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5-Chloro-2-nitrobenzaldehyde isonicotinoylhydrazone: a three-dimensional framework built from N—H···N and C—H···O hydrogen bonds

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.142
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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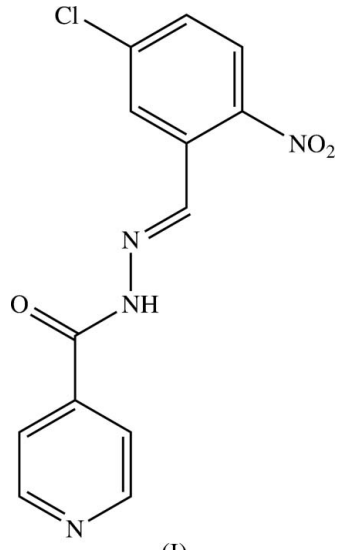
In the title compound, $C_{13}H_9ClN_4O_3$, the molecules are linked into a three-dimensional framework by one N—H···N hydrogen bond and three C—H···O hydrogen bonds.

Comment

We report here the molecular and supramolecular structure of the title compound, (I) (Fig. 1), originally synthesized as a potential antimycobacterial agent (Junior *et al.*, 2005).



(I)

The coordination of the hydrazine atom N1 is planar and the central spacer unit between C1 and C21 is nearly planar, as shown by the leading torsion angles (Table 1); however, the two rings are significantly twisted out of this plane, although the two rings remain nearly parallel.

The molecules of (I) are linked by a combination of N—H···N and C—H···O hydrogen bonds (Table 2) into a three-dimensional framework structure, whose formation is readily analysed in terms of a number of very simple one-dimensional substructures, each formed by the action of a single hydrogen bond.

Amino atom N1 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to pyridyl atom N4 in the molecule at $(-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, so forming a *C*(7) (Bernstein *et al.*, 1995) chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(0, y, \frac{3}{4})$ (Fig. 2). Atoms C3 and C24 in the molecule at (*x*, *y*, *z*) act as hydrogen-bond donors, respectively, to carbonyl atom O7 in the molecule at $(x, \frac{3}{2}-y, \frac{1}{2}+z)$, and nitro atom O221 in the molecule at $(x, \frac{1}{2}-y, -\frac{1}{2}+z)$, so forming two distinct *C*(6) chains running parallel to the

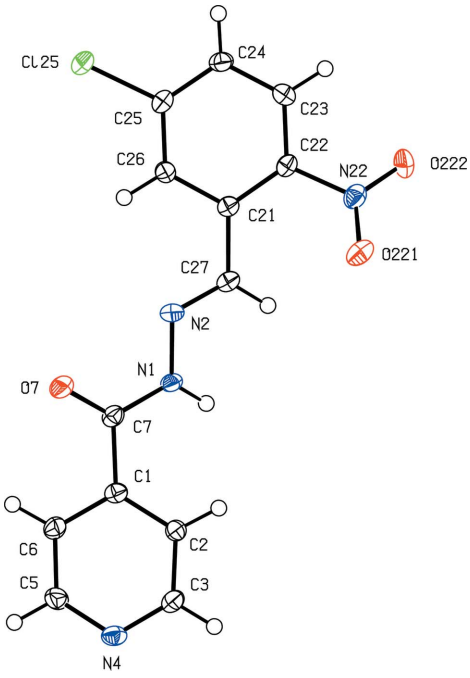


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

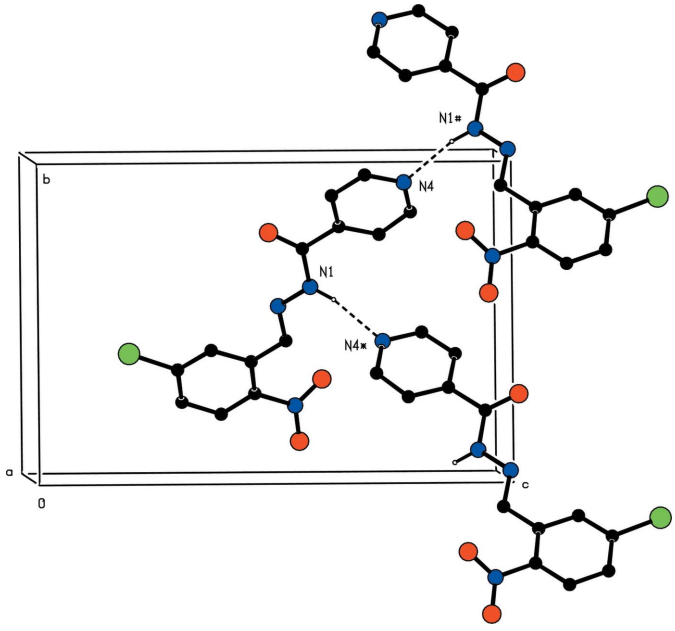


Figure 2
Part of the crystal structure of compound (I), showing the formation of a $C(7)$ chain along [010] built from N—H···N hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-x, -\frac{1}{2}+y, \frac{3}{2}-z)$ and $(-x, \frac{1}{2}+y, \frac{3}{2}-z)$, respectively.

[001] direction and generated respectively by the *c*-glide planes at $y = 0.75$ (Fig. 3) and $y = 0.25$ (Fig. 4). Finally, atom C5 in the molecule at (x, y, z) acts as hydrogen-bond donor to nitro atom O222 in the molecule at $(-1+x, 1+y, z)$, so generating by translation a $C(12)$ chain running parallel to the $[1\bar{1}0]$ direction (Fig. 5).

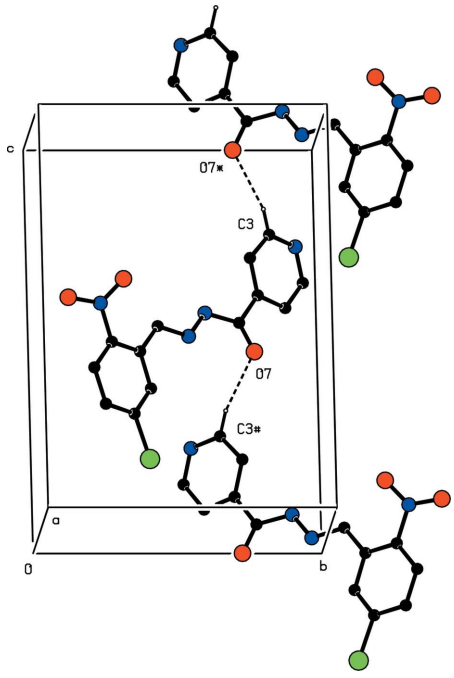


Figure 3
Part of the crystal structure of compound (I), showing the formation of a $C(6)$ chain along [001] built from C—H···O(carbonyl) hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, \frac{3}{2}-y, \frac{1}{2}+z)$ and $(x, \frac{3}{2}-y, -\frac{1}{2}+z)$, respectively.

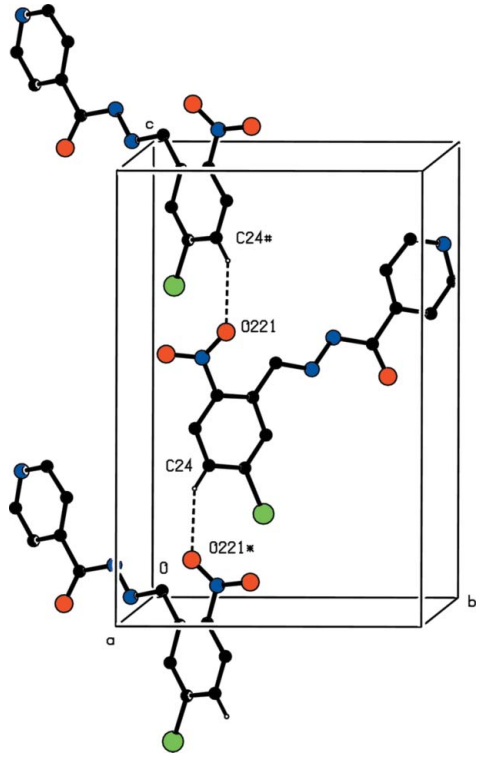


Figure 4
Part of the crystal structure of compound (I), showing the formation of a $C(6)$ chain along [001] built from C—H···O(nitro) hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, \frac{1}{2}-y, -\frac{1}{2}+z)$ and $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, respectively.

The combination of the [010], [001] and [1$\bar{1}$0] chains generates a single three-dimensional framework structure: it is notable that all three O atoms act as hydrogen-bond acceptors.

Experimental

Crystals of the title compound were prepared according to a published procedure (Junior *et al.*, 2005).

Crystal data

$C_{13}H_9ClN_4O_3$
M_r = 304.69
Monoclinic, $P2_1/c$
a = 8.0597 (2) Å
b = 10.4797 (4) Å
c = 15.4798 (6) Å
β = 97.383 (2)°
V = 1296.63 (8) Å^3
Z = 4
D_x = 1.561 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 120 (2) K
Lath, colourless
0.34 × 0.16 × 0.08 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.916, T_{max} = 0.976
17385 measured reflections
2980 independent reflections
2132 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.143
S = 1.09
2980 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0817P)^2 + 0.135P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected torsion angles (°).

C2—C1—C7—N1	24.3 (3)	N1—N2—C27—C21	179.18 (16)
C1—C7—N1—N2	−174.60 (17)	N2—C27—C21—C22	163.1 (2)
C7—N1—N2—C27	175.55 (18)	C21—C22—N22—O221	−29.5 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N4^{i}	0.88	2.14	3.002 (3)	168
C3—H3···O7^{ii}	0.95	2.46	3.371 (3)	161
C5—H5···O222^{iii}	0.95	2.35	3.175 (3)	145
C24—H24···O221^{iv}	0.95	2.47	3.327 (3)	151

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

All H atoms were located in difference maps, and then treated as riding atoms, with C—H = 0.95 Å, N—H = 0.88 Å and U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

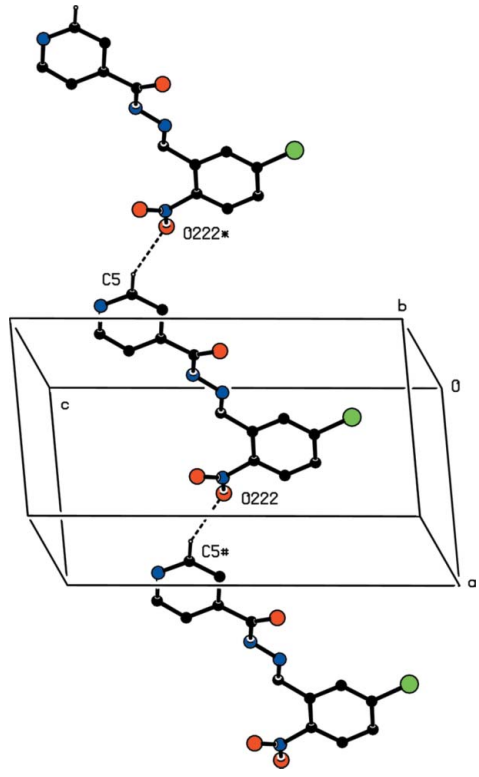


Figure 5
Part of the crystal structure of compound (I), showing the formation of a $C(12)$ chain along [1$\bar{1}$0] built from C—H···O(nitro) hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-1+x, 1+y, z)$ and $(1+x, -1+y, z)$, respectively.

X-ray data were collected at the EPSRC National Crystallography Service, University of Southampton, England. The authors thank the staff of the Service for all their help and advice. JLW thanks CNPq for financial support.

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supporting information

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Crystal data

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Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.0597$ (2) Å
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$c = 15.4798$ (6) Å
$\beta = 97.383$ (2)°
$V = 1296.63$ (8) Å^3
$Z = 4$
$F(000) = 624$
$D_x = 1.561$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2980 reflections
$\theta = 2.4$–27.5°
$\mu = 0.31$ mm^{-1}
$T = 120$ K
Lath, colourless
0.34 × 0.16 × 0.08 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.916$, $T_{max} = 0.976$
17385 measured reflections
2980 independent reflections
2132 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.4°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 13$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.143$
$S = 1.09$
2980 reflections
190 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
$w = 1/[\sigma^2(F_o^2) + (0.0817P)^2 + 0.135P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.0301 (3)	0.7986 (2)	0.63712 (13)	0.0170 (5)
C2	0.0839 (3)	0.7718 (2)	0.72369 (13)	0.0182 (5)
C3	0.0234 (3)	0.8436 (2)	0.78804 (14)	0.0201 (5)
N4	−0.0852 (2)	0.93930 (19)	0.77059 (12)	0.0212 (4)
C5	−0.1344 (3)	0.9650 (2)	0.68648 (15)	0.0237 (5)
C6	−0.0799 (3)	0.8991 (2)	0.61819 (14)	0.0206 (5)
C7	0.0889 (3)	0.7284 (2)	0.56203 (13)	0.0188 (5)
O7	0.0865 (2)	0.77907 (16)	0.49088 (10)	0.0298 (4)
N1	0.1468 (2)	0.60745 (16)	0.57975 (11)	0.0179 (4)
N2	0.2145 (2)	0.54538 (17)	0.51433 (11)	0.0186 (4)
C27	0.2790 (2)	0.4353 (2)	0.53226 (13)	0.0184 (5)
C21	0.3495 (2)	0.3683 (2)	0.46136 (13)	0.0162 (4)
C22	0.4603 (3)	0.2650 (2)	0.47262 (13)	0.0174 (5)
N22	0.5337 (2)	0.22436 (19)	0.56006 (12)	0.0222 (4)
O221	0.55542 (19)	0.30530 (16)	0.61789 (10)	0.0272 (4)
O222	0.5726 (2)	0.11140 (16)	0.57015 (11)	0.0324 (4)
C23	0.5128 (3)	0.1994 (2)	0.40315 (14)	0.0200 (5)
C24	0.4612 (3)	0.2393 (2)	0.31871 (14)	0.0208 (5)
C25	0.3551 (2)	0.3436 (2)	0.30634 (13)	0.0192 (5)
Cl25	0.28646 (7)	0.39720 (6)	0.20175 (3)	0.0280 (2)
C26	0.2974 (3)	0.4059 (2)	0.37533 (13)	0.0178 (5)
H2	0.1616	0.7048	0.7389	0.022*
H3	0.0609	0.8239	0.8472	0.024*
H5	−0.2116	1.0328	0.6729	0.028*
H6	−0.1171	0.9223	0.5596	0.025*
H1	0.1352	0.5678	0.6287	0.022*
H27	0.2814	0.3985	0.5885	0.022*
H23	0.5839	0.1272	0.4135	0.024*
H24	0.4976	0.1964	0.2705	0.025*
H26	0.2214	0.4750	0.3643	0.021*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0200 (10)	0.0147 (11)	0.0167 (11)	−0.0042 (9)	0.0039 (8)	−0.0017 (8)
C2	0.0241 (11)	0.0135 (11)	0.0172 (11)	−0.0003 (9)	0.0025 (9)	0.0003 (9)
C3	0.0263 (11)	0.0186 (12)	0.0152 (10)	−0.0041 (10)	0.0017 (9)	0.0000 (9)
N4	0.0221 (9)	0.0224 (10)	0.0190 (10)	−0.0006 (8)	0.0022 (7)	−0.0066 (8)
C5	0.0239 (11)	0.0231 (13)	0.0227 (12)	0.0051 (10)	−0.0028 (9)	−0.0062 (10)
C6	0.0226 (11)	0.0205 (12)	0.0173 (11)	−0.0010 (9)	−0.0025 (9)	−0.0027 (9)
C7	0.0217 (11)	0.0186 (12)	0.0157 (11)	−0.0025 (9)	0.0011 (8)	−0.0007 (9)
O7	0.0481 (11)	0.0256 (9)	0.0169 (8)	0.0077 (8)	0.0085 (7)	0.0031 (7)
N1	0.0230 (9)	0.0185 (10)	0.0133 (9)	0.0005 (8)	0.0058 (7)	−0.0006 (7)
N2	0.0208 (9)	0.0190 (10)	0.0165 (9)	−0.0006 (8)	0.0049 (7)	−0.0043 (8)
C27	0.0205 (11)	0.0206 (12)	0.0146 (10)	−0.0028 (9)	0.0035 (8)	−0.0010 (9)

C21	0.0167 (10)	0.0162 (11)	0.0158 (10)	−0.0027 (9)	0.0023 (8)	−0.0009 (8)
C22	0.0185 (10)	0.0184 (11)	0.0150 (10)	−0.0031 (9)	0.0009 (8)	0.0015 (9)
N22	0.0203 (9)	0.0286 (12)	0.0180 (9)	0.0000 (8)	0.0034 (8)	0.0035 (9)
O221	0.0276 (9)	0.0361 (10)	0.0174 (8)	−0.0046 (7)	0.0013 (7)	−0.0014 (7)
O222	0.0414 (10)	0.0277 (10)	0.0281 (10)	0.0133 (8)	0.0039 (8)	0.0102 (7)
C23	0.0193 (11)	0.0182 (12)	0.0227 (12)	0.0018 (9)	0.0034 (9)	−0.0017 (9)
C24	0.0226 (11)	0.0234 (12)	0.0170 (11)	0.0015 (9)	0.0052 (9)	−0.0031 (9)
C25	0.0198 (11)	0.0225 (12)	0.0150 (10)	−0.0019 (9)	0.0012 (8)	0.0015 (9)
Cl25	0.0349 (3)	0.0344 (4)	0.0150 (3)	0.0088 (3)	0.0045 (2)	0.0037 (2)
C26	0.0180 (10)	0.0170 (12)	0.0183 (11)	0.0012 (9)	0.0023 (8)	0.0006 (9)

Geometric parameters (Å, º)

C1—C2	1.383 (3)	C27—C21	1.477 (3)
C1—C6	1.384 (3)	C27—H27	0.95
C1—C7	1.503 (3)	C21—C22	1.400 (3)
C2—C3	1.386 (3)	C21—C26	1.400 (3)
C2—H2	0.95	C22—C23	1.387 (3)
C3—N4	1.336 (3)	C22—N22	1.469 (3)
C3—H3	0.95	N22—O221	1.229 (2)
N4—C5	1.339 (3)	N22—O222	1.229 (2)
C5—C6	1.380 (3)	C23—C24	1.385 (3)
C5—H5	0.95	C23—H23	0.95
C6—H6	0.95	C24—C25	1.386 (3)
C7—O7	1.221 (3)	C24—H24	0.95
C7—N1	1.366 (3)	C25—C26	1.382 (3)
N1—N2	1.374 (2)	C25—Cl25	1.736 (2)
N1—H1	0.88	C26—H26	0.95
N2—C27	1.281 (3)		
C2—C1—C6	118.19 (19)	N2—C27—H27	121.6
C2—C1—C7	123.99 (19)	C21—C27—H27	121.6
C6—C1—C7	117.77 (19)	C22—C21—C26	116.40 (19)
C1—C2—C3	119.4 (2)	C22—C21—C27	125.13 (19)
C1—C2—H2	120.3	C26—C21—C27	118.42 (18)
C3—C2—H2	120.3	C23—C22—C21	122.67 (19)
N4—C3—C2	123.0 (2)	C23—C22—N22	116.36 (18)
N4—C3—H3	118.5	C21—C22—N22	120.91 (18)
C2—C3—H3	118.5	O221—N22—O222	124.18 (19)
C3—N4—C5	116.87 (18)	O221—N22—C22	118.29 (18)
N4—C5—C6	124.1 (2)	O222—N22—C22	117.52 (19)
N4—C5—H5	117.9	C24—C23—C22	119.8 (2)
C6—C5—H5	117.9	C24—C23—H23	120.1
C5—C6—C1	118.4 (2)	C22—C23—H23	120.1
C5—C6—H6	120.8	C23—C24—C25	118.30 (19)
C1—C6—H6	120.8	C23—C24—H24	120.9
O7—C7—N1	123.4 (2)	C25—C24—H24	120.9
O7—C7—C1	121.0 (2)	C26—C25—C24	121.9 (2)

N1—C7—C1	115.62 (18)	C26—C25—Cl25	117.99 (17)
C7—N1—N2	116.68 (17)	C24—C25—Cl25	120.07 (16)
C7—N1—H1	122.6	C25—C26—C21	120.81 (19)
N2—N1—H1	120.5	C25—C26—H26	119.6
C27—N2—N1	117.08 (18)	C21—C26—H26	119.6
N2—C27—C21	116.84 (19)		

C6—C1—C2—C3	1.6 (3)	C26—C21—C22—C23	−2.1 (3)
C7—C1—C2—C3	179.1 (2)	C27—C21—C22—C23	175.0 (2)
C1—C2—C3—N4	−0.3 (3)	C26—C21—C22—N22	174.93 (18)
C2—C3—N4—C5	−0.5 (3)	C27—C21—C22—N22	−8.0 (3)
C3—N4—C5—C6	0.0 (3)	C23—C22—N22—O221	147.72 (19)
N4—C5—C6—C1	1.2 (3)	C21—C22—N22—O221	−29.5 (3)
C2—C1—C6—C5	−2.0 (3)	C23—C22—N22—O222	−30.9 (3)
C7—C1—C6—C5	−179.66 (19)	C21—C22—N22—O222	151.9 (2)
C2—C1—C7—O7	−154.4 (2)	C21—C22—C23—C24	3.0 (3)
C6—C1—C7—O7	23.1 (3)	N22—C22—C23—C24	−174.15 (19)
C2—C1—C7—N1	24.3 (3)	C22—C23—C24—C25	−1.2 (3)
C1—C7—N1—N2	−174.60 (17)	C23—C24—C25—C26	−1.5 (3)
C7—N1—N2—C27	175.55 (18)	C23—C24—C25—Cl25	−179.84 (16)
N1—N2—C27—C21	179.18 (16)	C24—C25—C26—C21	2.4 (3)
N2—C27—C21—C22	163.1 (2)	Cl25—C25—C26—C21	−179.24 (16)
C6—C1—C7—N1	−158.12 (18)	C22—C21—C26—C25	−0.6 (3)
O7—C7—N1—N2	4.2 (3)	C27—C21—C26—C25	−177.83 (19)
N2—C27—C21—C26	−19.9 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N4^{i}	0.88	2.14	3.002 (3)	168
C3—H3···O7^{ii}	0.95	2.46	3.371 (3)	161
C5—H5···O222^{iii}	0.95	2.35	3.175 (3)	145
C24—H24···O221^{iv}	0.95	2.47	3.327 (3)	151

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