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Guanidinium 4-chloro-3-nitrobenzoate monohydrate

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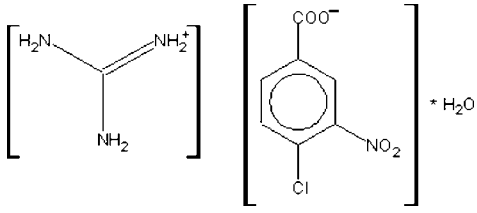
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.041; wR factor = 0.094; data-to-parameter ratio = 27.6.

The crystal packing of the title hydrated molecular salt, $CH_6N_3^+\cdot C_7H_3ClNO_4^-\cdot H_2O$, is stabilized by a three-dimensional network of N—H···O, O—H···O and N—H···Cl hydrogen bonds and aromatic π–π stacking interactions (centroid-to-centroid separation = 3.69 Å).

Related literature

For related literature, see: Abrahams *et al.* (2004); Burke *et al.* (2006); Cygler *et al.* (1976); Etter *et al.* (1990); Fülscher & Mehler (1988); Ishida & Fukunaga (2003); McKee & Najafpour (2007); Melo *et al.* (1999); Singh *et al.* (1987); Videnova-Adrabińska, Obara & Lis (2007).



Experimental

Crystal data

$CH_6N_3^+\cdot C_7H_3ClNO_4^-\cdot H_2O$
M_r = 278.66
Monoclinic, $P2_1/c$
a = 10.814 (4) Å
b = 7.040 (3) Å
c = 15.487 (6) Å
β = 97.68 (3)°
V = 1168.5 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 100 (2) K
0.60 × 0.18 × 0.09 mm

Data collection

Oxford Diffraction KM-4 CCD diffractometer
Absorption correction: none
17154 measured reflections
5166 independent reflections
3766 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.094
S = 1.01
5166 reflections
187 parameters
8 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.54 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
N10—H101···O1W^{i}	0.86	2.01	2.822 (2)	156
N10—H102···O1	0.86	2.04	2.858 (2)	158
N20—H201···O2^{ii}	0.86	2.11	2.875 (2)	147
N20—H202···O3^{iii}	0.86	2.51	2.964 (2)	114
N30—H301···O2^{ii}	0.86	2.10	2.876 (2)	150
N30—H301···Cl^{iv}	0.86	2.94	3.474 (2)	122
N30—H302···O1W^{i}	0.86	2.18	2.921 (2)	144
O1W—H1W···O1^{v}	0.82	1.93	2.742 (2)	170
O1W—H2W···O2	0.82	2.03	2.832 (2)	165
O1W—H2W···O1	0.82	2.62	3.249 (2)	134

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2489).

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supplementary materials

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M. M. Najafpour, M. Holynska and T. Lis

Comment

The crystal engineering of guanidinium salts has been widely explored and numerous supramolecular synthons have been found (Abrahams *et al.*, 2004). These structural units include, *e.g.* two-dimensional hydrogen-bonded networks in guanidinium hydrogen carboxylates (Videnova-Adrabińska *et al.*, 2007). The attempts to manipulate the hydrogen bonds formation include *e.g.* cation substitution in guanidinium sulfonates (Burke *et al.*, 2006). Thus gained knowledge is of help *e.g.* in the modelling of Arg–Glu or Arg–Asp side-chain interactions in proteins (Melo *et al.*, 1999; Fülscher & Mehler, 1988; Singh *et al.*, 1987).

In this paper we report on the synthesis and roentgenographic studies of the title compound, (I), containing 4-chloro-3-nitrobenzoate anions, guanidinium cations and water molecules in the molar ratio of 1:1:1 (Fig. 1). In the anion the carboxylate group lies approximately in the plane of the phenyl ring, whereas the nitro group plane is twisted with respect to the phenyl group plane (the twist angle with respect to the phenyl ring plane is 41.7 (1)°). The nitro group twist angle with respect to the phenyl ring plane is comparable to the analogous parameter reported for 4-chloro-3-nitrobenzoic acid (Ishida & Fukunaga, 2003). The guanidinium cation geometrical parameters are typical (Cygler *et al.*, 1976).

The crystal structure is stabilized mainly by a network of O—H···O, N—H···O and N—H···Cl hydrogen bonds (Table 1). In this network the carboxylate O atoms act as hydrogen bond acceptors, water O atoms act as donors as well as acceptors and guanidinium N atoms provide the most extensive part as donors. Each of the guanidinium H atoms is involved in hydrogen bonds as a donor. The well known synthon in which guanidinium amine group and carboxylate group are involved in hydrogen bonds to form a $R^2_2(6)$ ring (Videnova-Adrabińska *et al.*, 2007; McKee & Najafpour, 2007; Etter *et al.*, 1990) is not present in (I). Instead, a water molecule donates one of its H atoms (H2W) to form a bifurcated hydrogen bond. In this hydrogen bond the two carboxyl O atoms (O1 and O2) act as acceptors. The second water H1W atom is involved in the O1W—H1W···O1^{v} (see Table 1 for symmetry code) hydrogen bond which seems to be the strongest of all hydrogen bonds present (Table 1). The water O1W atom accepts two hydrogen bonds, N10—H101···O1W^{i} and N30—H302···O1W^{i} to form a $R^2_1(6)$ motif (Etter *et al.*, 1990). Furthermore, the carboxyl O1 atom is involved in one hydrogen bond as acceptor with H102 atom from the guanidinium cation amine group. The nitro O3^{iii} atom is bonded to the H262 atom *via* N—H···O hydrogen bond. The remaining nitro O4 atom participates in no other hydrogen bonds. The H201 and H301 atoms from two guanidinium amino groups participate in hydrogen bonds to the carboxyl O2^{ii} atom. The H301 atom is further bonded to the Cl^{iv} atom.

The phenyl rings form chains extending along [010] (the neighbouring phenyl rings constituting each chain are generated with the following symmetry operations: [vi] 1 − *x*, 2 − *y*, 1 − *z*; [vii] *x*, 1 + *y*, *z etc.*; Fig. 2). A weak stacking interaction stabilizes this pattern (3.69 Å distance between the neighbouring rings centroids). The phenyl ring chains are parallel to guanidinium cations and water molecules layers perpendicular to [100] which *via* hydrogen bonds create a three-dimensional crystal structure (Fig. 3).

Experimental

4-Chloro-3-nitrobenzoic acid (1 mmol, 0.201 g) was added to an aqueous solution (10 ml) of guanidinium carbonate (1 mmol, 0.180 g) with stirring. This solution yielded single crystals of (I) after 2 days.

Refinement

The H atoms from the water molecule as well as from the guanidinium cation were found in a difference map, then relocated in idealized positions (O—H = 0.82 Å, N—H = 0.86 Å) and refined as riding with U_{eq}(H) = 1.5U_{eq}(carrier). The C-bound H atoms were geometrically placed (C—H = 0.98 Å) and refined as riding with U_{eq}(H) = 1.2U_{eq}(C). The highest peak in the final difference map is situated on the C1—C2 bond.

Figures

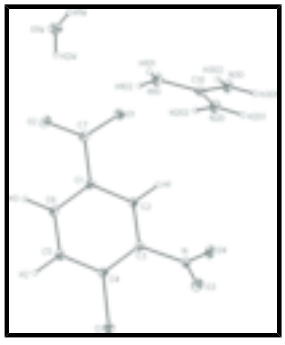

Fig. 1. View of the molecular structure of (I) with displacement ellipsoids drawn at 30% probability level (arbitrary spheres for the H atoms).

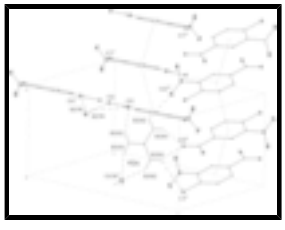

Fig. 2. Hydrogen bonding scheme and chains extending along [010] formed by phenyl rings from the 4-chloro-3-nitrobenzoate anions. For clarity, the displacement ellipsoids are visualized only for non-carbon, non-hydrogen atoms (20% probability level). The H atoms are presented as spheres of arbitrary radius. The hydrogen bonds and the weak stacking interactions are denoted with dashed and dotted lines, respectively. Symmetry codes: [i] –x, −*y* + 1, −*z* + 1; [ii] *x*, −*y* + 3/2, *z* + 1/2; [iii] –x+1, *y* + 1/2, −*z* + 3/2; [iv] –x+1, *y* − 1/2, −*z* + 3/2; [v] –x, −*y* + 2, −*z* + 1; [vi] 1 − *x*, 2 − *y*, 1 − *z*; [vii] *x*, 1 + *y*, *z*.

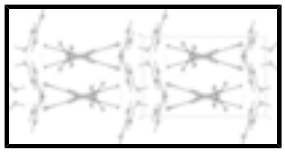

Fig. 3. View of the crystal structure of (I) along [001]. The hydrogen bonds are denoted with dashed lines.

Guanidinium 4-chloro-3-nitrobenzoate monohydrate

Crystal data

$CH_6N_3^+ \cdot C_7H_3ClNO_4^- \cdot H_2O$	F_{000} = 576
M_r = 278.66	D_x = 1.584 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 11041 reflections
a = 10.814 (4) Å	θ = 3.0–35.0º

b = 7.040 (3) Å	μ = 0.35 mm^{-1}
c = 15.487 (6) Å	T = 100 (2) K
β = 97.68 (3)º	Block, colourless
V = 1168.5 (8) Å^3	0.60 × 0.18 × 0.09 mm
Z = 4	

Data collection

Oxford Diffraction KM-4 CCD diffractometer	3766 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	R_{int} = 0.039
Monochromator: graphite	θ_{max} = 36.6º
T = 100(2) K	θ_{min} = 3.2º
ω scans	h = −17→15
Absorption correction: none	k = −11→9
17154 measured reflections	l = −25→25
5166 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.041	H-atom parameters constrained
$wR(F^2)$ = 0.094	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.01	$(\Delta/\sigma)_{max}$ = 0.001
5166 reflections	$\Delta\rho_{max}$ = 0.54 e Å^{-3}
187 parameters	$\Delta\rho_{min}$ = −0.26 e Å^{-3}
8 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl	0.79594 (2)	0.61834 (4)	0.582414 (16)	0.01727 (7)
O1	0.19850 (8)	0.90314 (12)	0.54668 (5)	0.01884 (16)
O2	0.22004 (8)	0.89017 (12)	0.40527 (5)	0.01845 (17)
C7	0.26099 (10)	0.87298 (14)	0.48485 (7)	0.01390 (19)

C2	0.44468 (10)	0.79857 (15)	0.59641 (6)	0.01337 (19)
H1	0.3957	0.8347	0.6403	0.016*
C5	0.59217 (10)	0.69974 (15)	0.46892 (6)	0.01446 (19)
H2	0.6424	0.6689	0.4250	0.017*
C4	0.64170 (10)	0.68633 (15)	0.55647 (6)	0.01310 (18)
C3	0.56635 (10)	0.73678 (15)	0.61942 (6)	0.01326 (19)
C1	0.39437 (10)	0.80762 (14)	0.50887 (6)	0.01273 (19)
O3	0.67402 (8)	0.59089 (13)	0.74134 (5)	0.02499 (19)
C6	0.46960 (10)	0.75806 (15)	0.44558 (6)	0.01430 (19)
H3	0.4363	0.7644	0.3857	0.017*
O4	0.58141 (9)	0.85905 (14)	0.75857 (5)	0.0289 (2)
N	0.61144 (9)	0.72820 (15)	0.71326 (6)	0.01803 (19)
N10	0.10087 (10)	0.55842 (15)	0.60786 (6)	0.0205 (2)
H101	0.0796	0.4460	0.5899	0.031*
H102	0.1187	0.6532	0.5767	0.031*
N20	0.17533 (10)	0.73976 (14)	0.72783 (6)	0.0198 (2)
H201	0.1983	0.748	0.7831	0.030*
H202	0.1871	0.8291	0.6920	0.030*
N30	0.11900 (10)	0.42771 (14)	0.74506 (6)	0.01893 (19)
H301	0.1390	0.443	0.8003	0.028*
H302	0.0987	0.3184	0.7228	0.028*
C10	0.13265 (10)	0.57518 (16)	0.69380 (7)	0.0150 (2)
O1W	−0.04003 (9)	0.83150 (13)	0.39911 (6)	0.02309 (19)
H1W	−0.0839	0.9069	0.4216	0.035*
H2W	0.0334	0.864	0.4075	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.01357 (13)	0.02021 (13)	0.01785 (12)	0.00384 (10)	0.00142 (8)	−0.00186 (9)
O1	0.0158 (4)	0.0226 (4)	0.0184 (4)	0.0039 (3)	0.0034 (3)	0.0021 (3)
O2	0.0186 (4)	0.0200 (4)	0.0151 (3)	0.0020 (3)	−0.0036 (3)	0.0012 (3)
C7	0.0141 (5)	0.0117 (4)	0.0152 (4)	−0.0010 (4)	−0.0006 (3)	0.0016 (3)
C2	0.0136 (5)	0.0149 (5)	0.0116 (4)	0.0007 (4)	0.0019 (3)	0.0009 (3)
C5	0.0161 (5)	0.0152 (5)	0.0124 (4)	0.0001 (4)	0.0029 (3)	−0.0015 (3)
C4	0.0121 (5)	0.0120 (4)	0.0150 (4)	0.0013 (4)	0.0010 (3)	−0.0004 (3)
C3	0.0145 (5)	0.0156 (5)	0.0094 (4)	0.0002 (4)	0.0006 (3)	0.0007 (3)
C1	0.0138 (5)	0.0120 (4)	0.0121 (4)	−0.0004 (4)	0.0005 (3)	0.0012 (3)
O3	0.0205 (5)	0.0324 (5)	0.0212 (4)	0.0048 (4)	−0.0005 (3)	0.0122 (3)
C6	0.0166 (5)	0.0143 (5)	0.0116 (4)	−0.0012 (4)	0.0005 (3)	−0.0001 (3)
O4	0.0261 (5)	0.0467 (6)	0.0133 (4)	0.0117 (4)	0.0004 (3)	−0.0082 (4)
N	0.0139 (5)	0.0281 (5)	0.0120 (4)	0.0016 (4)	0.0011 (3)	0.0028 (3)
N10	0.0260 (6)	0.0214 (5)	0.0136 (4)	−0.0046 (4)	0.0010 (3)	−0.0004 (3)
N20	0.0249 (5)	0.0180 (5)	0.0159 (4)	−0.0023 (4)	0.0011 (4)	−0.0011 (3)
N30	0.0236 (5)	0.0182 (4)	0.0146 (4)	−0.0033 (4)	0.0014 (3)	−0.0014 (3)
C10	0.0114 (5)	0.0187 (5)	0.0153 (4)	0.0006 (4)	0.0024 (3)	−0.0012 (4)
O1W	0.0169 (4)	0.0242 (4)	0.0282 (4)	−0.0020 (4)	0.0033 (3)	−0.0101 (3)

Geometric parameters (Å, °)

Cl—C4	1.7302 (12)	C4—C3	1.3974 (16)
O1—C7	1.2616 (14)	C3—N	1.4711 (14)
O2—C7	1.2585 (13)	C1—C6	1.3990 (16)
C7—C1	1.5123 (16)	O3—N	1.2259 (13)
C2—C3	1.3863 (15)	C6—H3	0.95
C2—C1	1.3932 (14)	O4—N	1.2277 (14)
C2—H1	0.95	N10—C10	1.3346 (15)
C5—C6	1.3886 (16)	N20—C10	1.3298 (15)
C5—C4	1.3929 (15)	N30—C10	1.3271 (15)
C5—H2	0.95		
O2—C7—O1	124.96 (10)	C5—C6—H3	119.5
O2—C7—C1	117.99 (10)	C1—C6—H3	119.5
O1—C7—C1	117.04 (9)	O3—N—O4	124.37 (9)
C3—C2—C1	119.89 (10)	O3—N—C3	118.50 (9)
C3—C2—H1	120.1	O4—N—C3	117.12 (9)
C1—C2—H1	120.1	C10—N10—H101	115
C6—C5—C4	120.20 (10)	C10—N10—H102	116
C6—C5—H2	119.9	H101—N10—H102	127
C4—C5—H2	119.9	C10—N20—H201	120
C5—C4—C3	118.53 (10)	C10—N20—H202	117
C5—C4—Cl	118.56 (9)	H201—N20—H202	122
C3—C4—Cl	122.84 (8)	C10—N30—H301	117
C2—C3—C4	121.49 (9)	C10—N30—H302	120
C2—C3—N	116.40 (9)	H301—N30—H302	121
C4—C3—N	122.11 (9)	N30—C10—N20	120.33 (10)
C2—C1—C6	118.84 (10)	N30—C10—N10	119.54 (10)
C2—C1—C7	119.26 (10)	N20—C10—N10	120.11 (10)
C6—C1—C7	121.89 (9)	H1W—O1W—H2W	111
C5—C6—C1	121.03 (9)		
C6—C5—C4—C3	−1.42 (16)	O1—C7—C1—C2	−5.10 (15)
C6—C5—C4—Cl	−178.53 (8)	O2—C7—C1—C6	−3.11 (15)
C1—C2—C3—C4	1.32 (16)	O1—C7—C1—C6	175.73 (10)
C1—C2—C3—N	−178.93 (9)	C4—C5—C6—C1	1.18 (16)
C5—C4—C3—C2	0.19 (16)	C2—C1—C6—C5	0.33 (16)
Cl—C4—C3—C2	177.16 (8)	C7—C1—C6—C5	179.50 (10)
C5—C4—C3—N	−179.55 (10)	C2—C3—N—O3	138.15 (11)
Cl—C4—C3—N	−2.58 (15)	C4—C3—N—O3	−42.10 (15)
C3—C2—C1—C6	−1.56 (15)	C2—C3—N—O4	−40.57 (14)
C3—C2—C1—C7	179.25 (10)	C4—C3—N—O4	139.18 (11)
O2—C7—C1—C2	176.06 (10)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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N30—H302···O1W^{i}	0.86	2.18	2.921 (2)	144
O1W—H1W···O1^{v}	0.82	1.93	2.742 (2)	170
O1W—H2W···O2	0.82	2.03	2.832 (2)	165
O1W—H2W···O1	0.82	2.62	3.249 (2)	134

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

Fig. 1

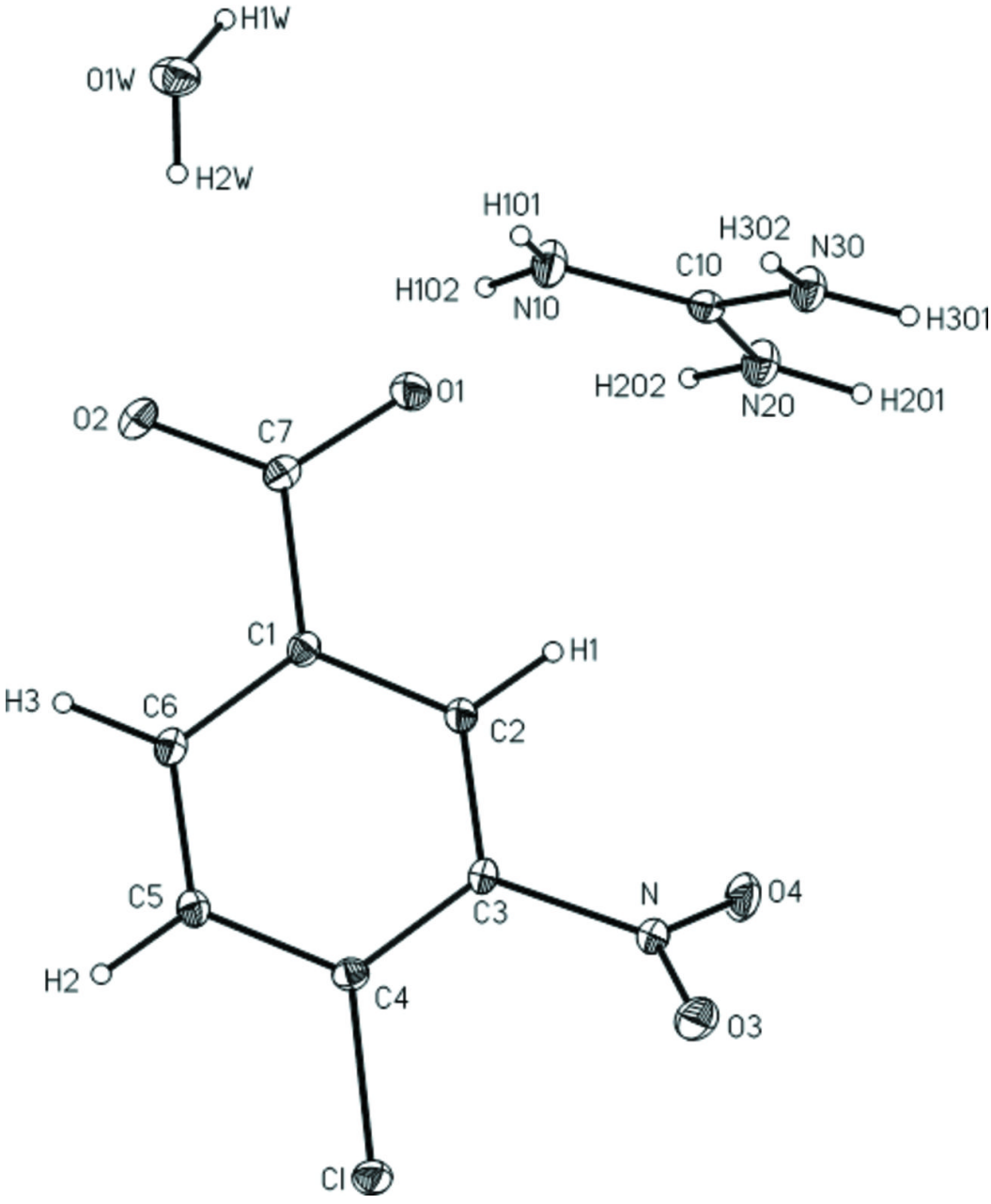
H1W
O1W
H2W
H101
H302
N30
C10
H102
N10
H301
H202
N20
H201
O1
O2
C7
C1
H1
H3
C6
C2
C5
C3
N
O4
H2
C4
O3
Cl

Fig. 2

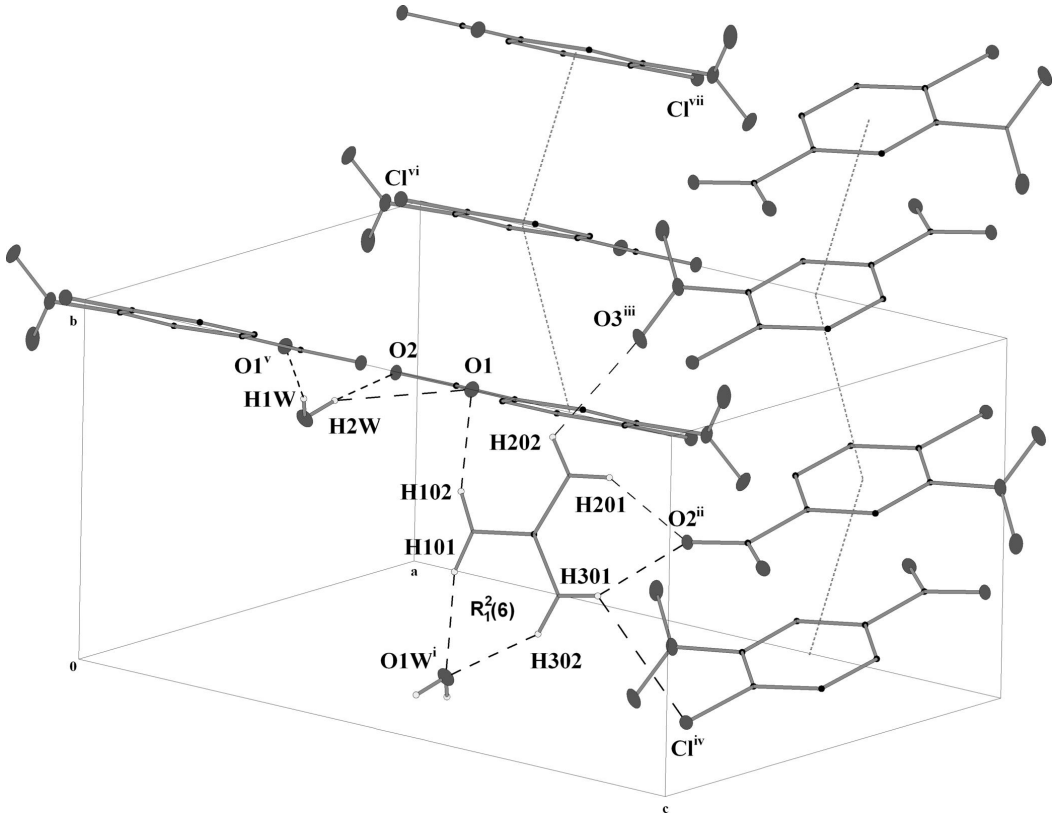
Cl^vii
Cl^vi
O3^iii
O1^v
O2
O1
H1W
H2W
H202
H102
H201
O2^ii
H101
H301
R²₁(6)
O1W^i
H302
Cl^iv
b
0
a
c

Fig. 3