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N-(5-Chloro-2-nitrobenzoyl)-*N*′-isonicotinoylhydrazine: a three-dimensional framework containing four types of hydrogen bond

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.008 Å
R factor = 0.051
wR factor = 0.102
Data-to-parameter ratio = 8.5

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

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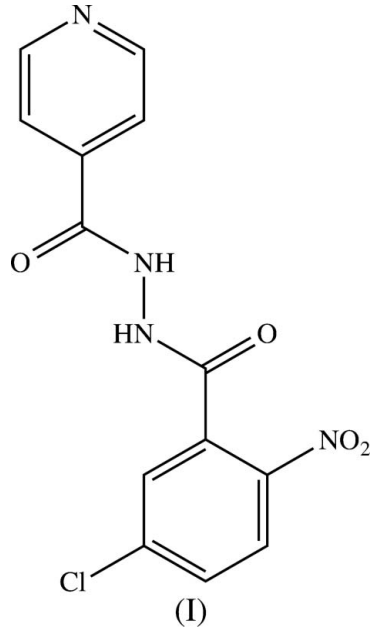
The title compound, $C_{13}H_9ClN_4O_4$, crystallizes with $Z' = 2$, and the two molecules have markedly different conformations. The molecules are linked into a three-dimensional framework by a combination of N—H···O, N—H···N, C—H···O and C—H···N hydrogen bonds.

Comment

We have recently reported the supramolecular structures of 4-[(4-chloro-3-nitrobenzoyl)hydrazinocarbonyl]pyridinium chloride and *N*-3,5-dinitrobenzoyl-*N*′-isonicotinoylhydrazine (Vasconcelos *et al.*, 2006). These compounds were prepared as part of a programme to test bactericidal activities, especially towards the Mycobacterium tuberculosis bacterium. Both compounds were found to exhibit significant activities (Junior *et al.*, 2006). The structure of a third member of this series, *N*-(5-chloro-2-nitrobenzoyl)-*N*′-isonicotinoylhydrazine, (I) (Fig. 1), is reported here.



(I)

Compound (I) crystallizes with $Z' = 2$ in space group *Fdd*2, with a unit cell of markedly tabular shape, as shown by the axial ratios *a*:*b*:*c* of 1.958:1:0.134, so that the ratio *c*/*a* is only 0.0686. The two independent molecules adopt significantly different conformations, as shown by the leading torsion angles (Table 1).

The molecules of (I) are linked by a combination of four types of hydrogen bond (Table 2) to form a fairly complex three-dimensional framework, whose formation is nonetheless

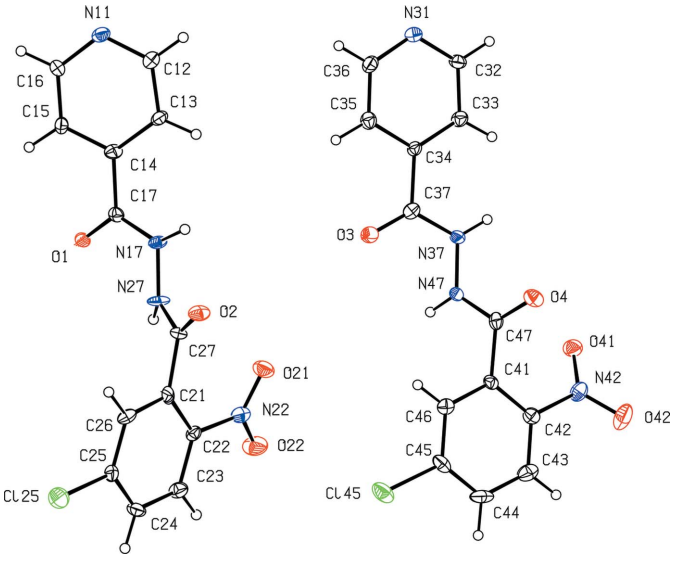


Figure 1
The structures of the two independent molecules of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

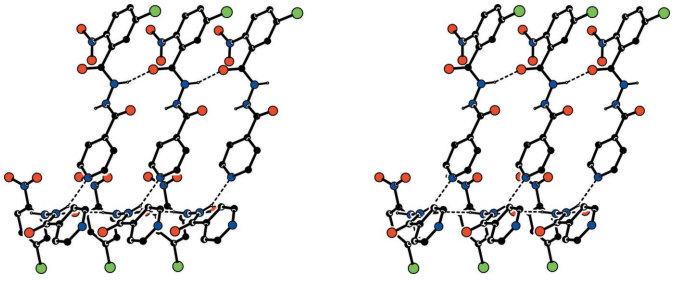


Figure 2
A stereoscopic view of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded (dashed lines) chain of $R_4^4(26)$ rings generated by translation along [001]. For the sake of clarity, the unit-cell outline and H atoms bonded to C atoms have been omitted.

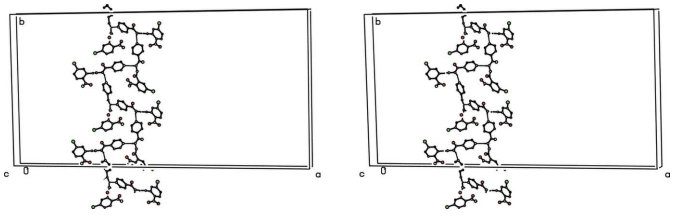


Figure 3
A stereoscopic view of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded (dashed lines) $C_2^2(14)$ chain along [01$\bar{1}$]. For the sake of clarity, H atoms bonded to C atoms have been omitted.

readily analysed in terms of three distinct substructures. Within the selected asymmetric unit, the two molecules are linked by an N—H···N hydrogen bond, possibly weakly augmented by a C—H···N hydrogen bond, and these bimolecular units are linked by two N—H···O hydrogen bonds into

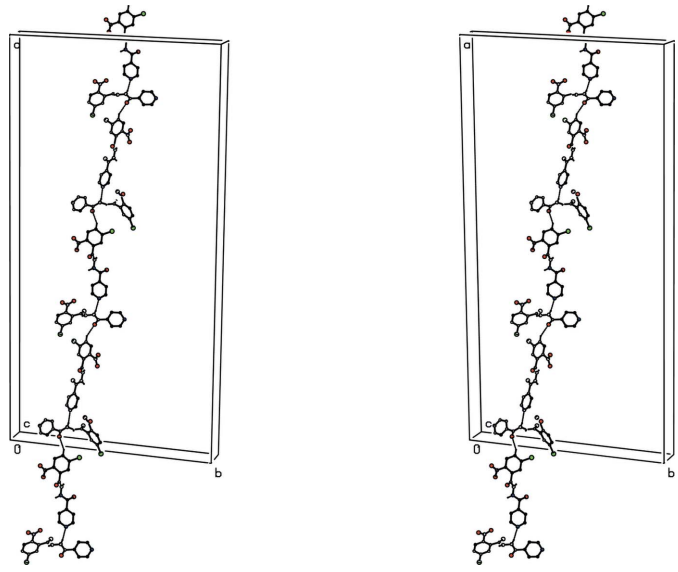


Figure 4
A stereoscopic view of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded (dashed lines) $C_2^2(17)$ chain along [107]. For the sake of clarity, H atoms bonded to C atoms but not involved in the motif shown have been omitted.

a chain of edge-fused $R_4^4(26)$ (Bernstein *et al.*, 1995) rings generated by translation along the [001] direction (Fig. 2). In the second substructure, the bimolecular units are linked by the second N—H···N hydrogen bond, in which atom N37 at (x, y, z) acts as donor to atom N11 at $(\frac{3}{4} - x, -\frac{1}{4} + y, \frac{1}{4} + z)$, so forming a $C_2^2(14)$ chain running parallel to the [01$\bar{1}$] direction and generated by the *d*-glide plane at $x = 0.375$ (Fig. 3). This chain may be weakly reinforced by a second C—H···N hydrogen bond. In the final substructure, atom C44 at (x, y, z) acts as hydrogen-bond donor to atom O1 at $(\frac{1}{4} + x, \frac{3}{4} - y, \frac{7}{4} + z)$, so forming a $C_2^2(17)$ chain running parallel to the [107] direction and generated by the *d*-glide plane at $y = 0.375$ (Fig. 4). The combination of the [001], [01$\bar{1}$] and [107] chains is sufficient to generate a single three-dimensional framework structure.

Experimental

5-Chloro-2-nitrobenzoyl chloride was prepared from the corresponding carboxylic acid (1 g) using thionyl chloride (3 molar equivalents) and *N*,*N*-dimethylformamide (0.1 equivalent) in dichloromethane (20 ml) at ambient temperature with stirring and in a dinitrogen atmosphere. After 6 h, the excess of thionyl chloride was removed under reduced pressure to leave the crude acyl chloride, which was used without purification in a reaction with isonicotinoylhydrazine (isoniazid, 1 molar equivalent) in refluxing tetrahydrofuran (20 ml). The mixture was then cooled and the solvent removed under reduced pressure. The crude solid product, (I), was purified by column chromatography on silica gel, using as eluant a hexane–ethyl acetate gradient. Recrystallization from ethanol gave crystals suitable for single-crystal X-ray diffraction [yield 75%, m.p. 543–545 K (decomposition)]. GC/MS *m*/*z* 320 $[M]^+$.

Crystal data

$C_{13}H_9ClN_4O_4$
M_r = 320.69
Orthorhombic, *Fdd*2
a = 67.786 (4) Å
b = 34.613 (2) Å
c = 4.6486 (2) Å
V = 10906.9 (10) Å^3
Z = 32
D_x = 1.562 Mg m^{-3}
Mo *Kα* radiation
μ = 0.31 mm^{-1}
T = 120 (2) K
Needle, colourless
0.20 × 0.04 × 0.02 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.955, T_{max} = 0.994
16346 measured reflections
3383 independent reflections
2656 reflections with $I > 2\sigma(I)$
R_{int} = 0.104
θ_{max} = 22.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.102
S = 1.05
3383 reflections
397 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 24.7113P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), with 1344 Friedel pairs
Flack parameter: 0.08 (10)

Table 1
Selected torsion angles (°).

C12—C13—C14—C17	−179.9 (5)	C32—C33—C34—C37	−179.6 (5)
C13—C14—C17—N17	27.6 (7)	C33—C34—C37—N37	2.7 (8)
C14—C17—N17—N27	176.5 (4)	C34—C37—N37—N47	176.3 (4)
C17—N17—N27—C27	−149.8 (5)	C37—N37—N47—C47	−128.3 (5)
N17—N27—C27—C21	169.8 (4)	N37—N47—C47—C41	−179.6 (4)
N27—C27—C21—C22	73.2 (7)	N47—C47—C41—C42	120.7 (5)
C21—C22—N22—O21	14.6 (7)	C41—C42—N42—O41	−32.2 (7)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N17—H17···N31	0.88	2.22	3.039 (6)	156
C13—H13···N31	0.95	2.56	3.448 (7)	156
N27—H27···O2^{i}	0.88	1.86	2.737 (6)	171
N47—H47···O4^{ii}	0.88	1.93	2.777 (6)	160
N37—H37···N11^{iii}	0.88	2.07	2.908 (6)	159
C33—H33···N11^{iii}	0.95	2.55	3.476 (7)	165
C44—H44···O1^{iv}	0.95	2.30	3.164 (7)	151

Symmetry codes: (i) $x, y, z-1$; (ii) $x, y, z+1$; (iii) $-x+\frac{3}{4}, y-\frac{1}{4}, z+\frac{1}{4}$; (iv) $x+\frac{1}{4}, -y+\frac{3}{4}, z+\frac{7}{4}$.

All H atoms were located in difference maps and then treated as riding, with C—H = 0.95 Å and N—H = 0.88 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N). The unit-cell dimensions posed some difficulties during the data collection, and there was effectively no scattering beyond θ = 22°.

Data collection: *COLLECT* (Nonius, 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).

The X-ray data were collected at the EPSRC National Crystallograpic 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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N-(5-Chloro-2-nitrobenzoyl)-N′-isonicotinoylhydrazine

Crystal data

$C_{13}H_9ClN_4O_4$
$M_r = 320.69$
Orthorhombic, *Fdd*2
Hall symbol: F 2 -2d
$a = 67.786$ (4) Å
$b = 34.613$ (2) Å
$c = 4.6486$ (2) Å
$V = 10906.9$ (10) Å^3
$Z = 32$
$F(000) = 5248$
$D_x = 1.562$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3383 reflections
$\theta = 3.0$–$22.5°$
$\mu = 0.31$ mm^{-1}
$T = 120$ K
Needle, colourless
0.20 × 0.04 × 0.02 mm

Data collection

Bruker Nonius KappaCCD area-detector 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)
$T_{min} = 0.955$, $T_{max} = 0.994$
16346 measured reflections
3383 independent reflections
2656 reflections with $I > 2\sigma(I)$
$R_{int} = 0.104$
$\theta_{max} = 22.5°$, $\theta_{min} = 3.0°$
$h = -72 \rightarrow 72$
$k = -29 \rightarrow 36$
$l = -4 \rightarrow 4$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.102$
$S = 1.05$
3383 reflections
397 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
$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 24.7113P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Absolute structure: Flack (1983), with 1344 Friedel pairs
Absolute structure parameter: 0.08 (10)

Special details

Experimental. GC/MS m/z 320 $[M]^+$; ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 11.48 (1H, s, NH), 11.13 (1H, s, NH), 8.99 (2H, d, J = 5.0 Hz), 8.94 (1H, d, J = 4.5 Hz), 8.20 (1H, s), 8.17 (2H, d, J = 5.0 Hz), 8.11 (1H, d, J = 4.5 Hz); ^{13}C NMR (DMSO-d_6, δ, p.p.m.): 163.1, 162.8, 148.0, 146.8, 145.6, 142.6, 138.2, 131.5, 129.2, 126.5, 123.2; IR (KBr disk, ν, cm^{-1}) 3091 (NH), 1703 (CO), 1668 (CO).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N11	0.32274 (6)	0.54404 (12)	0.6076 (9)	0.0274 (12)
C12	0.33700 (8)	0.51929 (15)	0.6811 (13)	0.0301 (14)
C13	0.33787 (8)	0.48147 (15)	0.5828 (11)	0.0267 (15)
C14	0.32318 (8)	0.46834 (15)	0.4031 (11)	0.0232 (13)
C15	0.30859 (8)	0.49394 (15)	0.3220 (11)	0.0244 (14)
C16	0.30883 (8)	0.53063 (15)	0.4320 (12)	0.0271 (14)
C17	0.32230 (7)	0.42828 (16)	0.2821 (13)	0.0217 (13)
O1	0.31415 (5)	0.42119 (10)	0.0530 (8)	0.0289 (9)
N17	0.33095 (6)	0.40022 (11)	0.4385 (9)	0.0243 (11)
N27	0.32920 (6)	0.36286 (11)	0.3350 (9)	0.0278 (11)
C27	0.32892 (7)	0.33276 (14)	0.5187 (13)	0.0217 (13)
O2	0.33100 (6)	0.33659 (10)	0.7804 (8)	0.0321 (10)
C21	0.32351 (7)	0.29506 (14)	0.3875 (11)	0.0203 (13)
C22	0.33456 (7)	0.27172 (14)	0.2074 (11)	0.0218 (13)
N22	0.35514 (7)	0.28219 (14)	0.1378 (11)	0.0339 (13)
O21	0.36322 (5)	0.30690 (11)	0.2866 (9)	0.0383 (10)
O22	0.36326 (6)	0.26550 (12)	−0.0632 (11)	0.0497 (12)
C23	0.32756 (8)	0.23772 (16)	0.0876 (12)	0.0303 (15)
C24	0.30871 (8)	0.22605 (15)	0.1591 (12)	0.0313 (15)
C25	0.29757 (7)	0.24784 (16)	0.3449 (12)	0.0266 (14)
Cl25	0.27397 (2)	0.23329 (4)	0.4317 (4)	0.0492 (5)
C26	0.30482 (8)	0.28213 (15)	0.4576 (12)	0.0262 (14)
N31	0.36416 (6)	0.40581 (13)	0.8757 (9)	0.0263 (11)
C32	0.37569 (8)	0.37612 (15)	0.8074 (12)	0.0279 (14)
C33	0.39446 (8)	0.37069 (15)	0.9265 (12)	0.0273 (14)
C34	0.40144 (7)	0.39704 (15)	1.1202 (12)	0.0215 (13)
C35	0.38935 (8)	0.42736 (15)	1.1948 (12)	0.0277 (14)
C36	0.37124 (8)	0.43104 (16)	1.0637 (12)	0.0291 (14)
C37	0.42157 (7)	0.39452 (16)	1.2631 (13)	0.0251 (14)
O3	0.42663 (5)	0.41836 (11)	1.4393 (9)	0.0355 (10)
N37	0.43315 (6)	0.36508 (12)	1.1805 (9)	0.0260 (11)
N47	0.45204 (6)	0.36366 (11)	1.2963 (10)	0.0233 (11)
C47	0.46750 (8)	0.36012 (14)	1.1193 (14)	0.0242 (14)
O4	0.46603 (5)	0.35841 (10)	0.8564 (8)	0.0332 (10)
C41	0.48709 (7)	0.35861 (15)	1.2688 (11)	0.0221 (13)
C42	0.49991 (8)	0.32735 (16)	1.2428 (11)	0.0274 (14)
N42	0.49372 (8)	0.29281 (13)	1.0876 (10)	0.0341 (13)
O41	0.47619 (6)	0.28373 (10)	1.0942 (8)	0.0366 (10)
O42	0.50662 (6)	0.27417 (12)	0.9587 (11)	0.0571 (13)
C43	0.51840 (8)	0.32683 (18)	1.3700 (12)	0.0380 (16)

C44	0.52428 (8)	0.35888 (19)	1.5291 (14)	0.0411 (17)
C45	0.51170 (8)	0.38943 (16)	1.5572 (11)	0.0314 (15)
Cl45	0.51843 (2)	0.42921 (5)	1.7631 (3)	0.0468 (5)
C46	0.49313 (7)	0.39002 (15)	1.4267 (11)	0.0240 (13)
H12	0.3471	0.5280	0.8073	0.036*
H13	0.3484	0.4650	0.6384	0.032*
H15	0.2985	0.4862	0.1918	0.029*
H16	0.2984	0.5476	0.3797	0.033*
H17	0.3375	0.4015	0.6014	0.029*
H27	0.3307	0.3562	0.1536	0.033*
H23	0.3355	0.2229	−0.0397	0.036*
H24	0.3035	0.2029	0.0797	0.038*
H26	0.2968	0.2969	0.5846	0.031*
H32	0.3710	0.3578	0.6717	0.034*
H33	0.4022	0.3490	0.8733	0.033*
H35	0.3935	0.4456	1.3354	0.033*
H36	0.3634	0.4529	1.1105	0.035*
H37	0.4291	0.3472	1.0599	0.031*
H47	0.4537	0.3648	1.4838	0.028*
H43	0.5269	0.3051	1.3491	0.046*
H44	0.5369	0.3595	1.6173	0.049*
H46	0.4848	0.4119	1.4469	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N11	0.027 (3)	0.018 (3)	0.038 (3)	0.000 (2)	0.007 (2)	0.001 (2)
C12	0.028 (3)	0.027 (3)	0.036 (4)	0.005 (3)	−0.001 (3)	−0.002 (3)
C13	0.034 (4)	0.019 (3)	0.028 (4)	0.008 (3)	−0.006 (3)	−0.003 (3)
C14	0.032 (3)	0.023 (3)	0.015 (3)	0.002 (3)	0.002 (3)	−0.006 (3)
C15	0.020 (3)	0.027 (3)	0.027 (3)	0.004 (3)	−0.005 (3)	−0.001 (3)
C16	0.022 (3)	0.026 (4)	0.034 (4)	−0.002 (3)	−0.006 (3)	−0.003 (3)
C17	0.017 (3)	0.022 (3)	0.025 (3)	−0.004 (3)	0.005 (3)	−0.001 (3)
O1	0.033 (2)	0.023 (2)	0.030 (2)	0.0020 (18)	−0.011 (2)	−0.0064 (18)
N17	0.041 (3)	0.016 (3)	0.016 (2)	0.003 (2)	−0.005 (2)	−0.003 (2)
N27	0.054 (3)	0.011 (3)	0.019 (3)	−0.002 (2)	0.000 (2)	−0.006 (2)
C27	0.026 (3)	0.015 (3)	0.025 (4)	−0.005 (3)	−0.001 (3)	−0.004 (3)
O2	0.054 (3)	0.025 (2)	0.017 (2)	0.001 (2)	−0.005 (2)	−0.0051 (19)
C21	0.021 (3)	0.021 (3)	0.019 (3)	0.001 (3)	−0.005 (3)	0.004 (3)
C22	0.021 (3)	0.018 (3)	0.026 (3)	0.002 (3)	0.003 (3)	0.004 (3)
N22	0.036 (3)	0.023 (3)	0.043 (3)	0.001 (3)	0.000 (3)	−0.003 (3)
O21	0.035 (2)	0.031 (2)	0.049 (3)	−0.011 (2)	0.004 (2)	−0.006 (2)
O22	0.043 (3)	0.042 (3)	0.064 (3)	−0.001 (2)	0.023 (3)	−0.020 (3)
C23	0.032 (4)	0.024 (3)	0.034 (4)	0.002 (3)	0.006 (3)	−0.003 (3)
C24	0.037 (4)	0.020 (3)	0.037 (4)	−0.008 (3)	−0.009 (3)	−0.002 (3)
C25	0.018 (3)	0.025 (3)	0.037 (4)	0.001 (3)	−0.002 (3)	0.001 (3)
Cl25	0.0278 (8)	0.0388 (9)	0.0809 (13)	−0.0087 (7)	0.0070 (9)	0.0028 (9)
C26	0.034 (4)	0.020 (3)	0.025 (3)	0.007 (3)	0.007 (3)	−0.002 (3)

N31	0.023 (3)	0.027 (3)	0.029 (3)	0.001 (2)	−0.002 (2)	0.003 (2)
C32	0.025 (3)	0.025 (3)	0.033 (4)	0.002 (3)	−0.010 (3)	−0.002 (3)
C33	0.025 (3)	0.020 (3)	0.036 (4)	0.002 (3)	−0.002 (3)	−0.001 (3)
C34	0.019 (3)	0.018 (3)	0.027 (3)	0.000 (3)	0.001 (3)	−0.002 (3)
C35	0.032 (3)	0.023 (3)	0.029 (4)	0.001 (3)	0.000 (3)	−0.001 (3)
C36	0.027 (3)	0.034 (4)	0.026 (3)	0.007 (3)	0.003 (3)	−0.001 (3)
C37	0.023 (3)	0.024 (4)	0.028 (4)	−0.001 (3)	0.005 (3)	0.005 (3)
O3	0.031 (2)	0.036 (2)	0.040 (2)	0.0066 (19)	−0.008 (2)	−0.019 (2)
N37	0.021 (3)	0.023 (3)	0.034 (3)	0.001 (2)	−0.008 (3)	−0.009 (2)
N47	0.023 (3)	0.026 (3)	0.021 (3)	0.004 (2)	−0.003 (2)	−0.003 (2)
C47	0.032 (4)	0.015 (3)	0.026 (4)	0.001 (3)	0.001 (3)	−0.002 (3)
O4	0.036 (2)	0.037 (3)	0.027 (3)	−0.0037 (19)	−0.003 (2)	0.0007 (19)
C41	0.025 (3)	0.024 (3)	0.017 (3)	0.001 (3)	−0.002 (3)	0.001 (3)
C42	0.027 (3)	0.027 (3)	0.028 (3)	−0.004 (3)	0.000 (3)	0.001 (3)
N42	0.037 (3)	0.024 (3)	0.042 (3)	0.009 (3)	0.002 (3)	0.001 (2)
O41	0.032 (2)	0.030 (2)	0.047 (3)	0.002 (2)	−0.007 (2)	−0.003 (2)
O42	0.054 (3)	0.046 (3)	0.071 (3)	0.012 (2)	0.019 (3)	−0.013 (3)
C43	0.030 (4)	0.043 (4)	0.041 (4)	0.009 (3)	−0.001 (3)	0.008 (3)
C44	0.019 (3)	0.062 (5)	0.042 (4)	−0.001 (4)	−0.009 (3)	0.009 (4)
C45	0.034 (4)	0.037 (4)	0.023 (3)	−0.013 (3)	−0.003 (3)	−0.002 (3)
Cl45	0.0420 (9)	0.0615 (11)	0.0368 (9)	−0.0228 (9)	−0.0024 (8)	−0.0074 (8)
C46	0.022 (3)	0.026 (3)	0.024 (3)	−0.005 (3)	0.005 (3)	0.006 (3)

Geometric parameters (Å, º)

N11—C16	1.331 (6)	N31—C36	1.325 (6)
N11—C12	1.336 (6)	N31—C32	1.329 (6)
C12—C13	1.388 (7)	C32—C33	1.400 (7)
C12—H12	0.95	C32—H32	0.95
C13—C14	1.377 (7)	C33—C34	1.366 (7)
C13—H13	0.95	C33—H33	0.95
C14—C15	1.380 (7)	C34—C35	1.376 (7)
C14—C17	1.498 (7)	C34—C37	1.520 (7)
C15—C16	1.369 (7)	C35—C36	1.377 (7)
C15—H15	0.95	C35—H35	0.95
C16—H16	0.95	C36—H36	0.95
C17—O1	1.224 (6)	C37—O3	1.212 (6)
C17—N17	1.347 (6)	C37—N37	1.343 (6)
N17—N27	1.385 (5)	N37—N47	1.389 (5)
N17—H17	0.88	N37—H37	0.88
N27—C27	1.347 (6)	N47—C47	1.338 (6)
N27—H27	0.88	N47—H47	0.88
C27—O2	1.232 (6)	C47—O4	1.227 (6)
C27—C21	1.486 (7)	C47—C41	1.500 (7)
C21—C26	1.382 (7)	C41—C46	1.374 (7)
C21—C22	1.384 (7)	C41—C42	1.393 (7)
C22—C23	1.385 (7)	C42—C43	1.386 (7)
C22—N22	1.477 (6)	C42—N42	1.458 (7)

N22—O22	1.228 (6)	N42—O41	1.230 (5)
N22—O21	1.229 (5)	N42—O42	1.241 (6)
C23—C24	1.381 (7)	C43—C44	1.391 (8)
C23—H23	0.95	C43—H43	0.95
C24—C25	1.373 (7)	C44—C45	1.365 (7)
C24—H24	0.95	C44—H44	0.95
C25—C26	1.387 (7)	C45—C46	1.397 (7)
C25—Cl25	1.725 (5)	C45—Cl45	1.738 (5)
C26—H26	0.95	C46—H46	0.95

C16—N11—C12	116.5 (5)	C36—N31—C32	117.0 (5)
N11—C12—C13	123.5 (5)	N31—C32—C33	122.9 (5)
N11—C12—H12	118.3	N31—C32—H32	118.5
C13—C12—H12	118.3	C33—C32—H32	118.5
C14—C13—C12	118.7 (5)	C34—C33—C32	119.1 (5)
C14—C13—H13	120.6	C34—C33—H33	120.5
C12—C13—H13	120.6	C32—C33—H33	120.5
C13—C14—C15	118.2 (5)	C33—C34—C35	118.0 (5)
C13—C14—C17	124.2 (5)	C33—C34—C37	124.1 (5)
C15—C14—C17	117.6 (5)	C35—C34—C37	117.9 (5)
C16—C15—C14	119.0 (5)	C34—C35—C36	119.4 (5)
C16—C15—H15	120.5	C34—C35—H35	120.3
C14—C15—H15	120.5	C36—C35—H35	120.3
N11—C16—C15	124.2 (5)	N31—C36—C35	123.6 (5)
N11—C16—H16	117.9	N31—C36—H36	118.2
C15—C16—H16	117.9	C35—C36—H36	118.2
O1—C17—N17	121.4 (5)	O3—C37—N37	123.0 (5)
O1—C17—C14	122.0 (5)	O3—C37—C34	120.7 (5)
N17—C17—C14	116.6 (5)	N37—C37—C34	116.3 (5)
C17—N17—N27	116.7 (4)	C37—N37—N47	117.1 (4)
C17—N17—H17	130.4	C37—N37—H37	122.2
N27—N17—H17	112.9	N47—N37—H37	120.8
C27—N27—N17	120.2 (4)	C47—N47—N37	119.1 (4)
C27—N27—H27	114.1	C47—N47—H47	120.7
N17—N27—H27	124.5	N37—N47—H47	120.2
O2—C27—N27	122.7 (5)	O4—C47—N47	123.6 (5)
O2—C27—C21	121.9 (5)	O4—C47—C41	122.1 (5)
N27—C27—C21	115.0 (5)	N47—C47—C41	114.3 (5)
C26—C21—C22	116.7 (5)	C46—C41—C42	118.3 (5)
C26—C21—C27	114.4 (5)	C46—C41—C47	119.0 (5)
C22—C21—C27	128.9 (5)	C42—C41—C47	122.6 (5)
C21—C22—C23	123.6 (5)	C43—C42—C41	122.5 (5)
C21—C22—N22	120.0 (5)	C43—C42—N42	117.4 (5)
C23—C22—N22	116.4 (5)	C41—C42—N42	120.0 (5)
O22—N22—O21	123.8 (5)	O41—N42—O42	124.1 (5)
O22—N22—C22	118.3 (5)	O41—N42—C42	118.4 (5)
O21—N22—C22	117.9 (5)	O42—N42—C42	117.5 (5)
C24—C23—C22	118.0 (5)	C42—C43—C44	118.4 (5)

C24—C23—H23	121.0	C42—C43—H43	120.8
C22—C23—H23	121.0	C44—C43—H43	120.8
C25—C24—C23	120.0 (5)	C45—C44—C43	119.3 (5)
C25—C24—H24	120.0	C45—C44—H44	120.3
C23—C24—H24	120.0	C43—C44—H44	120.3
C24—C25—C26	120.8 (5)	C44—C45—C46	122.2 (5)
C24—C25—Cl25	119.8 (4)	C44—C45—Cl45	120.2 (5)
C26—C25—Cl25	119.3 (4)	C46—C45—Cl45	117.6 (5)
C21—C26—C25	120.8 (5)	C41—C46—C45	119.3 (5)
C21—C26—H26	119.6	C41—C46—H46	120.4
C25—C26—H26	119.6	C45—C46—H46	120.4
C16—N11—C12—C13	0.4 (8)	C36—N31—C32—C33	0.6 (8)
N11—C12—C13—C14	−0.9 (8)	N31—C32—C33—C34	−0.5 (8)
C12—C13—C14—C15	2.0 (7)	C32—C33—C34—C35	1.6 (8)
C12—C13—C14—C17	−179.9 (5)	C32—C33—C34—C37	−179.6 (5)
C13—C14—C15—C16	−2.7 (7)	C33—C34—C35—C36	−2.9 (8)
C17—C14—C15—C16	179.1 (5)	C37—C34—C35—C36	178.3 (5)
C12—N11—C16—C15	−1.1 (8)	C32—N31—C36—C35	−2.0 (8)
C14—C15—C16—N11	2.3 (8)	C34—C35—C36—N31	3.2 (8)
C13—C14—C17—O1	−152.5 (5)	C33—C34—C37—O3	−178.0 (5)
C15—C14—C17—O1	25.6 (7)	C35—C34—C37—O3	0.8 (8)
C13—C14—C17—N17	27.6 (7)	C33—C34—C37—N37	2.7 (8)
C15—C14—C17—N17	−154.3 (5)	C35—C34—C37—N37	−178.5 (5)
O1—C17—N17—N27	−3.4 (7)	O3—C37—N37—N47	−3.0 (7)
C14—C17—N17—N27	176.5 (4)	C34—C37—N37—N47	176.3 (4)
C17—N17—N27—C27	−149.8 (5)	C37—N37—N47—C47	−128.3 (5)
N17—N27—C27—O2	−3.2 (8)	N37—N47—C47—O4	0.8 (8)
N17—N27—C27—C21	169.8 (4)	N37—N47—C47—C41	−179.6 (4)
O2—C27—C21—C26	66.3 (7)	O4—C47—C41—C46	117.0 (6)
N27—C27—C21—C26	−106.8 (5)	N47—C47—C41—C46	−62.6 (6)
O2—C27—C21—C22	−113.8 (6)	O4—C47—C41—C42	−59.7 (8)
N27—C27—C21—C22	73.2 (7)	N47—C47—C41—C42	120.7 (5)
C26—C21—C22—C23	2.9 (8)	C46—C41—C42—C43	0.1 (8)
C27—C21—C22—C23	−177.1 (5)	C47—C41—C42—C43	176.8 (5)
C26—C21—C22—N22	−175.9 (4)	C46—C41—C42—N42	177.4 (5)
C27—C21—C22—N22	4.1 (8)	C47—C41—C42—N42	−5.9 (8)
C21—C22—N22—O22	−166.1 (5)	C43—C42—N42—O41	145.2 (5)
C23—C22—N22—O22	15.0 (7)	C41—C42—N42—O41	−32.2 (7)
C21—C22—N22—O21	14.6 (7)	C43—C42—N42—O42	−34.2 (7)
C23—C22—N22—O21	−164.3 (5)	C41—C42—N42—O42	148.4 (5)
C21—C22—C23—C24	−1.9 (8)	C41—C42—C43—C44	−0.1 (8)
N22—C22—C23—C24	176.9 (5)	N42—C42—C43—C44	−177.4 (5)
C22—C23—C24—C25	−0.4 (8)	C42—C43—C44—C45	0.6 (8)
C23—C24—C25—C26	1.5 (8)	C43—C44—C45—C46	−1.2 (8)
C23—C24—C25—Cl25	179.6 (4)	C43—C44—C45—Cl45	178.2 (4)
C22—C21—C26—C25	−1.6 (7)	C42—C41—C46—C45	−0.6 (7)
C27—C21—C26—C25	178.3 (5)	C47—C41—C46—C45	−177.5 (5)

C24—C25—C26—C21	−0.5 (8)	C44—C45—C46—C41	1.2 (8)
Cl25—C25—C26—C21	−178.6 (4)	Cl45—C45—C46—C41	−178.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N17—H17···N31	0.88	2.22	3.039 (6)	156
C13—H13···N31	0.95	2.56	3.448 (7)	156
N27—H27···O2^{i}	0.88	1.86	2.737 (6)	171
N47—H47···O4^{ii}	0.88	1.93	2.777 (6)	160
N37—H37···N11^{iii}	0.88	2.07	2.908 (6)	159
C33—H33···N11^{iii}	0.95	2.55	3.476 (7)	165
C44—H44···O1^{iv}	0.95	2.30	3.164 (7)	151

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) *x*, *y*, *z*+1; (iii) −*x*+3/4, *y*−1/4, *z*+1/4; (iv) *x*+1/4, −*y*+3/4, *z*+7/4.