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7-Chloro-4-[(*E*)-(3-chlorobenzylidene)-hydrazinyl]-1λ^4-quinolinium 3-chlorobenzoate

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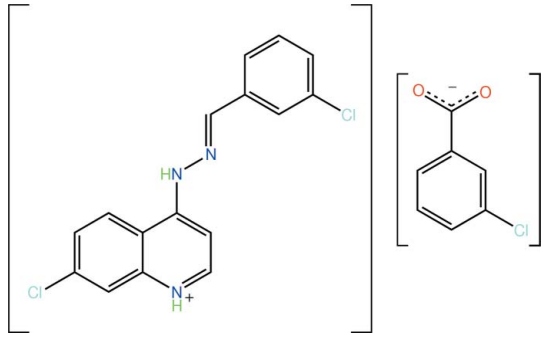
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.003 Å; R factor = 0.047; wR factor = 0.104; data-to-parameter ratio = 16.8.

The title salt, $C_{16}H_{12}Cl_2N_3^+\cdot C_7H_4ClO_2^-$, features a non-planar cation, the dihedral angle between the quinolinium and benzene residues being 18.98 (10)°. The cation adopts an *E* conformation about the C—N bond, and the amine group is oriented towards the quinolinium residue. In the crystal, N—H···O hydrogen bonds link two cations with two anions, forming a 20-membered $\{\cdots OCO\cdots HNC_3NH\}_2$ synthon. The dimeric units are connected into a linear supramolecular chain along [100] *via* π–π interactions [centroid–centroid distance = 3.5625 (13) Å].

Related literature

For background information on the pharmacological activity of quinoline derivatives, see: Elslager *et al.* (1969); Font *et al.* (1997); Kaminsky & Meltzer (1968); Musiol *et al.* (2006); Nakamura *et al.* (1999); Palmer *et al.* (1993); Ridley (2002); Sloboda *et al.* (1991); Tanenbaum & Tuffanelli (1980); Warshakoon *et al.* (2006). For recent studies into quinoline-based anti-malarials, see: Andrade *et al.* (2007); Cunico *et al.* (2006); da Silva *et al.* (2003); de Souza (2005). For a related crystallographic study on neutral species related to the title compound, see: Kaiser *et al.* (2009).



Experimental

Crystal data

$C_{16}H_{12}Cl_2N_3^+\cdot C_7H_4ClO_2^-$
M_r = 472.74
Triclinic, $P\overline{1}$
a = 8.8777 (2) Å
b = 10.7064 (3) Å
c = 11.9807 (3) Å
α = 112.5318 (12)°
β = 91.6382 (15)°
γ = 97.4362 (15)°
V = 1039.17 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.47 mm^{-1}
T = 120 K
0.06 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.922, T_{max} = 1.000
16836 measured reflections
4746 independent reflections
3949 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.104
S = 1.07
4746 reflections
283 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1n···O2^{i}	0.89 (3)	1.76 (3)	2.641 (3)	175 (3)
N2—H2n···O1^{ii}	0.88	2.00	2.809 (3)	152

Symmetry codes: (i) $x-1, y-1, z$; (ii) $-x+1, -y+1, -z+1$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2605).

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References

Andrade, A. A., Varotti, F. D., de Freitas, I. Q., de Souza, M. V. N., Vasconcelos, T. R. A., Boechat, N. & Krettli, A. U. (2007). *Eur. J. Pharm.* **558**, 194–198.

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Cunico, W., Cechinel, C. A., Bonacorso, H. G., Martins, G. M. A. P., Zanetta, N., de Souza, M. V. N., Freitas, I. Q., Soares, R. P. P. & Krettli, A. U. (2006). *Bioorg. Med. Chem. Lett.* **16**, 649–653.

Elslager, E. F., Tendick, F. H. & Werbel, L. M. (1969). *J. Med. Chem.* **12**, 600–607.

Font, M., Monge, A., Ruiz, I. & Heras, B. (1997). *Drug. Des. Disc.* **14**, 259–272.

Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Kaiser, C. R., Pais, K. C., de Souza, M. V. N., Wardell, J. L., Wardell, S. M. S. V. & Tiekink, E. R. T. (2009). *CrystEngComm*, **11**, 1133–1140.

Kaminsky, D. & Meltzer, R. I. (1968). *J. Med. Chem.* **11**, 160–163.

Musiol, R., Jampilek, J., Buchta, V., Silva, L., Halina, H., Podeszwa, B., Palka, A., Majerz-Maniecka, K., Oleksyn, B. & Polanski, J. (2006). *Bioorg. Med. Chem.* **14**, 3592–3598.

Nakamura, T., Oka, M., Aizawa, K., Soda, H., Fukuda, M., Terashi, K., Ikeda, K., Mizuta, Y., Noguchi, Y., Kimura, Y., Tsuruo, T. & Kohno, S. (1999). *Biochem. Biophys. Res. Commun.* **255**, 618–624.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Palmer, K. J., Holliday, S. M. **&** and Brogden, R. N. (1993). *Drugs*, **45**, 430–475.

Ridley, R. G. (2002). *Nature* (London), **415**, 686–693.

Sheldrick, G. M. (2007). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Silva, A. D. da, de Almeida, M. V., de Souza, M. V. N. & Couri, M. R. C. (2003). *Curr. Med. Chem.* **10**, 21–39.

Sloboda, A. E., Powell, D., Poletto, J. F., Pickett, W. C., Gibbons, J. J., Bell, D. H., Oronsky, A. L. & Kerwar, S. S. (1991). *J. Rheumatol.* **18**, 855–860.

Souza, M. V. N. de (2005). *Mini Rev. Med. Chem.* **5**, 1009–1017.

Tanenbaum, L. & Tuffanelli, D. L. (1980). *Arch. Dermatol.* **116**, 587–591.

Warshakoon, N. C., Sheville, J., Bhatt, R. T., Ji, W., Mendez-Andino, J. L., Meyers, K. M., Kim, N., Wos, J. A., Mitchell, C., Paris, J. L., Pinney, B. B. O., Reizes, O. & Hu, X. E. (2006). *Bioorg. Med. Chem. Lett.* **16**, 5207–5211.

Westrip, S. P. (2009). *publCIF*. In preparation.

supporting information

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S1. Comment

The majority of anti-malarial drugs, such as chloroquine (Tanenbaum & Tuffanelli, 1980), mefloquine (Palmer *et al.*, 1993), primaquine (Elslager *et al.*, 1969) and amodiaquine (Ridley, 2002), possess a quinoline ring, the mainstay of malaria chemotherapy for much of the past 40 years (Font *et al.*, 1997; Kaminsky & Meltzer, 1968; Musiol *et al.*, 2006; Nakamura *et al.*, 1999; Sloboda *et al.*, 1991; Warshakoon *et al.*, 2006). The above motivates our studies aimed towards the development anti-malarial compounds based on the quinoline nucleus (Andrade *et al.*, 2007; Cunico *et al.*, 2006; da Silva *et al.*, 2003; de Souza *et al.*, 2005. The title salt, (I), was prepared as a part of these investigations.

The cation in (I) is twisted about the N2–N3 bond, Fig. 1, as seen in the C3–N2–N3–C10 torsion angle of -168.3 (2) °. This is also reflected in the dihedral angle formed between the quinolinium (maximum deviation = 0.043 (2) for the C2 atom) and benzene planes of 18.98 (10) °. The conformation about the C10═N3 bond is *E*, and the amine-H is oriented towards the quinolinium residue as seen in related structures (Kaiser *et al.*, 2009). The benzoate anion, Fig. 2, is planar with the O1–C17–C18–C19 torsion angle being -10.0 (3) °. The C17–O1, O2 distances in the carboxylate residue are 1.250 (3) and 1.269 (3) Å, respectively, consistent with deprotonation.

The crystal packing is dominated by N–H···O hydrogen bonding, Table 1. A pair of centrosymmetrically related benzoate anions each bridge the quinolinium-H and amine-H atoms of a cation to form a centrosymmetric 20-membered $\{\cdots OCO\cdots HNC_3NH\}_2$ synthon, Fig. 3. The dimeric units face each other to allow the formation of π–π interactions between the quinolinium residues with the *Cg*(N1, C1—C4, C9)···*Cg*(C4—C9)^{i} distance = 3.5625 (13) Å for i: -*x*, -*y*, 1 - *z*. The net result is the formation of linear supramolecular chains aligned along [1 0 0], Fig. 4.

S2. Experimental

A solution of 7-chloro-4-hydrazinylquinoline (0.20 g, 1.0 mmol) and 3-chorobenzaldehyde (1.2 mmol) in EtOH (5 ml) was maintained at room temperature overnight and rotary evaporated. The solid residue was washed with cold Et_2O (3 *x* 10 ml) and recrystallized from EtOH m. pt. 463–465 K, yield 0.24 g The sample for the X-ray study was slowly grown from moist EtOH and the compound isolated was found to be the salt with 3-chlorobenzoic acid. MS/ESI: 315 [$C_{16}H_{10}Cl_2N_3$], based on ^{35}Cl. IR [KBr, cm^{-1}] *v* 3197 (NH), 1611 and 1552 (CN), 1362 (C—O). The 3-chlorobenzoic acid was subsequently found to be an impurity in the 3-chlorobenzaldehyde reagent.

S3. Refinement

The quinolinium- and C-bound H atoms were geometrically placed (N–H = 0.88 Å and C–H = 0.95 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The amine-bound H atom was located from a difference map and refined (N–H = 0.89 (3) Å) with U_{iso}(H) = 1.2U_{eq}(N).

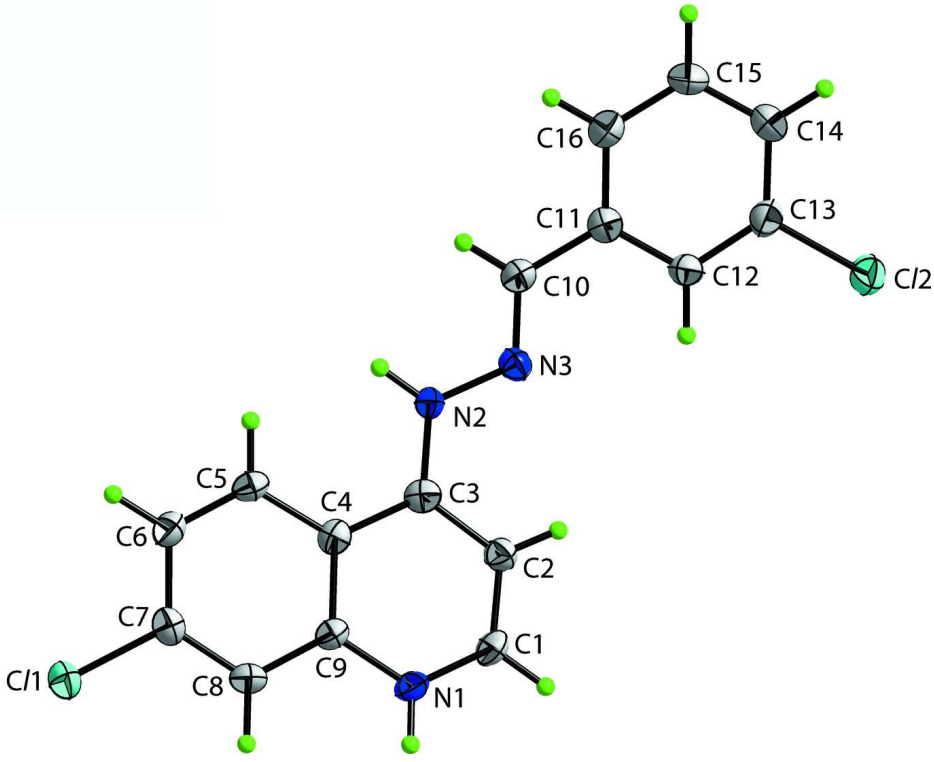

Figure 1

The molecular structure of the cation in (I) showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

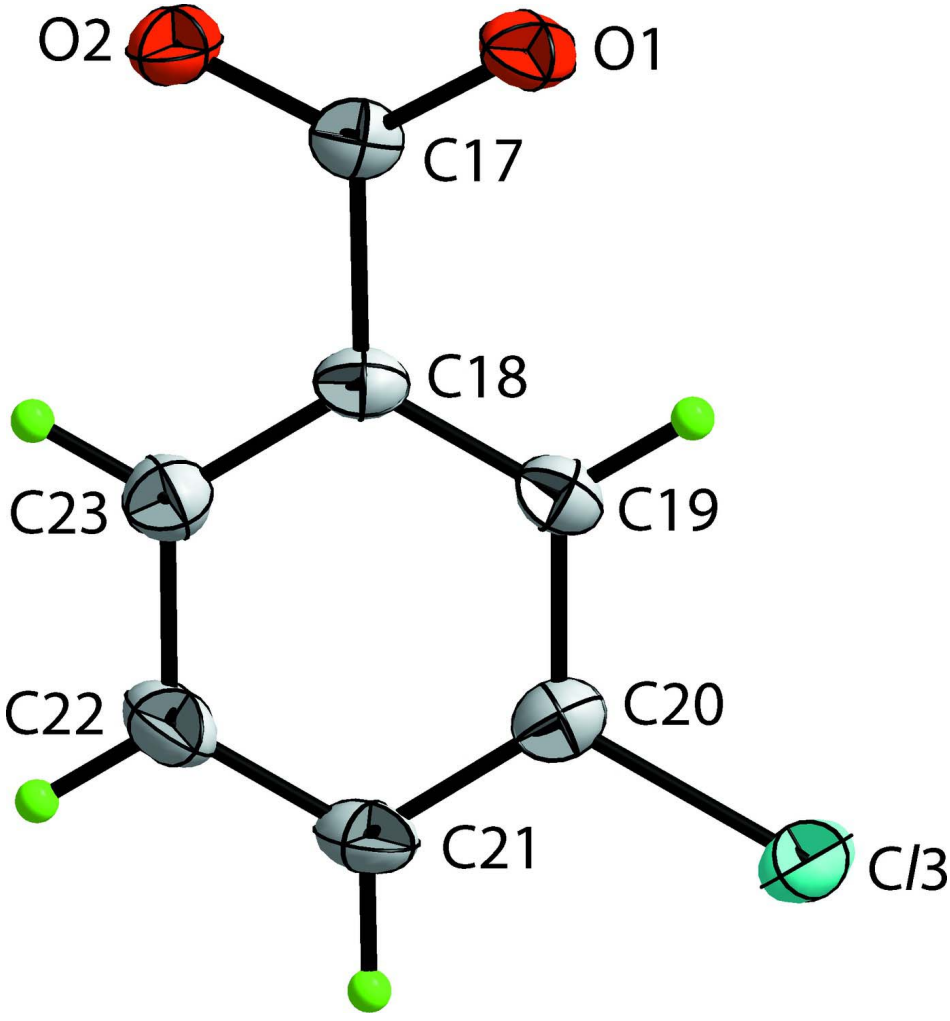

Figure 2

The molecular structure of the anion in (I) showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

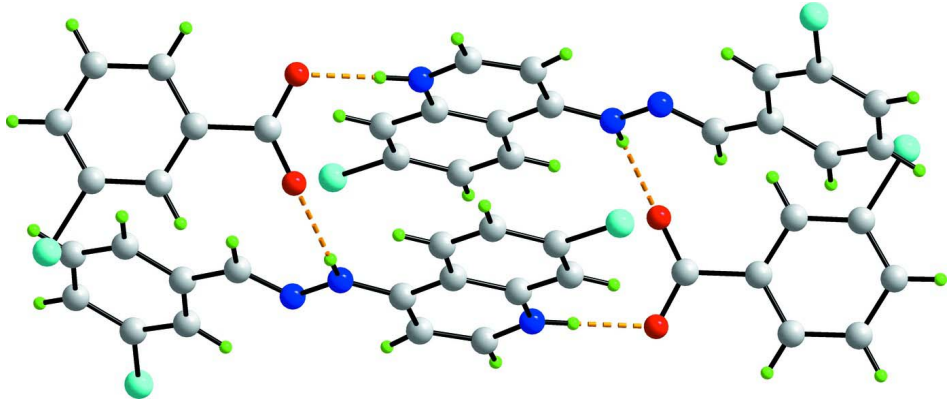

Figure 3

View of the centrosymmetric 20-membered $\{\cdots OCO\cdots HNC_3NH\}_2$ synthon in (I) showing the N–H···O hydrogen bonding as orange dashed lines. Colour code: Cl, cyan; O, red; N, blue; C, grey; and H, green.

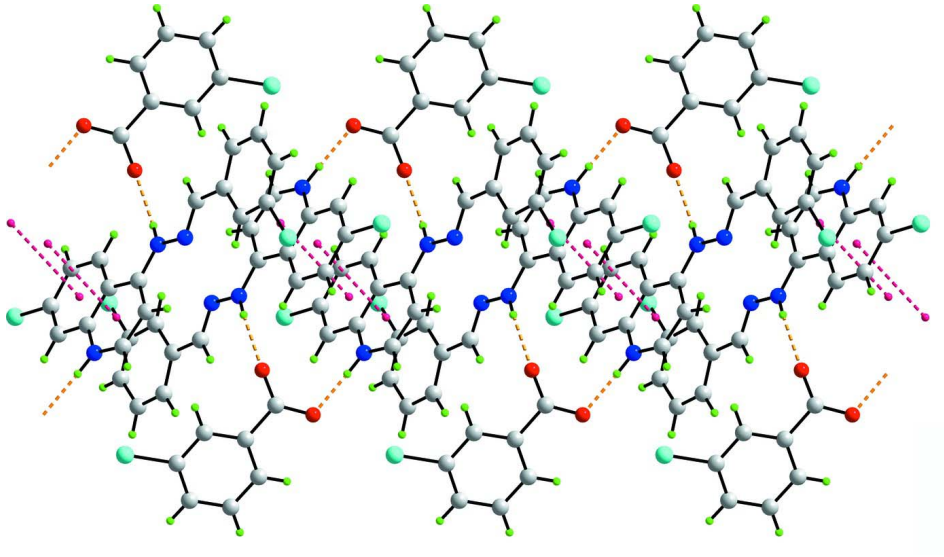

Figure 4

A view of the linear supramolecular chain aligned along [1 0 0] in (I) where the dimeric aggregates illustrated in Fig. 3 are linked by π–π interactions (pink dashed lines).

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Crystal data

$C_{16}H_{12}Cl_2N_3^+\cdot C_7H_4ClO_2^-$
M_r = 472.74
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.8777 (2) Å
b = 10.7064 (3) Å
c = 11.9807 (3) Å
α = 112.5318 (12)°
β = 91.6382 (15)°
γ = 97.4362 (15)°
V = 1039.17 (5) Å^3
Z = 2
F(000) = 484
D_x = 1.511 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 16230 reflections
θ = 2.9–27.5°
μ = 0.47 mm^{-1}
T = 120 K
Block, yellow
0.06 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: Enraf Nonius FR591 rotating anode
10 cm confocal mirrors monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.922, T_{max} = 1.000
16836 measured reflections
4746 independent reflections
3949 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −11→11
k = −13→13
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.104
S = 1.07
4746 reflections
283 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 atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0078P)^2 + 1.9095P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.20629 (7)	−0.15682 (6)	0.12224 (5)	0.02306 (14)
Cl2	0.85051 (7)	0.10932 (6)	1.02577 (5)	0.02465 (15)
N1	0.0669 (2)	−0.2783 (2)	0.43607 (18)	0.0167 (4)
H1N	−0.007 (3)	−0.349 (3)	0.417 (2)	0.020*
N2	0.3644 (2)	0.08652 (19)	0.57378 (17)	0.0161 (4)
H2N	0.3580	0.1499	0.5448	0.019*
N3	0.4690 (2)	0.1101 (2)	0.67007 (17)	0.0165 (4)
C1	0.1764 (3)	−0.2566 (2)	0.5229 (2)	0.0176 (5)
H1	0.1815	−0.3246	0.5550	0.021*
C2	0.2826 (3)	−0.1393 (2)	0.5677 (2)	0.0169 (5)
H2	0.3619	−0.1290	0.6269	0.020*
C3	0.2724 (2)	−0.0350 (2)	0.5250 (2)	0.0150 (4)
C4	0.1584 (2)	−0.0590 (2)	0.4281 (2)	0.0152 (4)
C5	0.1406 (3)	0.0354 (2)	0.3736 (2)	0.0160 (4)
H5	0.2070	0.1203	0.4012	0.019*
C6	0.0291 (3)	0.0063 (2)	0.2819 (2)	0.0178 (5)
H6	0.0173	0.0709	0.2469	0.021*
C7	−0.0678 (3)	−0.1204 (2)	0.2400 (2)	0.0174 (5)
C8	−0.0558 (3)	−0.2149 (2)	0.2900 (2)	0.0163 (4)
H8	−0.1226	−0.2996	0.2607	0.020*
C9	0.0570 (2)	−0.1842 (2)	0.3852 (2)	0.0148 (4)
C10	0.5321 (3)	0.2345 (2)	0.7240 (2)	0.0183 (5)
H10	0.5072	0.3008	0.6948	0.022*
C11	0.6420 (3)	0.2766 (2)	0.8300 (2)	0.0190 (5)
C12	0.6897 (3)	0.1816 (2)	0.8718 (2)	0.0178 (5)
H12	0.6519	0.0869	0.8313	0.021*
C13	0.7928 (3)	0.2280 (2)	0.9730 (2)	0.0197 (5)
C14	0.8501 (3)	0.3651 (3)	1.0350 (2)	0.0262 (6)
H14	0.9208	0.3945	1.1043	0.031*

C15	0.8015 (3)	0.4585 (3)	0.9931 (2)	0.0316 (6)
H15	0.8388	0.5532	1.0346	0.038*
C16	0.6988 (3)	0.4153 (3)	0.8908 (2)	0.0274 (6)
H16	0.6673	0.4803	0.8625	0.033*
Cl3	0.12274 (6)	0.37851 (6)	0.30843 (6)	0.02426 (14)
O1	0.67939 (19)	0.66372 (16)	0.43847 (15)	0.0212 (4)
O2	0.84256 (18)	0.51324 (17)	0.36860 (16)	0.0216 (4)
C17	0.7100 (3)	0.5460 (2)	0.3827 (2)	0.0165 (5)
C18	0.5784 (3)	0.4312 (2)	0.3217 (2)	0.0164 (4)
C19	0.4291 (3)	0.4533 (2)	0.3442 (2)	0.0173 (5)
H19	0.4091	0.5382	0.4019	0.021*
C20	0.3100 (3)	0.3500 (2)	0.2816 (2)	0.0182 (5)
C21	0.3357 (3)	0.2254 (2)	0.1967 (2)	0.0218 (5)
H21	0.2526	0.1564	0.1535	0.026*
C22	0.4848 (3)	0.2028 (3)	0.1756 (2)	0.0243 (5)
H22	0.5041	0.1175	0.1183	0.029*
C23	0.6058 (3)	0.3051 (2)	0.2385 (2)	0.0206 (5)
H23	0.7077	0.2889	0.2245	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0229 (3)	0.0245 (3)	0.0229 (3)	−0.0014 (2)	−0.0066 (2)	0.0127 (2)
Cl2	0.0323 (3)	0.0204 (3)	0.0219 (3)	0.0074 (2)	−0.0037 (2)	0.0082 (2)
N1	0.0171 (10)	0.0126 (9)	0.0215 (10)	0.0015 (7)	0.0001 (8)	0.0081 (8)
N2	0.0163 (9)	0.0142 (9)	0.0183 (10)	0.0005 (7)	−0.0038 (7)	0.0080 (8)
N3	0.0153 (9)	0.0180 (10)	0.0158 (9)	0.0014 (7)	−0.0011 (7)	0.0067 (8)
C1	0.0199 (11)	0.0147 (11)	0.0211 (12)	0.0062 (9)	0.0018 (9)	0.0092 (9)
C2	0.0163 (11)	0.0156 (11)	0.0181 (11)	0.0020 (9)	−0.0011 (9)	0.0061 (9)
C3	0.0127 (10)	0.0143 (11)	0.0177 (11)	0.0041 (8)	0.0035 (8)	0.0051 (9)
C4	0.0141 (10)	0.0159 (11)	0.0165 (11)	0.0047 (8)	0.0028 (8)	0.0065 (9)
C5	0.0173 (11)	0.0125 (10)	0.0178 (11)	0.0025 (8)	0.0033 (9)	0.0052 (9)
C6	0.0210 (12)	0.0159 (11)	0.0188 (11)	0.0043 (9)	0.0030 (9)	0.0087 (9)
C7	0.0162 (11)	0.0200 (12)	0.0156 (11)	0.0033 (9)	0.0003 (9)	0.0067 (9)
C8	0.0161 (11)	0.0132 (10)	0.0177 (11)	−0.0001 (8)	0.0014 (9)	0.0048 (9)
C9	0.0159 (11)	0.0128 (10)	0.0162 (11)	0.0025 (8)	0.0019 (8)	0.0060 (9)
C10	0.0195 (11)	0.0164 (11)	0.0195 (12)	0.0004 (9)	−0.0005 (9)	0.0085 (9)
C11	0.0211 (12)	0.0179 (11)	0.0179 (11)	0.0009 (9)	−0.0007 (9)	0.0075 (9)
C12	0.0183 (11)	0.0150 (11)	0.0177 (11)	−0.0006 (9)	−0.0001 (9)	0.0050 (9)
C13	0.0231 (12)	0.0198 (12)	0.0190 (12)	0.0044 (9)	0.0018 (9)	0.0103 (10)
C14	0.0321 (14)	0.0227 (13)	0.0207 (12)	−0.0044 (11)	−0.0088 (10)	0.0083 (10)
C15	0.0453 (17)	0.0165 (12)	0.0277 (14)	−0.0068 (11)	−0.0131 (12)	0.0077 (11)
C16	0.0376 (15)	0.0193 (12)	0.0257 (13)	−0.0007 (11)	−0.0082 (11)	0.0115 (11)
Cl3	0.0161 (3)	0.0240 (3)	0.0307 (3)	0.0009 (2)	−0.0005 (2)	0.0094 (3)
O1	0.0227 (9)	0.0133 (8)	0.0253 (9)	0.0007 (6)	−0.0033 (7)	0.0061 (7)
O2	0.0170 (8)	0.0168 (8)	0.0296 (10)	0.0006 (6)	−0.0019 (7)	0.0085 (7)
C17	0.0195 (11)	0.0154 (11)	0.0166 (11)	0.0018 (9)	−0.0025 (9)	0.0092 (9)
C18	0.0180 (11)	0.0145 (11)	0.0175 (11)	−0.0012 (8)	−0.0011 (9)	0.0085 (9)

C19	0.0208 (11)	0.0145 (11)	0.0165 (11)	0.0020 (9)	−0.0003 (9)	0.0065 (9)
C20	0.0168 (11)	0.0195 (12)	0.0205 (11)	0.0012 (9)	0.0002 (9)	0.0108 (9)
C21	0.0222 (12)	0.0180 (12)	0.0208 (12)	−0.0049 (9)	−0.0012 (10)	0.0054 (10)
C22	0.0279 (13)	0.0158 (11)	0.0233 (13)	−0.0006 (10)	0.0033 (10)	0.0024 (10)
C23	0.0208 (12)	0.0195 (12)	0.0211 (12)	0.0019 (9)	0.0029 (9)	0.0077 (10)

Geometric parameters (Å, º)

Cl1—C7	1.735 (2)	C11—C16	1.395 (3)
Cl2—C13	1.744 (2)	C11—C12	1.398 (3)
N1—C1	1.334 (3)	C12—C13	1.383 (3)
N1—C9	1.373 (3)	C12—H12	0.9500
N1—H1N	0.89 (3)	C13—C14	1.384 (3)
N2—C3	1.348 (3)	C14—C15	1.386 (4)
N2—N3	1.383 (3)	C14—H14	0.9500
N2—H2N	0.8800	C15—C16	1.392 (4)
N3—C10	1.277 (3)	C15—H15	0.9500
C1—C2	1.379 (3)	C16—H16	0.9500
C1—H1	0.9500	Cl3—C20	1.745 (2)
C2—C3	1.407 (3)	O1—C17	1.250 (3)
C2—H2	0.9500	O2—C17	1.269 (3)
C3—C4	1.440 (3)	C17—C18	1.517 (3)
C4—C9	1.416 (3)	C18—C19	1.392 (3)
C4—C5	1.420 (3)	C18—C23	1.394 (3)
C5—C6	1.371 (3)	C19—C20	1.385 (3)
C5—H5	0.9500	C19—H19	0.9500
C6—C7	1.408 (3)	C20—C21	1.385 (3)
C6—H6	0.9500	C21—C22	1.389 (4)
C7—C8	1.372 (3)	C21—H21	0.9500
C8—C9	1.405 (3)	C22—C23	1.392 (3)
C8—H8	0.9500	C22—H22	0.9500
C10—C11	1.465 (3)	C23—H23	0.9500
C10—H10	0.9500		
C1—N1—C9	120.8 (2)	C16—C11—C10	118.8 (2)
C1—N1—H1N	119.7 (17)	C12—C11—C10	121.6 (2)
C9—N1—H1N	119.0 (17)	C13—C12—C11	118.9 (2)
C3—N2—N3	119.06 (18)	C13—C12—H12	120.6
C3—N2—H2N	120.5	C11—C12—H12	120.6
N3—N2—H2N	120.5	C12—C13—C14	122.4 (2)
C10—N3—N2	114.66 (19)	C12—C13—Cl2	118.72 (18)
N1—C1—C2	122.5 (2)	C14—C13—Cl2	118.83 (19)
N1—C1—H1	118.8	C13—C14—C15	118.2 (2)
C2—C1—H1	118.8	C13—C14—H14	120.9
C1—C2—C3	119.4 (2)	C15—C14—H14	120.9
C1—C2—H2	120.3	C14—C15—C16	120.9 (2)
C3—C2—H2	120.3	C14—C15—H15	119.6
N2—C3—C2	121.7 (2)	C16—C15—H15	119.6

N2—C3—C4	119.7 (2)	C15—C16—C11	120.0 (2)
C2—C3—C4	118.6 (2)	C15—C16—H16	120.0
C9—C4—C5	117.9 (2)	C11—C16—H16	120.0
C9—C4—C3	118.0 (2)	O1—C17—O2	125.9 (2)
C5—C4—C3	124.1 (2)	O1—C17—C18	118.0 (2)
C6—C5—C4	121.1 (2)	O2—C17—C18	116.1 (2)
C6—C5—H5	119.4	C19—C18—C23	119.6 (2)
C4—C5—H5	119.4	C19—C18—C17	120.1 (2)
C5—C6—C7	119.3 (2)	C23—C18—C17	120.1 (2)
C5—C6—H6	120.4	C20—C19—C18	119.3 (2)
C7—C6—H6	120.4	C20—C19—H19	120.4
C8—C7—C6	121.8 (2)	C18—C19—H19	120.4
C8—C7—Cl1	119.40 (18)	C19—C20—C21	121.6 (2)
C6—C7—Cl1	118.75 (17)	C19—C20—Cl3	119.25 (18)
C7—C8—C9	118.8 (2)	C21—C20—Cl3	119.13 (18)
C7—C8—H8	120.6	C20—C21—C22	119.1 (2)
C9—C8—H8	120.6	C20—C21—H21	120.5
N1—C9—C8	118.6 (2)	C22—C21—H21	120.5
N1—C9—C4	120.5 (2)	C21—C22—C23	120.0 (2)
C8—C9—C4	120.9 (2)	C21—C22—H22	120.0
N3—C10—C11	121.2 (2)	C23—C22—H22	120.0
N3—C10—H10	119.4	C22—C23—C18	120.4 (2)
C11—C10—H10	119.4	C22—C23—H23	119.8
C16—C11—C12	119.6 (2)	C18—C23—H23	119.8

C3—N2—N3—C10	−168.3 (2)	C11—C12—C13—C14	0.3 (4)
C9—N1—C1—C2	1.3 (3)	C11—C12—C13—Cl2	179.37 (18)
N1—C1—C2—C3	2.9 (3)	C12—C13—C14—C15	0.0 (4)
N3—N2—C3—C2	−1.5 (3)	Cl2—C13—C14—C15	−179.1 (2)
N3—N2—C3—C4	177.33 (19)	C13—C14—C15—C16	−0.5 (4)
C1—C2—C3—N2	173.8 (2)	C14—C15—C16—C11	0.7 (4)
C1—C2—C3—C4	−5.1 (3)	C12—C11—C16—C15	−0.4 (4)
N2—C3—C4—C9	−175.6 (2)	C10—C11—C16—C15	178.9 (2)
C2—C3—C4—C9	3.3 (3)	O1—C17—C18—C19	−10.0 (3)
N2—C3—C4—C5	3.8 (3)	O2—C17—C18—C19	172.1 (2)
C2—C3—C4—C5	−177.3 (2)	O1—C17—C18—C23	166.8 (2)
C9—C4—C5—C6	−0.3 (3)	O2—C17—C18—C23	−11.1 (3)
C3—C4—C5—C6	−179.7 (2)	C23—C18—C19—C20	−1.1 (3)
C4—C5—C6—C7	−0.9 (3)	C17—C18—C19—C20	175.7 (2)
C5—C6—C7—C8	1.2 (3)	C18—C19—C20—C21	−0.3 (3)
C5—C6—C7—Cl1	−178.96 (18)	C18—C19—C20—Cl3	−179.20 (17)
C6—C7—C8—C9	−0.3 (3)	C19—C20—C21—C22	1.2 (4)
Cl1—C7—C8—C9	179.89 (17)	Cl3—C20—C21—C22	−179.88 (19)
C1—N1—C9—C8	176.9 (2)	C20—C21—C22—C23	−0.7 (4)
C1—N1—C9—C4	−3.2 (3)	C21—C22—C23—C18	−0.7 (4)
C7—C8—C9—N1	179.0 (2)	C19—C18—C23—C22	1.7 (4)
C7—C8—C9—C4	−1.0 (3)	C17—C18—C23—C22	−175.2 (2)
C5—C4—C9—N1	−178.7 (2)	C2—C3—N2—N3	−1.5 (3)

C3—C4—C9—N1	0.8 (3)	C4—C3—N2—N3	177.33 (19)
C5—C4—C9—C8	1.3 (3)	N3—C10—C11—C12	4.1 (4)
C3—C4—C9—C8	−179.3 (2)	N3—C10—C11—C16	−175.2 (2)
N2—N3—C10—C11	178.2 (2)	C19—C18—C17—O1	−10.0 (3)
N3—C10—C11—C16	−175.2 (2)	C19—C18—C17—O2	172.1 (2)
N3—C10—C11—C12	4.1 (4)	C23—C18—C17—O1	166.8 (2)
C16—C11—C12—C13	−0.1 (4)	C23—C18—C17—O2	−11.1 (3)
C10—C11—C12—C13	−179.4 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1n···O2^{i}	0.89 (3)	1.76 (3)	2.641 (3)	175 (3)
N2—H2n···O1^{ii}	0.88	2.00	2.809 (3)	152

Symmetry codes: (i) $x-1, y-1, z$; (ii) $-x+1, -y+1, -z+1$.