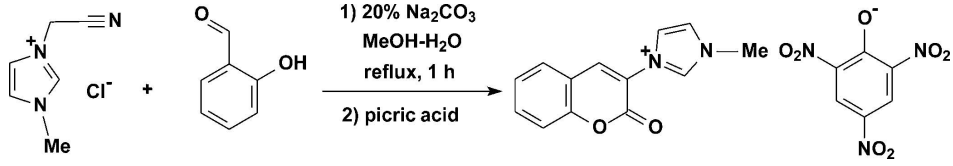

Figure 1

The domino reaction of 3-(cyanomethyl)-1-methylimidazolium chloride with salicylic aldehyde.

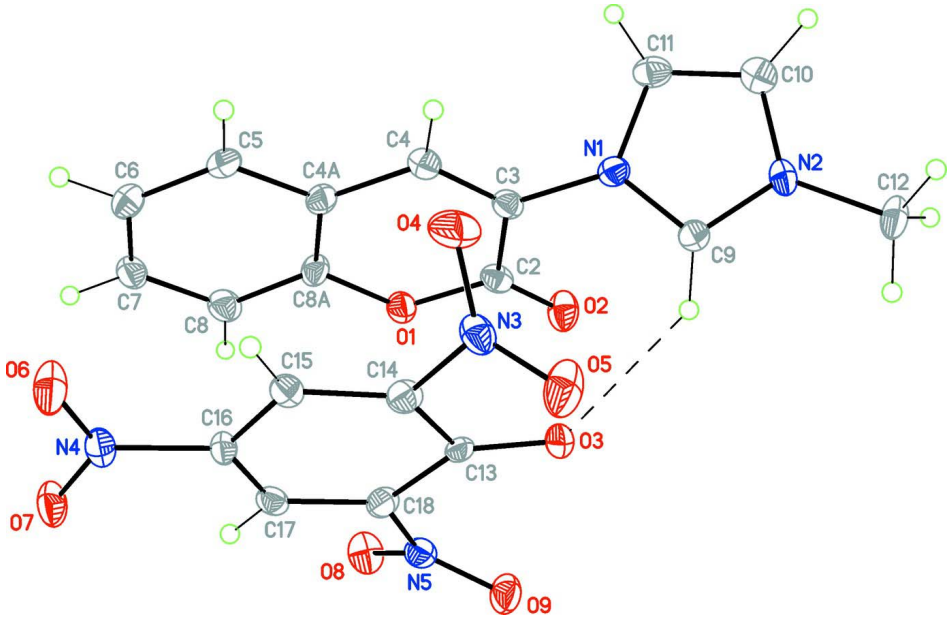

Figure 2

The molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius. Dashed line indicates the (N)C(N^+)—H···O^- hydrogen bond between cation and anion.

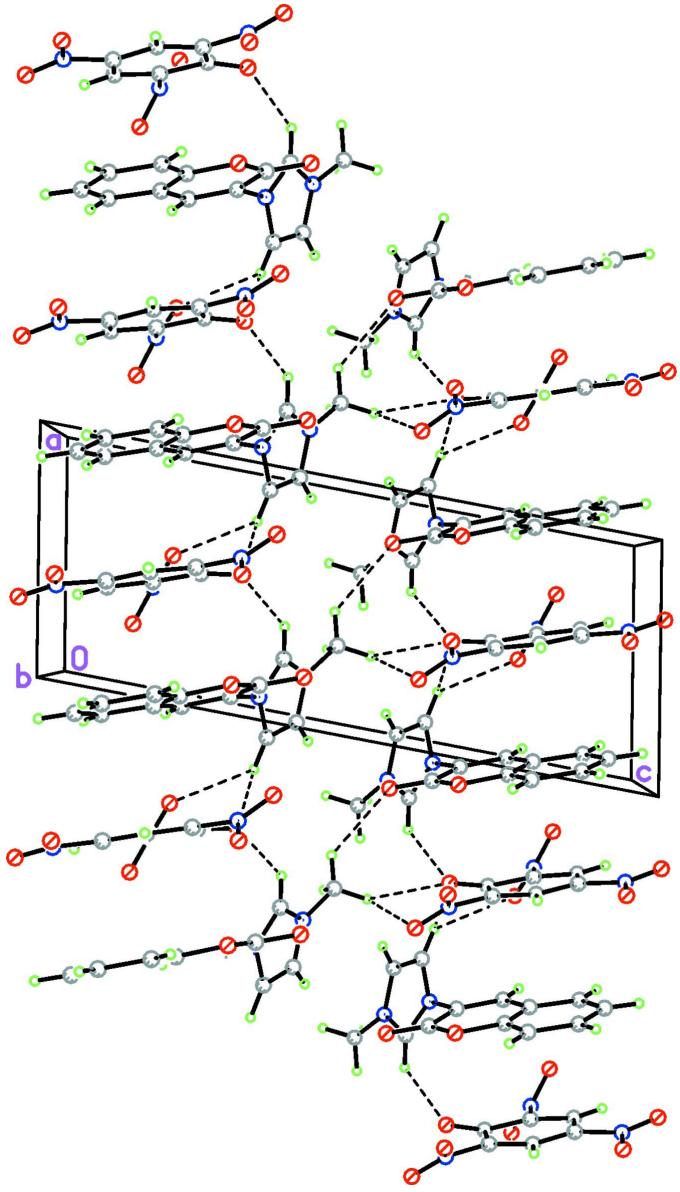

Figure 3

A portion of crystal packing of the title compound demonstrating the stacks along the *a* axis. Dashed lines indicate the intermolecular C—H···O hydrogen bonds.

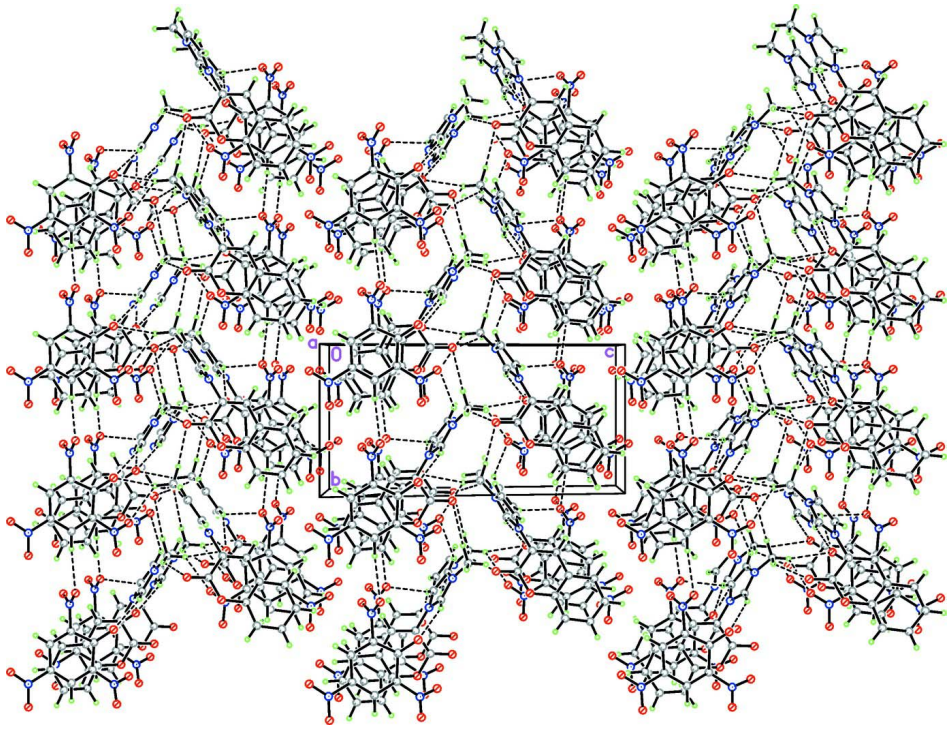

Figure 4

The two-tier layers of the title compound parallel to (001). Dashed lines indicate the intermolecular C—H···O hydrogen bonds.

1-Methyl-3-(2-oxo-2*H*-chromen-3-yl)-1*H*-imidazol-3-ium picrate

Crystal data

$C_{13}H_{11}N_2O_2^+·C_6H_2N_3O_7^-$
M_r = 455.34
Monoclinic, $P2_1$
Hall symbol: P 2yb
a = 6.8142 (12) Å
b = 8.1942 (14) Å
c = 16.832 (3) Å
β = 100.081 (4)°
V = 925.3 (3) Å^3
Z = 2
$F(000)$ = 468
D_x = 1.634 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3018 reflections
θ = 2.5–30.2°
μ = 0.13 mm^{-1}
T = 100 K
Plate, yellow
0.30 × 0.21 × 0.03 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, 2003)
T_{min} = 0.961, T_{max} = 0.996
10390 measured reflections
4415 independent reflections
3734 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 28.0°, θ_{min} = 2.5°
h = −9→9
k = −10→10
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.165$
$S = 1.00$
4415 reflections
299 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 1.86P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ 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}
O1	0.8777 (4)	0.6678 (3)	0.68430 (15)	0.0183 (5)
O2	0.8003 (4)	0.5232 (4)	0.57153 (15)	0.0233 (6)
N1	0.9223 (4)	0.2275 (4)	0.64703 (18)	0.0166 (6)
N2	0.8021 (5)	0.0278 (4)	0.57071 (17)	0.0166 (6)
C2	0.8643 (5)	0.5224 (5)	0.6430 (2)	0.0168 (7)
C3	0.9351 (5)	0.3784 (5)	0.6911 (2)	0.0161 (7)
C4	1.0105 (5)	0.3861 (5)	0.7702 (2)	0.0171 (7)
H4	1.0561	0.2899	0.7992	0.021*
C4A	1.0217 (5)	0.5408 (5)	0.8103 (2)	0.0165 (7)
C5	1.0926 (5)	0.5595 (5)	0.8937 (2)	0.0178 (7)
H5	1.1365	0.4666	0.9257	0.021*
C6	1.0989 (5)	0.7124 (5)	0.9295 (2)	0.0205 (8)
H6	1.1461	0.7240	0.9857	0.025*
C7	1.0352 (6)	0.8501 (5)	0.8821 (2)	0.0223 (8)
H7	1.0420	0.9552	0.9063	0.027*
C8	0.9623 (6)	0.8333 (5)	0.8001 (2)	0.0208 (8)
H8	0.9169	0.9257	0.7681	0.025*
C8A	0.9570 (5)	0.6794 (5)	0.7661 (2)	0.0172 (7)
C9	0.7529 (5)	0.1610 (5)	0.6077 (2)	0.0163 (7)
H9	0.6218	0.2018	0.6064	0.020*
C10	1.0046 (6)	0.0076 (5)	0.5862 (2)	0.0198 (7)
H10	1.0772	−0.0786	0.5671	0.024*
C11	1.0826 (5)	0.1338 (5)	0.6341 (2)	0.0200 (7)
H11	1.2195	0.1536	0.6546	0.024*
C12	0.6615 (6)	−0.0810 (5)	0.5195 (2)	0.0218 (8)
H12A	0.5247	−0.0517	0.5245	0.033*

H12B	0.6878	−0.1942	0.5369	0.033*
H12C	0.6784	−0.0694	0.4632	0.033*
O3	0.4485 (4)	0.3812 (3)	0.67659 (15)	0.0185 (5)
O4	0.7273 (4)	0.1650 (4)	0.85805 (18)	0.0293 (7)
O5	0.4224 (5)	0.1338 (4)	0.79424 (19)	0.0310 (7)
O6	0.6970 (5)	0.6752 (4)	1.02204 (16)	0.0283 (7)
O7	0.5824 (4)	0.8942 (3)	0.95546 (17)	0.0245 (6)
O8	0.4486 (4)	0.8736 (3)	0.66647 (16)	0.0239 (6)
O9	0.2690 (4)	0.6684 (4)	0.61602 (16)	0.0257 (6)
N3	0.5653 (5)	0.2192 (4)	0.82445 (19)	0.0197 (6)
N4	0.6210 (5)	0.7472 (4)	0.95962 (18)	0.0183 (6)
N5	0.3876 (5)	0.7341 (4)	0.67024 (19)	0.0185 (6)
C13	0.4738 (5)	0.4649 (4)	0.7400 (2)	0.0134 (7)
C14	0.5419 (5)	0.3960 (5)	0.8190 (2)	0.0173 (7)
C15	0.5962 (5)	0.4837 (4)	0.8896 (2)	0.0155 (7)
H15	0.6481	0.4310	0.9391	0.019*
C16	0.5717 (5)	0.6527 (5)	0.8853 (2)	0.0159 (7)
C17	0.5037 (5)	0.7321 (5)	0.8138 (2)	0.0161 (7)
H17	0.4908	0.8476	0.8125	0.019*
C18	0.4542 (5)	0.6419 (5)	0.7437 (2)	0.0170 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0207 (13)	0.0180 (13)	0.0157 (12)	0.0025 (11)	0.0020 (9)	−0.0013 (10)
O2	0.0339 (16)	0.0201 (14)	0.0150 (12)	−0.0014 (12)	0.0016 (11)	0.0006 (11)
N1	0.0142 (14)	0.0172 (15)	0.0181 (14)	−0.0001 (12)	0.0019 (11)	−0.0001 (12)
N2	0.0237 (16)	0.0131 (14)	0.0130 (13)	−0.0004 (12)	0.0036 (11)	−0.0013 (11)
C2	0.0155 (17)	0.0147 (16)	0.0212 (17)	0.0007 (14)	0.0062 (13)	0.0011 (14)
C3	0.0155 (16)	0.0133 (16)	0.0195 (17)	0.0007 (13)	0.0035 (13)	−0.0003 (14)
C4	0.0178 (16)	0.0163 (17)	0.0175 (16)	0.0021 (14)	0.0042 (13)	0.0010 (14)
C4A	0.0121 (16)	0.0192 (18)	0.0181 (16)	−0.0026 (14)	0.0024 (13)	−0.0024 (14)
C5	0.0141 (17)	0.0206 (18)	0.0175 (17)	0.0014 (14)	−0.0002 (13)	0.0014 (14)
C6	0.0167 (17)	0.022 (2)	0.0212 (18)	−0.0030 (14)	−0.0002 (13)	−0.0036 (15)
C7	0.0167 (18)	0.022 (2)	0.028 (2)	−0.0007 (15)	0.0040 (15)	−0.0101 (16)
C8	0.0208 (19)	0.0158 (18)	0.0256 (19)	0.0011 (14)	0.0038 (15)	−0.0010 (14)
C8A	0.0176 (17)	0.0215 (18)	0.0117 (15)	−0.0002 (14)	0.0010 (12)	−0.0012 (14)
C9	0.0165 (16)	0.0163 (17)	0.0157 (16)	0.0008 (14)	0.0018 (12)	−0.0001 (13)
C10	0.0222 (18)	0.0217 (19)	0.0169 (16)	0.0009 (15)	0.0072 (13)	0.0022 (14)
C11	0.0163 (17)	0.0250 (19)	0.0192 (18)	0.0025 (15)	0.0047 (13)	0.0031 (14)
C12	0.029 (2)	0.0186 (19)	0.0155 (17)	−0.0051 (15)	−0.0025 (14)	−0.0030 (14)
O3	0.0197 (13)	0.0201 (13)	0.0150 (12)	0.0018 (11)	0.0011 (9)	−0.0049 (11)
O4	0.0266 (15)	0.0243 (15)	0.0361 (16)	0.0091 (12)	0.0032 (12)	0.0054 (13)
O5	0.0455 (18)	0.0140 (14)	0.0279 (15)	−0.0041 (13)	−0.0089 (13)	0.0022 (11)
O6	0.0429 (17)	0.0229 (15)	0.0172 (13)	−0.0014 (13)	0.0000 (12)	−0.0038 (11)
O7	0.0348 (15)	0.0170 (14)	0.0207 (13)	−0.0002 (12)	0.0022 (11)	−0.0069 (11)
O8	0.0346 (16)	0.0162 (13)	0.0212 (13)	−0.0008 (12)	0.0061 (11)	0.0041 (11)
O9	0.0310 (15)	0.0231 (14)	0.0195 (13)	0.0036 (12)	−0.0057 (11)	−0.0036 (11)
N3	0.0268 (17)	0.0144 (15)	0.0179 (15)	0.0034 (13)	0.0041 (12)	0.0003 (12)
N4	0.0204 (15)	0.0182 (16)	0.0172 (15)	−0.0036 (12)	0.0060 (12)	−0.0042 (12)

N5	0.0173 (15)	0.0213 (16)	0.0170 (15)	0.0028 (13)	0.0036 (12)	−0.0008 (12)
C13	0.0079 (16)	0.0186 (18)	0.0135 (15)	−0.0004 (12)	0.0015 (12)	−0.0022 (12)
C14	0.0168 (17)	0.0131 (17)	0.0212 (18)	0.0002 (14)	0.0011 (13)	0.0017 (14)
C15	0.0147 (17)	0.0144 (17)	0.0184 (17)	−0.0013 (13)	0.0051 (13)	−0.0006 (13)
C16	0.0157 (16)	0.0160 (17)	0.0159 (16)	−0.0011 (14)	0.0023 (12)	−0.0057 (14)
C17	0.0129 (16)	0.0159 (17)	0.0205 (17)	−0.0002 (14)	0.0062 (13)	−0.0020 (14)
C18	0.0148 (17)	0.0170 (18)	0.0182 (17)	−0.0003 (14)	0.0002 (13)	0.0003 (14)

Geometric parameters (Å, º)

O1—C2	1.374 (5)	C10—C11	1.361 (6)
O1—C8A	1.391 (4)	C10—H10	0.9500
O2—C2	1.206 (5)	C11—H11	0.9500
N1—C9	1.342 (5)	C12—H12A	0.9800
N1—C11	1.383 (5)	C12—H12B	0.9800
N1—C3	1.437 (5)	C12—H12C	0.9800
N2—C9	1.328 (5)	O3—C13	1.255 (4)
N2—C10	1.369 (5)	O4—N3	1.232 (4)
N2—C12	1.472 (5)	O5—N3	1.235 (4)
C2—C3	1.464 (5)	O6—N4	1.237 (4)
C3—C4	1.342 (5)	O7—N4	1.232 (4)
C4—C4A	1.433 (5)	O8—N5	1.222 (4)
C4—H4	0.9500	O9—N5	1.232 (4)
C4A—C8A	1.387 (5)	N3—C14	1.458 (5)
C4A—C5	1.410 (5)	N4—C16	1.460 (4)
C5—C6	1.387 (6)	N5—C18	1.452 (5)
C5—H5	0.9500	C13—C14	1.445 (5)
C6—C7	1.405 (6)	C13—C18	1.458 (5)
C6—H6	0.9500	C14—C15	1.383 (5)
C7—C8	1.389 (6)	C15—C16	1.395 (5)
C7—H7	0.9500	C15—H15	0.9500
C8—C8A	1.383 (5)	C16—C17	1.376 (5)
C8—H8	0.9500	C17—C18	1.383 (5)
C9—H9	0.9500	C17—H17	0.9500
C2—O1—C8A	122.7 (3)	C11—C10—H10	126.4
C9—N1—C11	109.4 (3)	N2—C10—H10	126.4
C9—N1—C3	125.0 (3)	C10—C11—N1	106.1 (3)
C11—N1—C3	125.5 (3)	C10—C11—H11	126.9
C9—N2—C10	109.8 (3)	N1—C11—H11	126.9
C9—N2—C12	125.5 (3)	N2—C12—H12A	109.5
C10—N2—C12	124.7 (3)	N2—C12—H12B	109.5
O2—C2—O1	118.7 (3)	H12A—C12—H12B	109.5
O2—C2—C3	125.7 (4)	N2—C12—H12C	109.5
O1—C2—C3	115.6 (3)	H12A—C12—H12C	109.5
C4—C3—N1	122.0 (3)	H12B—C12—H12C	109.5
C4—C3—C2	122.9 (4)	O4—N3—O5	124.3 (3)
N1—C3—C2	115.1 (3)	O4—N3—C14	117.8 (3)
C3—C4—C4A	119.3 (4)	O5—N3—C14	117.9 (3)
C3—C4—H4	120.4	O7—N4—O6	124.6 (3)

C4A—C4—H4	120.4	O7—N4—C16	117.1 (3)
C8A—C4A—C5	117.8 (3)	O6—N4—C16	118.3 (3)
C8A—C4A—C4	119.1 (3)	O8—N5—O9	123.7 (3)
C5—C4A—C4	123.1 (4)	O8—N5—C18	118.2 (3)
C6—C5—C4A	120.6 (4)	O9—N5—C18	118.0 (3)
C6—C5—H5	119.7	O3—C13—C14	122.9 (3)
C4A—C5—H5	119.7	O3—C13—C18	125.4 (3)
C5—C6—C7	119.7 (3)	C14—C13—C18	111.5 (3)
C5—C6—H6	120.1	C15—C14—C13	125.6 (3)
C7—C6—H6	120.1	C15—C14—N3	116.9 (3)
C8—C7—C6	120.3 (4)	C13—C14—N3	117.4 (3)
C8—C7—H7	119.8	C14—C15—C16	117.4 (3)
C6—C7—H7	119.8	C14—C15—H15	121.3
C8A—C8—C7	118.7 (4)	C16—C15—H15	121.3
C8A—C8—H8	120.6	C17—C16—C15	122.3 (3)
C7—C8—H8	120.6	C17—C16—N4	119.4 (3)
C8—C8A—C4A	122.8 (3)	C15—C16—N4	118.3 (3)
C8—C8A—O1	116.8 (3)	C16—C17—C18	119.2 (3)
C4A—C8A—O1	120.5 (3)	C16—C17—H17	120.4
N2—C9—N1	107.4 (3)	C18—C17—H17	120.4
N2—C9—H9	126.3	C17—C18—N5	116.2 (3)
N1—C9—H9	126.3	C17—C18—C13	123.9 (3)
C11—C10—N2	107.3 (3)	N5—C18—C13	119.9 (3)

C8A—O1—C2—O2	−177.4 (3)	C12—N2—C10—C11	178.7 (3)
C8A—O1—C2—C3	1.3 (5)	N2—C10—C11—N1	0.6 (4)
C9—N1—C3—C4	120.5 (4)	C9—N1—C11—C10	−0.5 (4)
C11—N1—C3—C4	−64.0 (5)	C3—N1—C11—C10	−176.6 (3)
C9—N1—C3—C2	−60.9 (5)	O3—C13—C14—C15	171.5 (4)
C11—N1—C3—C2	114.6 (4)	C18—C13—C14—C15	−4.2 (5)
O2—C2—C3—C4	177.9 (4)	O3—C13—C14—N3	−5.2 (5)
O1—C2—C3—C4	−0.7 (5)	C18—C13—C14—N3	179.1 (3)
O2—C2—C3—N1	−0.7 (5)	O4—N3—C14—C15	−50.5 (5)
O1—C2—C3—N1	−179.4 (3)	O5—N3—C14—C15	130.3 (4)
N1—C3—C4—C4A	179.1 (3)	O4—N3—C14—C13	126.5 (4)
C2—C3—C4—C4A	0.6 (5)	O5—N3—C14—C13	−52.7 (5)
C3—C4—C4A—C8A	−1.0 (5)	C13—C14—C15—C16	4.2 (5)
C3—C4—C4A—C5	177.9 (3)	N3—C14—C15—C16	−179.1 (3)
C8A—C4A—C5—C6	−0.7 (5)	C14—C15—C16—C17	−2.4 (5)
C4—C4A—C5—C6	−179.6 (3)	C14—C15—C16—N4	177.7 (3)
C4A—C5—C6—C7	−0.4 (5)	O7—N4—C16—C17	6.1 (5)
C5—C6—C7—C8	1.3 (6)	O6—N4—C16—C17	−174.2 (3)
C6—C7—C8—C8A	−1.1 (6)	O7—N4—C16—C15	−174.1 (3)
C7—C8—C8A—C4A	−0.1 (6)	O6—N4—C16—C15	5.6 (5)
C7—C8—C8A—O1	178.3 (3)	C15—C16—C17—C18	1.2 (5)
C5—C4A—C8A—C8	1.0 (5)	N4—C16—C17—C18	−179.0 (3)
C4—C4A—C8A—C8	179.9 (4)	C16—C17—C18—N5	−178.7 (3)
C5—C4A—C8A—O1	−177.3 (3)	C16—C17—C18—C13	−1.5 (5)
C4—C4A—C8A—O1	1.6 (5)	O8—N5—C18—C17	27.9 (5)

C2—O1—C8A—C8	179.8 (3)	O9—N5—C18—C17	−150.4 (3)
C2—O1—C8A—C4A	−1.8 (5)	O8—N5—C18—C13	−149.4 (3)
C10—N2—C9—N1	0.1 (4)	O9—N5—C18—C13	32.3 (5)
C12—N2—C9—N1	−179.0 (3)	O3—C13—C18—C17	−172.8 (3)
C11—N1—C9—N2	0.3 (4)	C14—C13—C18—C17	2.8 (5)
C3—N1—C9—N2	176.4 (3)	O3—C13—C18—N5	4.3 (5)
C9—N2—C10—C11	−0.4 (4)	C14—C13—C18—N5	179.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O7^{i}	0.95	2.58	3.349 (4)	138
C9—H9···O3	0.95	2.33	3.122 (5)	140
C10—H10···O9^{ii}	0.95	2.51	3.303 (5)	141
C11—H11···O3^{iii}	0.95	2.42	3.196 (5)	139
C11—H11···O5^{iii}	0.95	2.51	3.231 (5)	132
C12—H12*A*···O2^{iv}	0.98	2.58	3.360 (5)	137
C12—H12*B*···O2^{v}	0.98	2.48	3.448 (5)	171
C12—H12*C*···O3^{iv}	0.98	2.39	3.269 (4)	148
C12—H12*C*···O9^{iv}	0.98	2.42	3.160 (5)	132
C17—H17···O5^{vi}	0.95	2.40	3.345 (5)	172

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