Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structures of four isomeric hydrogen-bonded co-crystals of 6-methylquinoline with 2-chloro-4-nitrobenzoic acid, 2-chloro-5-nitrobenzoic acid, 3-chloro-2-nitrobenzoic acid and 4-chloro-2-nitrobenzoic acid

Received 26 September 2020
Accepted 29 September 2020

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; 2-chloro-4-nitrobenzoic acid; 2-chloro-5-nitrobenzoic acid; 3-chloro-2-nitrobenzoic acid; 4-chloro-2-nitrobenzoic acid; 6-methylquinoline; hydrogen bond; disorder; Hirshfeld surface.

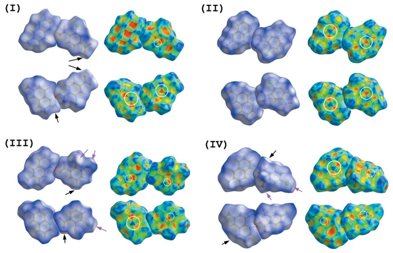
CCDC references: 2034476; 2034475; 2034474; 2034473

Supporting information: this article has supporting information at journals.iucr.org/e

Kazuma Gotoh and Hiroyuki Ishida*

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan. *Correspondence e-mail: ishidah@cc.okayama-u.ac.jp

The structures of the four isomeric compounds of 6-methylquinoline with chloro- and nitro-substituted benzoic acids, $C_7H_4ClNO_4\cdot C_{10}H_9N$, namely, 2-chloro-4-nitrobenzoic acid–6-methylquinoline (1/1), (I), 2-chloro-5-nitrobenzoic acid–6-methylquinoline (1/1), (II), 3-chloro-2-nitrobenzoic acid–6-methylquinoline (1/1), (III), and 4-chloro-2-nitrobenzoic acid–6-methylquinoline (1/1), (IV), have been determined at 185–190 K. In each compound, the acid and base molecules are linked by a short hydrogen bond between a carboxyl O atom and an N atom of the base. The $O\cdots N$ distances are 2.5452 (12), 2.6569 (13), 2.5640 (17) and 2.514 (2) Å, respectively, for compounds (I)–(IV). In the hydrogen-bonded acid–base units of (I), (III) and (IV), the H atoms are each disordered over two positions with O site:N site occupancies of 0.65 (3):0.35 (3), 0.59 (4):0.41 (4) and 0.48 (5):0.52 (5), respectively, for (I), (III) and (IV). The H atom in the hydrogen-bonded unit of (II) is located at the O-atom site. In all of the crystals of (I)–(IV), π–π interactions between the quinoline ring system and the benzene ring of the acid molecule are observed. In addition, a π–π interaction between the benzene rings of adjacent acid molecules and a $C-H\cdots O$ hydrogen bond are observed in the crystal of (I), and $C-H\cdots O$ hydrogen bonds and $O\cdots Cl$ contacts occur in the crystals of (III) and (IV). These intermolecular interactions connect the acid and base molecules, forming a layer structure parallel to the *bc* plane in (I), a column along the *a*-axis direction in (II), a layer parallel to the *ab* plane in (III) and a three-dimensional network in (IV). Hirshfeld surfaces for the title compounds mapped over d_{norm} and shape index were generated to visualize the weak intermolecular interactions.

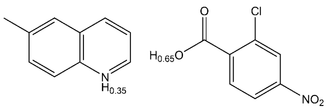


1. Chemical context

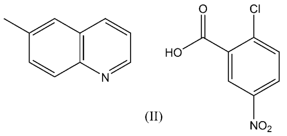
Properties of hydrogen bonds formed between organic acids and organic bases depend on the pK_a values of the acids and bases as well as intermolecular interactions in the crystals. In our ongoing study on crystal structures of the system of quinoline derivatives–chloro- and nitro-substituted benzoic acids, we have shown that three compounds of quinoline with 3-chloro-2-nitrobenzoic acid, 4-chloro-2-nitrobenzoic acid and 5-chloro-2-nitrobenzoic acid, the ΔpK_a [pK_a(base) − pK_a(acid)] values of which are 3.08, 2.93 and 3.04, respectively, have a short double-well $O-H\cdots N$/$O\cdots H-N$ hydrogen bond between the carboxy O atom and the aromatic N atom (Gotoh & Ishida, 2009). On the other hand, in 2-chloro-5-nitrobenzoic acid–quinoline (1/1) (ΔpK_a = 2.68; Gotoh & Ishida, 2009), 2-chloro-4-nitrobenzoic acid–

https://doi.org/10.1107/S2056989020013134

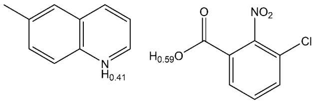
quinoline (1/1) ($\Delta pK_a = 2.86$; Gotoh & Ishida, 2011), 3-chloro-2-nitrobenzoic acid–6-nitroquinolune (1/1) (ΔpK_a = 1.42), 8-hydroxyquinolinium 3-chloro-2-nitrobenzoate (ΔpK_a = 3.02) and 3-chloro-2-nitrobenzoic acid–5-nitroquinoline (1/1) (ΔpK_a = 0.98) (Gotoh & Ishida, 2019*a*), 2-chloro-4-nitrobenzoic acid–5-nitroquinoline (1/1) ($\Delta pK_a = 0.76$), 5-chloro-2-nitrobenzoic acid–5-nitroquinoline (1/1) (ΔpK_a = 0.94) (Gotoh & Ishida, 2019*b*), such a short disordered hydrogen bond was not observed. We report here crystal structures of title four isomeric compounds, namely, 2-chloro-4-nitrobenzoic acid–6-methylquinoline (1/1), (I), 2-chloro-5-nitrobenzoic acid–6-methylquinoline (1/1), (II), 3-chloro-2-nitrobenzoic acid–6-methylquinoline (1/1), (III), and 4-chloro-2-nitrobenzoic acid–6-methylquinoline (1/1), (IV), in order to extend our studies of short hydrogen bonding and weak intermolecular interactions in the system of quinoline derivatives–chloro- and nitro-substituted benzoic acids. The ΔpK_a values are 3.16, 2.98, 3.38 and 3.23, respectively, for (I)–(IV).



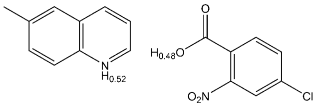
(I)



(II)



(III)



(IV)

2. Structural commentary

The molecular structures of compounds (I)–(IV) are shown in Fig. 1. In each compound, the acid and base molecules are linked by a hydrogen bond between the carboxy group and the N atom of the base. In (I), (III) and (IV), short hydrogen bonds are observed with N$\cdots$O distances of 2.5452 (12), 2.5640 (17) and 2.515 (2) Å, respectively. (Tables 1, 3 and 4). In these hydrogen bonds, the H atoms are each disordered over two sites; the occupancies of the O site and the N site refined to 0.65 (3) and 0.35 (3), 0.59 (4) and 0.41 (4), and 0.48 (5) and 0.52 (5), respectively, for (I), (III) and (IV). In (II), the H atom in the hydrogen bond is located at the O site with an N$\cdots$O distance of 2.6569 (13) Å (Table 2), being longer than those in (I), (III) and (IV). Weak C—H$\cdots$O hydrogen bonds are each observed in the acid–base unit of (II) (C15—H15$\cdots$O2; Table 2) and the unit of (III) (C8—H8$\cdots$O2; Table 3).

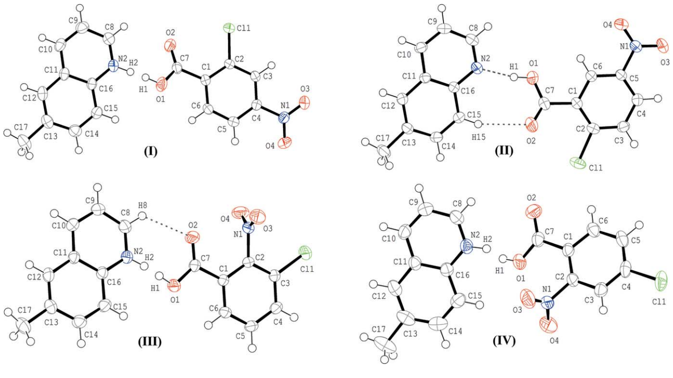


Figure 1
Molecular structures of the title compounds (I)–(IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. In the hydrogen bonds between the carboxy group and the N atom of the base of compounds (I), (III) and (IV), the H atoms are each disordered over two positions. Dashed lines in (II) and (III) indicate the O—H$\cdots$N and C—H$\cdots$O hydrogen bonds.

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1—H1$\cdots$N2	0.85 (2)	1.70 (2)	2.5452 (12)	174 (3)
N2—H2$\cdots$O1	0.88 (3)	1.66 (3)	2.5452 (12)	176 (3)
C8—H8$\cdots$O4^{i}	0.95	2.59	3.2307 (13)	125

Symmetry code: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1—H1$\cdots$N2	0.89 (2)	1.78 (2)	2.6569 (13)	169 (2)
C15—H15$\cdots$O2	0.95	2.46	3.3211 (14)	151

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1—H1$\cdots$N2	0.85 (3)	1.72 (3)	2.5640 (17)	174 (3)
N2—H2$\cdots$O1	0.88 (4)	1.69 (4)	2.5640 (17)	170 (4)
C5—H5$\cdots$O2^{i}	0.95	2.44	3.3245 (19)	155
C8—H8$\cdots$O2	0.95	2.46	3.1438 (19)	129

Symmetry code: (i) $x, y+1, z$.

Table 4
Hydrogen-bond geometry (Å, °) for (IV).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1—H1$\cdots$N2	0.84 (7)	1.70 (6)	2.514 (2)	163 (7)
N2—H2$\cdots$O1	0.87 (4)	1.67 (5)	2.514 (2)	162 (4)
C10—H10$\cdots$O2^{i}	0.95	2.54	3.364 (3)	145

Symmetry code: (i) $x, -y+1, z+\frac{1}{2}$.

In the hydrogen-bonded acid–base unit of compound (I), the quinoline ring system (N2/C8–C16) and the benzene ring (C1–C6) are almost coplanar with a dihedral angle of 1.11 (4)°, while the quinoline ring system and the carboxy group (O1/C7/O2) of the acid are twisted to each other with a dihedral angle of 28.59 (12)°. In the acid molecule, the benzene ring makes dihedral angles of 29.36 (12) and 8.24 (11)°, respectively, with the carboxy group and the nitro group (O3/N1/O4).

Similar to (I), the quinoline ring system (N2/C8–C16) in the hydrogen-bonded acid–base unit of (II) makes dihedral angles of 2.15 (4) and 24.51 (15)°, respectively, with the benzene ring and the carboxy group. The benzene ring makes dihedral angles of 22.63 (15) and 0.77 (14)°, respectively, with the carboxy group and the nitro group.

Compound (III) crystallizes in the non-centrosymmetric space group $P2_12_12_1$. In the acid–base unit, the quinoline ring system and the benzene ring of the acid are slightly twisted to each other with a dihedral angle of 14.50 (5)°. The quinoline ring system and the carboxy group are also slightly twisted with a dihedral angle of 12.55 (18)°. The benzene ring makes dihedral angles of 3.14 (18) and 85.04 (11)°, respectively, with the carboxy group and the nitro group.

Compound (IV) crystallizes in the non-centrosymmetric space group *Cc*. In the acid–base unit, the quinoline ring system and the benzene ring of the acid are twisted to each other with a dihedral angle of 30.39 (9)°. The quinoline ring system and the carboxy group are also twisted with a dihedral angle of 21.7 (3)°. The benzene ring makes dihedral angles of 16.4 (3) and 74.4 (3)°, respectively, with the carboxy group and the nitro group.

3. Supramolecular features

In the crystal of (I), the hydrogen-bonded acid-base units are linked by a C—H···O hydrogen bond (C8—H8···O4^{i}; symmetry code as given in Table 1), forming a zigzag chain propagating along the *c*-axis direction (Fig. 2). The acid–base units, which are related to each other by an inversion center, are linked together *via* π–π interactions between the quinoline ring system and the benzene ring of the acid molecule, forming a centrosymmetric dimeric unit (Fig. 3); the centroid–centroid distances are 3.7217 (6) and 3.7216 (6) Å, respectively, for $Cg1\cdots Cg2^{iii}$ and $Cg1\cdots Cg3^{iii}$, where *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, N2/C8–C11/C16 and C11–C16 rings, respectively [symmetry code: (iii) $-x + 1, -y + 1, -z + 1$]. The dimeric units are further linked into a column structure stacked along the *b*-axis direction through a weak π–π interaction between the benzene rings with $Cg1\cdots Cg1^{iv}$ = 3.9401 (6) Å [symmetry code: (iv) $-x + 1, -y + 2, -z + 1$]. The molecular chains are thus stacked into a layer parallel to the *bc* plane *via* these π–π interactions.

In the crystal of (II), the acid and base molecules are alternately stacked in a column *via* π–π interactions between the acid benzene ring and the quinoline ring system, so that the hydrogen-bonded acid–base units related by an inversion center are linked into a column structure along the *a*-axis direction (Fig. 4). The centroid–centroid distances are 3.6438 (6), 3.5745 (6), 3.6560 (6) and 3.7375 (6) Å, respectively, for $Cg1\cdots Cg2^{i}$, $Cg1\cdots Cg2^{ii}$, $Cg1\cdots Cg3^{i}$ and $Cg1\cdots Cg3^{ii}$, where *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, N2/C8–C11/C16 and C11–C16 rings, respectively [symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$]. There are no significant interactions between the columns.

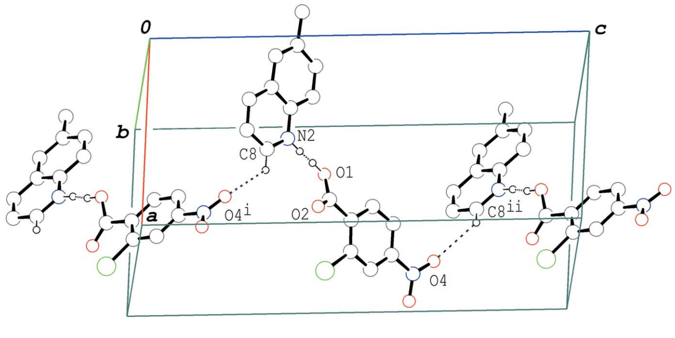


Figure 2
A packing diagram of (I), showing the hydrogen-bonded chain structure formed *via* the O—H···N/O····H—N and C—H···O hydrogen bonds (dashed lines). H atoms not involved in the hydrogen bonds are omitted for clarity. Symmetry codes: (i) $x, -y + \frac{2}{3}, z - \frac{1}{2}$; (ii) $x, -y + \frac{3}{2}, -z + \frac{1}{2}$.

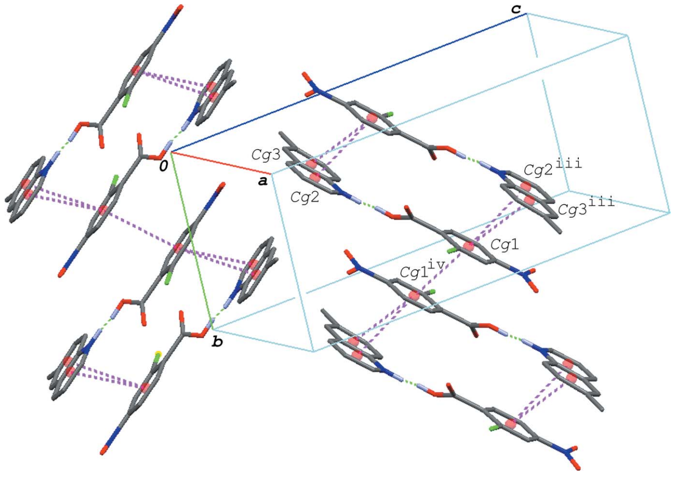


Figure 3
A packing diagram of (I), showing the column structure formed *via* the π–π interactions (magenta dashed lines). H atoms except for in the O—H···N/O····H—N hydrogen bonds (green dashed lines) are omitted for clarity. *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, N2/C8–C11/C16 and C11–C16 rings, respectively. Symmetry codes: (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, -y + 2, -z + 1$.

In the crystal of (III), the hydrogen-bonded acid–base units are linked by a C—H···O hydrogen bond (C5—H5···O2^{i};

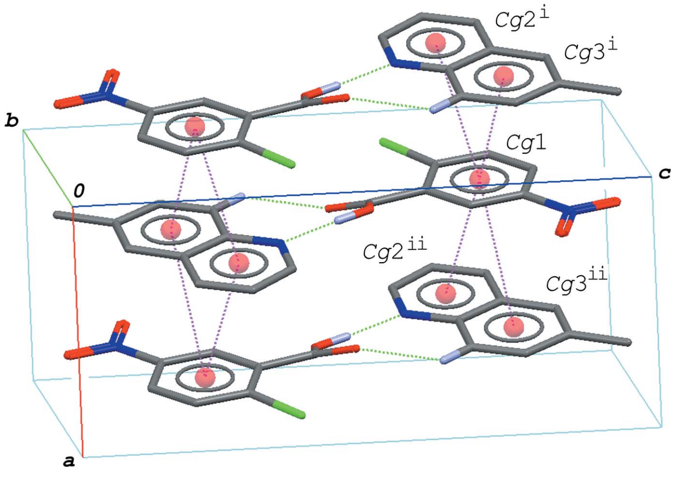


Figure 4
A packing diagram of (II), showing the column structure formed *via* the π–π interactions (magenta dashed lines). H atoms not involved in the O—H···N and C—H···O hydrogen bonds (green dashed lines) are omitted for clarity. *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, N2/C8–C11/C16 and C11–C16 rings, respectively. Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$.

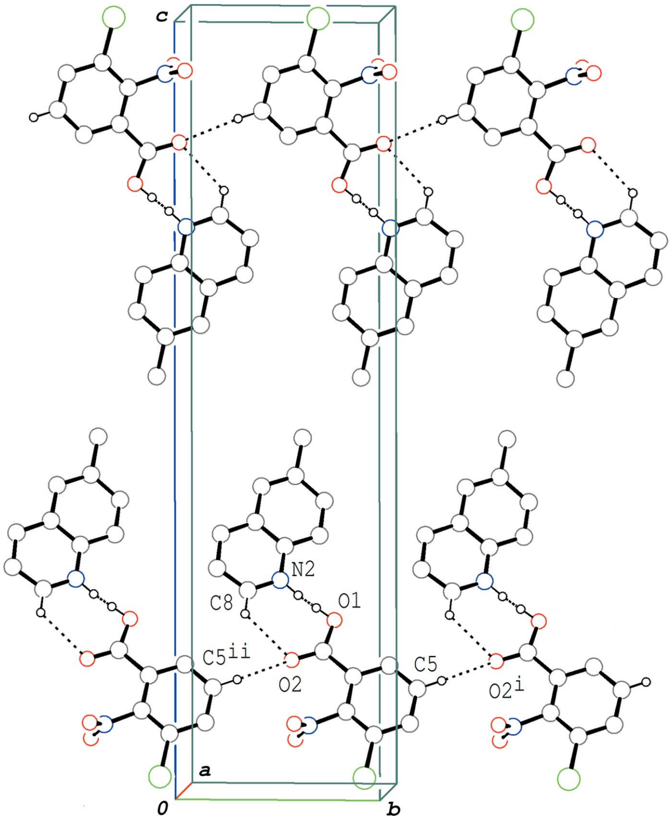


Figure 5
A packing diagram of (III), showing two tape structures (top and bottom) related by an inversion symmetry to each other, formed by O—H···N/O···H—N and C—H···O hydrogen bonds (dashed lines). H atoms not involved in the hydrogen bonds are omitted for clarity. Symmetry codes: (i) $x, y + 1, z$; (ii) $x, y - 1, z$.

symmetry code as in Table 3), forming a tape structure propagating along the *b*-axis direction (Fig. 5). The acid and base molecules are alternately stacked in a column along the *a* axis direction *via* π–π interactions between the acid ring and the quinoline ring system (Fig. 6), and thus the hydrogen-bonded acid–base units form a layer lying parallel to the *ab* plane. The centroid–centroid distances are 3.6415 (8), 3.6126 (8) and 3.6393 (8) Å, respectively, for $Cg1\cdots Cg2^{iii}$, $Cg1\cdots Cg3^{iii}$ and $Cg1\cdots Cg3^{iv}$, where *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, N2/C8–C11/C16 and C11–C16 rings, respectively [symmetry codes: (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$]. A short O···Cl contact [$O3\cdots Cl1^{v}$ = 3.0934 (14) Å; symmetry code: (v) $x - \frac{1}{2}, -y + \frac{3}{2}, -z$] is observed between the layers.

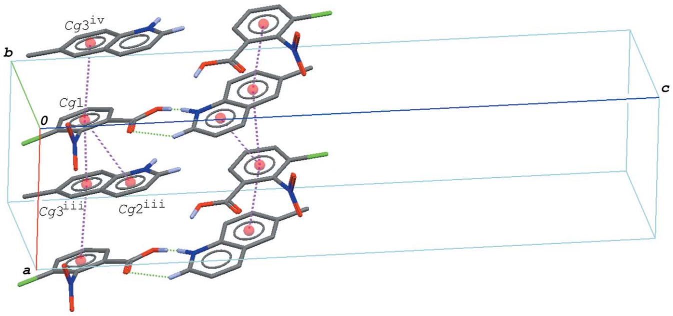


Figure 6
A packing diagram of (III), showing the column structure formed *via* the π–π interactions (magenta dashed lines). H atoms not involved in the O—H···N/O···H—N and C—H···O hydrogen bonds (green dashed lines) are omitted for clarity. *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, N2/C8–C11/C16 and C11–C16 rings, respectively. Symmetry codes: (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

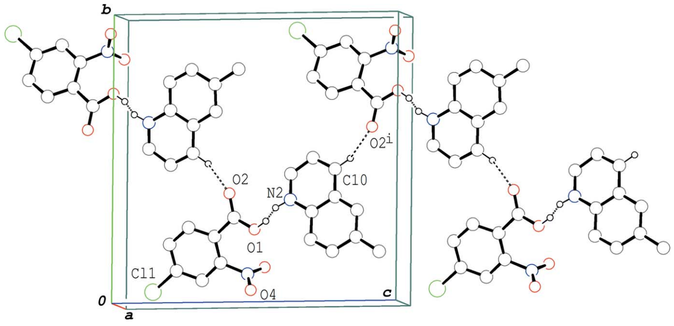


Figure 7
A packing diagram of (IV), showing the zigzag chain structure along the *c* axis *via* O—H···N/O···H—N and C—H···O hydrogen bonds. H atoms not involved in the hydrogen bonds are omitted for clarity. Symmetry code: (i) $x, -y + 1, z + \frac{1}{2}$.

In the crystal of (IV), the hydrogen-bonded acid–base units are linked into a zigzag chain structure propagating along the *c*-axis direction (Fig. 7) *via* C—H···O hydrogen bonds ($C10—H10\cdots O2^{i}$; symmetry code as in Table 4). The chains are further linked into a sheet parallel to the *bc* plane *via* an O···Cl short contact [$O4\cdots Cl1^{ii}$ = 3.017 (3) Å; (ii) $x, -y, z + \frac{1}{2}$]. Similar to (III), the acid and base molecules are alternately stacked in a column along the *a*-axis direction *via* π–π interactions between the acid ring and the quinoline ring system (Fig. 8), and thus the above sheets form a three-dimensional network. The centroid–centroid distances are 3.5813 (13), 3.7987 (14) and 3.7382 (14) Å, respectively, for $Cg1\cdots Cg2^{iii}$, $Cg1\cdots Cg3^{iii}$ and $Cg1\cdots Cg3^{iv}$, where *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, N2/C8–C11/C16 and C11–C16 rings,

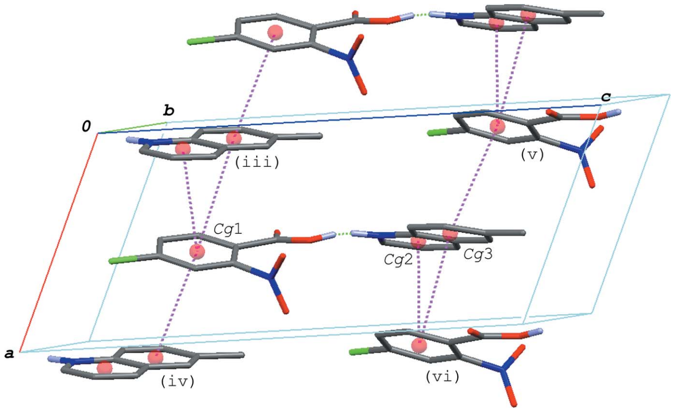


Figure 8
A packing diagram of (IV), showing the column structure formed *via* the π–π interactions (magenta dashed lines). H atoms not involved in the O—H···N/O···H—N hydrogen bonds (green dashed lines) are omitted for clarity. *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, N2/C8–C11/C16 and C11–C16 rings, respectively. Symmetry codes: (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - 1/2$: (v) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

respectively [symmetry codes: (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$].

Hirshfeld surfaces for compounds (I)–(IV) mapped over $d_{\rm norm}$ and shape index (Turner *et al.*, 2017; McKinnon *et al.*, 2004, 2007) are shown in Fig. 9. The C—H⋯O interactions in (I), (III) and (IV) are viewed as faint-red spots on the $d_{\rm norm}$ surfaces (black arrows in Fig. 9). In addition to these interactions, the O⋯Cl contacts in (III) and (IV) are shown as faint-red spots (magenta arrows). The π–π interactions between the acid ring and the quinoline ring system in (I)–(IV) are indicated by blue and red triangles on the shape index surfaces (white circles in Fig. 9).

4. Database survey

A search of the Cambridge Structural Database (Version 5.41, last update May 2020; Groom *et al.*, 2016) for organic co-crystals/salts of 6-methylquinoline with carboxylic acid derivatives showed two structures, namely, 6-methylquinoline hemikis(*trans*-but-2-enedioic acid) (Cambridge Structural Database refcode LASGUJ; Bekö *et al.*, 2012), sesquikis(6-methylquinoline) hemikis(quinoline) *trans*-but-2-enedioic acid (LASHAQ; Beko *et al.*, 2012). A search for organic co-crystals/salts of 2-chloro-4-nitrobenzoic acid, 2-chloro-5-nitrobenzoic acid, 3-chloro-2-nitrobenzoic acid and 4-chloro-2-nitrobenzoic acid gave 61, 12, 9 and 9 structures, respectively. Limiting the search for quinoline derivatives of these compounds gave 3, 2, 4 and 2 compounds, namely, for 2-chloro-4-nitrobenzoic acid: 2-chloro-4-nitrobenzoic acid–5-nitroquinoline (NUBHEA; Gotoh & Ishida, 2019*b*), 8-hydroxyquinolinium 2-chloro-4-nitrobenzoate (WOPDEM; Babu & Chandrasekaran, 2014), 2-chloro-4-nitrobenzoic acid–quinoline (1/1) (YAGFAP; Gotoh & Ishida, 2011), for 2-chloro-5-nitrobenzoic acid: 2-chloro-5-nitrobenzoic acid–quinoline (1/1) (AJIWIA; Gotoh & Ishida, 2009), 8-hydroxy-2-methylquinolinium 2-chloro-5-nitrobenzoate dihydrate (HIHPIY; Tan, 2007), for 3-chloro-2-nitrobenzoic acid: 3-chloro-2-nitrobenzoic acid–quinoline (1/1) (AJIWOG, Gotoh & Ishida, 2009), 3-chloro-2-nitrobenzoic acid–5-nitroquinoline (1/1) (XOWVUD; Gotoh & Ishida, 2019*a*), 3-chloro-2-nitrobenzoic acid–6-nitroquinoline (1/1) (XOWWAK, Gotoh & Ishida, 2019*a*), 8-hydroxyquinolin-1-ium 3-chloro-2-nitrobenzoate (XOWWEO; Gotoh & Ishida, 2019*a*), and for 4-chloro-2-nitrobenzoic acid: 4-chloro-2-nitrobenzoic acid–quinoline (AJIWUM; Gotoh & Ishida, 2009), 4-hydroxyquinolin-1-ium 4-chloro-2-nitrobenzoate (WOVZOZ; Gotoh & Ishida, 2019*c*). Of these compounds, AJIWOG and AJIWUM show disordered O—H⋯N/O⋯H—N hydrogen bonds, while WOVZOZ shows a disorder structure in the O—H⋯O hydrogen bond accompanied by a keto–enol tautomerization in the base molecule.

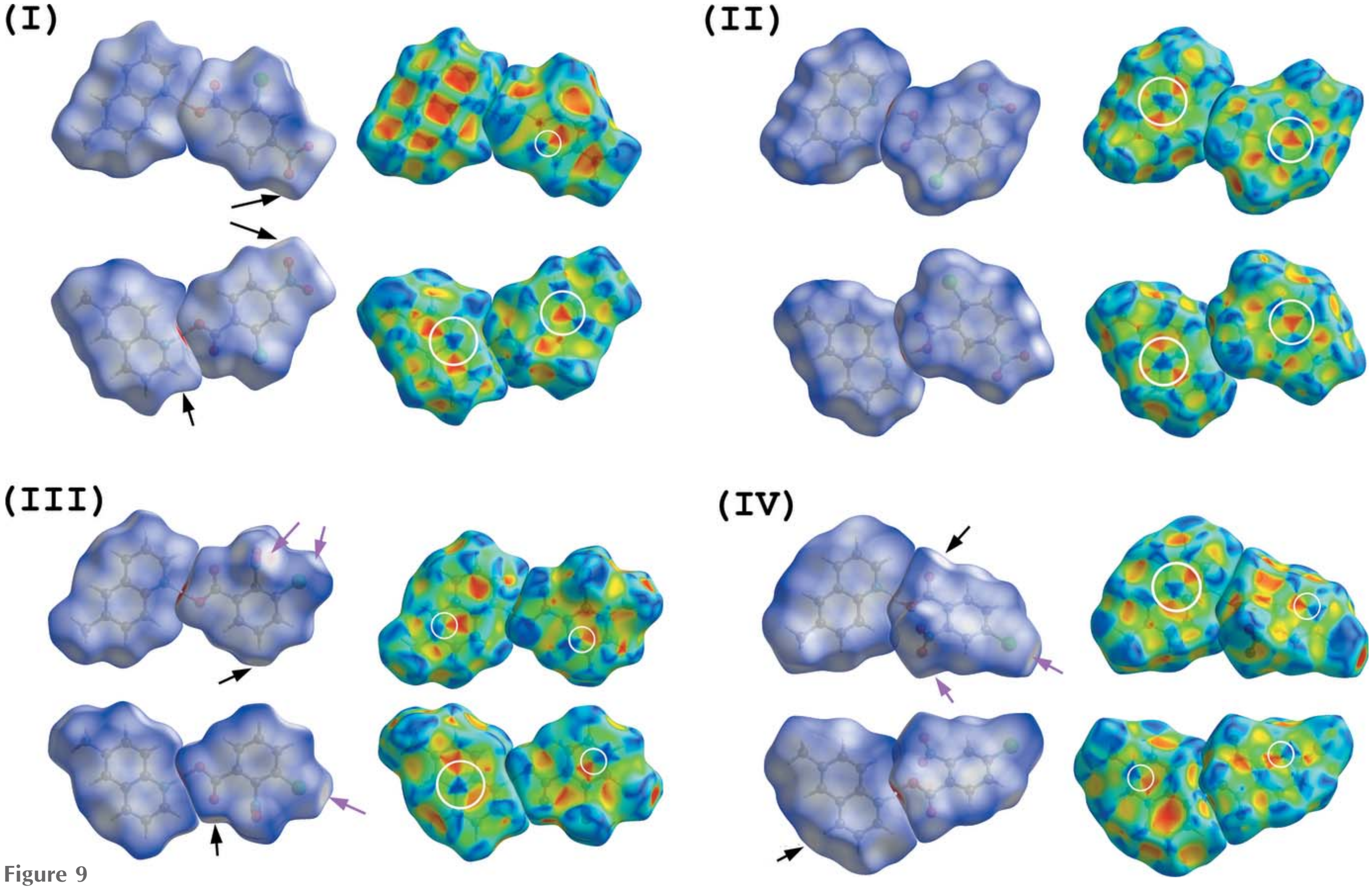


Figure 9
Hirshfeld surfaces [front (top) and back (bottom) views] for the compounds of (I)–(IV) mapped over $d_{\rm norm}$ and shape index, indicating the C—H⋯O interactions (black arrows), O⋯Cl contacts (magenta arrows) and π–π interactions (white circles).

Table 5
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	$C_7H_{3.65}ClNO_4\cdot C_{10}H_{9.35}N$	$C_7H_4ClNO_4\cdot C_{10}H_9N$	$C_7H_{3.59}ClNO_4\cdot C_{10}H_{9.41}N$	$C_7H_{3.48}ClNO_4\cdot C_{10}H_{9.52}N$
M_r	344.74	344.74	344.75	344.75
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$	Orthorhombic, $P2_12_12_1$	Monoclinic, Cc
Temperature (K)	185	186	190	185
a, b, c (Å)	9.5055 (2), 8.3019 (4), 19.5865 (4)	6.8693 (3), 7.6482 (4), 15.1195 (4)	7.1156 (4), 7.5854 (4), 28.8599 (14)	7.4271 (6), 14.4348 (6), 16.2208 (7)
α, β, γ (°)	90, 95.7214 (7), 90	78.218 (3), 81.1923 (18), 77.754 (3)	90, 90, 90	90, 113.203 (3), 90
V (Å^3)	1537.94 (8)	754.89 (6)	1557.70 (14)	1598.35 (16)
Z	4	2	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.27	0.28	0.27	0.26
Crystal size (mm)	0.40 × 0.35 × 0.35	0.45 × 0.35 × 0.30	0.30 × 0.30 × 0.17	0.28 × 0.25 × 0.20
Data collection				
Diffractometer	Rigaku R-AXIS RAPIDII	Rigaku R-AXIS RAPIDII	Rigaku R-AXIS RAPIDII	Rigaku R-AXIS RAPIDII
Absorption correction	Numerical (*NUMABS*; Higashi, 1999)	Numerical (*NUMABS*; Higashi, 1999)	Numerical (*NUMABS*; Higashi, 1999)	Numerical (*NUMABS*; Higashi, 1999)
T_{min}, T_{max}	0.887, 0.909	0.891, 0.920	0.938, 0.955	0.931, 0.949
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30539, 4487, 4065	15404, 4381, 3868	30061, 4532, 4365	16695, 4645, 4158
R_{int}	0.025	0.023	0.017	0.015
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.704	0.703	0.703	0.703
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.096, 1.06	0.036, 0.108, 1.05	0.028, 0.079, 1.06	0.030, 0.081, 1.09
No. of reflections	4487	4381	4532	4645
No. of parameters	225	222	225	225
No. of restraints	2	0	2	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.22	0.48, −0.26	0.31, −0.26	0.35, −0.16
Absolute structure	–	–	Flack x determined using 1821 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	Flack x determined using 1899 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	–	−0.014 (8)	−0.023 (9)

Computer programs: *PROCESS-AUTO* (Rigaku, 2006), *SHELXT* (Sheldrick, 2015*a*), *SHELXS97* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020), *CrystalStructure* (Rigaku, 2018) and *PLATON* (Spek, 2020).

5. Synthesis and crystallization

Single crystals of the title compounds (I)–(IV) were obtained by slow evaporation from acetonitrile solutions of 6-methylquinoline with chloro-nitrobenzoic acids in a 1:1 molar ratio at room temperature [80 ml acetonitrile solution of 6-methylquinoline (0.20 g) and chloro-nitrobenzoic acid (0.28 g for each acid)].

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. All H atoms in compounds (I)–(IV) were found in difference-Fourier maps. The O-bound H atom in (II) was refined freely; the refined distance is given in Table 2. For (I), (III) and (IV), H atoms in the N···H···O hydrogen bonds were found to be disordered over two positions in difference-Fourier maps. Since the site-occupancy factors and isotropic displacement parameters are strongly collated, the positional parameters and occupancy factors were refined, with bond length restraints of N—H = 0.88 (1) Å and O—H = 0.84 (1) Å, and with $U_{iso}(H) = 1.5U_{eq}(N \text{ or } O)$; the refined distances are given in Tables 1, 3 and 4. Other H atoms were positioned geometrically (C—H = 0.95 Å) and treated as riding, with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$.

References

Babu, B. & Chandrasekaran, J. (2014). Private Communication (refcode WOPDEM). CCDC, Cambridge, England.

Bekö, S. L., Schmidt, M. U. & Bond, A. D. (2012). *CrystEngComm*, **14**, 1967–1971.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Gotoh, K. & Ishida, H. (2009). *Acta Cryst.* C**65**, o534–o538.

Gotoh, K. & Ishida, H. (2011). *Acta Cryst.* E**67**, o2883.

Gotoh, K. & Ishida, H. (2019*a*). *Acta Cryst.* E**75**, 1552–1557.

Gotoh, K. & Ishida, H. (2019*b*). *Acta Cryst.* E**75**, 1694–1699.

Gotoh, K. & Ishida, H. (2019*c*). *Acta Cryst.* E**75**, 1853–1856.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.

Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

McKinnon, J. J., Spackman, M. A. & Mitchell, A. S. (2004). *Acta Cryst.* B**60**, 627–668.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

Rigaku (2006). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku (2018). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.

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

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.

Tan, T. (2007). *J. Mol. Struct.* **840**, 6–13.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia. http://hirshfeldsurface.net.

supporting information

Acta Cryst. (2020). E**76**, 1701-1707   [https://doi.org/10.1107/S2056989020013134]

Crystal structures of four isomeric hydrogen-bonded co-crystals of 6-methylquinoline with 2-chloro-4-nitrobenzoic acid, 2-chloro-5-nitrobenzoic acid, 3-chloro-2-nitrobenzoic acid and 4-chloro-2-nitrobenzoic acid

Kazuma Gotoh and Hiroyuki Ishida

Computing details

For all structures, data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO* (Rigaku, 2006); data reduction: *PROCESS-AUTO* (Rigaku, 2006). Program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*) for (I), (II); *SHELXS97* (Sheldrick, 2008) for (III), (IV). Program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015*b*) for (I); *SHELXL-2018/3* (Sheldrick, 2015*b*) for (II); *SHELXL2016/6* (Sheldrick, 2015b) for (III); *SHELXL2016/6* (Sheldrick, 2015*b*) for (IV). For all structures, molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2018) and *PLATON* (Spek, 2020).

2-Chloro-4-nitrobenzoic acid–6-methylquinoline (1/1) (I)

Crystal data

$C_7H_{3.65}ClNO_4·C_{10}H_{9.35}N$
$M_r = 344.74$
Monoclinic, $P2_1/c$
$a = 9.5055$ (2) Å
$b = 8.3019$ (4) Å
$c = 19.5865$ (4) Å
$\beta = 95.7214$ (7)°
$V = 1537.94$ (8) Å^3
$Z = 4$
$F(000) = 712.00$
$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 26323 reflections
$\theta = 3.1–30.2°$
$\mu = 0.27$ mm^{-1}
$T = 185$ K
Block, colorless
0.40 × 0.35 × 0.35 mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
$T_{min} = 0.887$, $T_{max} = 0.909$
30539 measured reflections
4487 independent reflections
4065 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 30.0°$, $\theta_{min} = 3.2°$
$h = -13 \rightarrow 12$
$k = -11 \rightarrow 11$
$l = -27 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.096$
$S = 1.06$
4487 reflections
225 parameters
2 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.329P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.87370 (3)	0.79426 (3)	0.44087 (2)	0.03134 (8)	
O1	0.42961 (8)	0.64577 (11)	0.42646 (5)	0.03635 (19)	
H1	0.401 (3)	0.576 (3)	0.3967 (11)	0.055*	0.65 (3)
O2	0.64551 (9)	0.55323 (11)	0.41332 (5)	0.0415 (2)	
O3	0.85703 (9)	1.17879 (11)	0.64471 (4)	0.03715 (19)	
O4	0.67137 (9)	1.12532 (11)	0.69548 (4)	0.03875 (19)	
N1	0.74667 (9)	1.10600 (10)	0.64913 (4)	0.02564 (17)	
N2	0.32928 (9)	0.44919 (10)	0.33444 (4)	0.02445 (16)	
H2	0.364 (4)	0.521 (4)	0.3649 (17)	0.037*	0.35 (3)
C1	0.61850 (9)	0.76377 (11)	0.49454 (4)	0.02042 (16)	
C2	0.75219 (9)	0.83696 (11)	0.49820 (4)	0.02126 (17)	
C3	0.79336 (9)	0.95089 (11)	0.54813 (5)	0.02240 (17)	
H3	0.883075	1.001906	0.549641	0.027*	
C4	0.70028 (10)	0.98778 (11)	0.59541 (4)	0.02162 (17)	
C5	0.56791 (10)	0.91744 (12)	0.59456 (5)	0.02394 (18)	
H5	0.506368	0.944280	0.628184	0.029*	
C6	0.52786 (10)	0.80690 (11)	0.54331 (5)	0.02350 (18)	
H6	0.436619	0.759387	0.541313	0.028*	
C7	0.56641 (10)	0.64206 (11)	0.44026 (5)	0.02361 (17)	
C8	0.40800 (11)	0.39905 (13)	0.28726 (5)	0.0284 (2)	
H8	0.500827	0.441308	0.287010	0.034*	
C9	0.36003 (12)	0.28509 (13)	0.23709 (5)	0.0314 (2)	
H9	0.418985	0.252719	0.203149	0.038*	
C10	0.22700 (12)	0.22130 (12)	0.23779 (5)	0.0291 (2)	
H10	0.193332	0.143923	0.204340	0.035*	
C11	0.14049 (10)	0.27092 (11)	0.28827 (5)	0.02387 (18)	
C12	0.00279 (11)	0.20841 (12)	0.29329 (5)	0.0285 (2)	
H12	−0.034075	0.128787	0.261562	0.034*	
C13	−0.07753 (11)	0.26074 (13)	0.34293 (6)	0.0294 (2)	
C14	−0.02173 (11)	0.38120 (13)	0.38945 (6)	0.0299 (2)	
H14	−0.078279	0.419813	0.423309	0.036*	
C15	0.11154 (11)	0.44368 (12)	0.38702 (5)	0.02705 (19)	

H15	0.146830	0.523118	0.419192	0.032*
C16	0.19535 (10)	0.38878 (11)	0.33634 (5)	0.02220 (17)
C17	−0.22358 (12)	0.19441 (16)	0.34909 (8)	0.0408 (3)
H17A	−0.290638	0.283656	0.350772	0.061*
H17B	−0.222599	0.130421	0.391184	0.061*
H17C	−0.252335	0.126106	0.309332	0.061*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02668 (13)	0.03764 (15)	0.03157 (13)	−0.00822 (9)	0.01214 (9)	−0.01037 (9)
O1	0.0247 (4)	0.0378 (4)	0.0445 (4)	0.0002 (3)	−0.0067 (3)	−0.0172 (3)
O2	0.0293 (4)	0.0412 (5)	0.0547 (5)	−0.0052 (3)	0.0083 (3)	−0.0239 (4)
O3	0.0343 (4)	0.0387 (4)	0.0387 (4)	−0.0130 (3)	0.0050 (3)	−0.0133 (3)
O4	0.0452 (5)	0.0433 (5)	0.0297 (4)	−0.0057 (4)	0.0133 (3)	−0.0115 (3)
N1	0.0282 (4)	0.0247 (4)	0.0239 (4)	−0.0008 (3)	0.0022 (3)	−0.0028 (3)
N2	0.0244 (4)	0.0227 (4)	0.0254 (4)	−0.0023 (3)	−0.0015 (3)	−0.0010 (3)
C1	0.0196 (4)	0.0194 (4)	0.0219 (4)	−0.0016 (3)	0.0006 (3)	0.0011 (3)
C2	0.0195 (4)	0.0228 (4)	0.0219 (4)	−0.0016 (3)	0.0043 (3)	−0.0005 (3)
C3	0.0197 (4)	0.0235 (4)	0.0241 (4)	−0.0042 (3)	0.0024 (3)	−0.0010 (3)
C4	0.0235 (4)	0.0200 (4)	0.0211 (4)	−0.0012 (3)	0.0011 (3)	−0.0012 (3)
C5	0.0219 (4)	0.0258 (4)	0.0247 (4)	−0.0006 (3)	0.0055 (3)	−0.0004 (3)
C6	0.0193 (4)	0.0246 (4)	0.0268 (4)	−0.0033 (3)	0.0034 (3)	0.0000 (3)
C7	0.0247 (4)	0.0213 (4)	0.0247 (4)	−0.0042 (3)	0.0019 (3)	−0.0004 (3)
C8	0.0274 (4)	0.0280 (5)	0.0297 (5)	−0.0020 (4)	0.0029 (4)	0.0016 (4)
C9	0.0375 (5)	0.0320 (5)	0.0256 (4)	0.0002 (4)	0.0072 (4)	−0.0014 (4)
C10	0.0389 (5)	0.0267 (5)	0.0212 (4)	−0.0027 (4)	0.0000 (4)	−0.0031 (3)
C11	0.0276 (4)	0.0214 (4)	0.0214 (4)	−0.0014 (3)	−0.0038 (3)	0.0008 (3)
C12	0.0286 (5)	0.0257 (4)	0.0295 (5)	−0.0047 (3)	−0.0060 (4)	0.0000 (3)
C13	0.0238 (4)	0.0268 (4)	0.0366 (5)	−0.0010 (4)	−0.0017 (4)	0.0065 (4)
C14	0.0280 (5)	0.0274 (5)	0.0346 (5)	0.0035 (4)	0.0052 (4)	0.0015 (4)
C15	0.0292 (5)	0.0234 (4)	0.0282 (4)	0.0006 (3)	0.0011 (3)	−0.0032 (3)
C16	0.0237 (4)	0.0197 (4)	0.0223 (4)	−0.0004 (3)	−0.0023 (3)	0.0003 (3)
C17	0.0269 (5)	0.0399 (6)	0.0553 (7)	−0.0065 (4)	0.0026 (5)	0.0073 (5)

Geometric parameters (Å, º)

Cl1—C2	1.7262 (9)	C8—C9	1.4069 (14)
O1—C7	1.3019 (12)	C8—H8	0.9500
O1—H1	0.847 (10)	C9—C10	1.3722 (16)
O2—C7	1.2111 (13)	C9—H9	0.9500
O3—N1	1.2211 (12)	C10—C11	1.4091 (14)
O4—N1	1.2215 (11)	C10—H10	0.9500
N1—C4	1.4739 (12)	C11—C12	1.4206 (14)
N2—C8	1.3134 (13)	C11—C16	1.4205 (12)
N2—C16	1.3722 (12)	C12—C13	1.3656 (16)
N2—H2	0.883 (10)	C12—H12	0.9500
C1—C6	1.3954 (13)	C13—C14	1.4196 (15)

C1—C2	1.4039 (12)	C13—C17	1.5096 (15)
C1—C7	1.5137 (12)	C14—C15	1.3741 (15)
C2—C3	1.3884 (12)	C14—H14	0.9500
C3—C4	1.3774 (13)	C15—C16	1.4090 (14)
C3—H3	0.9500	C15—H15	0.9500
C4—C5	1.3857 (13)	C17—H17A	0.9800
C5—C6	1.3851 (13)	C17—H17B	0.9800
C5—H5	0.9500	C17—H17C	0.9800
C6—H6	0.9500		

C7—O1—H1	112.0 (19)	C10—C9—C8	119.17 (10)
O3—N1—O4	123.98 (9)	C10—C9—H9	120.4
O3—N1—C4	118.49 (8)	C8—C9—H9	120.4
O4—N1—C4	117.53 (8)	C9—C10—C11	119.80 (9)
C8—N2—C16	119.89 (8)	C9—C10—H10	120.1
C8—N2—H2	119 (3)	C11—C10—H10	120.1
C16—N2—H2	121 (3)	C10—C11—C12	123.23 (9)
C6—C1—C2	118.13 (8)	C10—C11—C16	117.72 (9)
C6—C1—C7	118.10 (8)	C12—C11—C16	119.05 (9)
C2—C1—C7	123.77 (8)	C13—C12—C11	121.16 (9)
C3—C2—C1	121.40 (8)	C13—C12—H12	119.4
C3—C2—Cl1	115.99 (7)	C11—C12—H12	119.4
C1—C2—Cl1	122.60 (7)	C12—C13—C14	118.79 (9)
C4—C3—C2	118.04 (8)	C12—C13—C17	121.65 (10)
C4—C3—H3	121.0	C14—C13—C17	119.56 (10)
C2—C3—H3	121.0	C15—C14—C13	122.03 (10)
C3—C4—C5	122.79 (8)	C15—C14—H14	119.0
C3—C4—N1	117.48 (8)	C13—C14—H14	119.0
C5—C4—N1	119.73 (8)	C14—C15—C16	119.36 (9)
C6—C5—C4	118.14 (8)	C14—C15—H15	120.3
C6—C5—H5	120.9	C16—C15—H15	120.3
C4—C5—H5	120.9	N2—C16—C15	119.48 (8)
C5—C6—C1	121.48 (8)	N2—C16—C11	120.93 (9)
C5—C6—H6	119.3	C15—C16—C11	119.59 (9)
C1—C6—H6	119.3	C13—C17—H17A	109.5
O2—C7—O1	125.07 (9)	C13—C17—H17B	109.5
O2—C7—C1	122.59 (9)	H17A—C17—H17B	109.5
O1—C7—C1	112.34 (8)	C13—C17—H17C	109.5
N2—C8—C9	122.47 (9)	H17A—C17—H17C	109.5
N2—C8—H8	118.8	H17B—C17—H17C	109.5
C9—C8—H8	118.8		

C6—C1—C2—C3	−0.91 (13)	C16—N2—C8—C9	0.66 (15)
C7—C1—C2—C3	178.41 (8)	N2—C8—C9—C10	−1.13 (16)
C6—C1—C2—Cl1	−179.86 (7)	C8—C9—C10—C11	0.25 (16)
C7—C1—C2—Cl1	−0.55 (13)	C9—C10—C11—C12	−178.73 (9)
C1—C2—C3—C4	1.56 (14)	C9—C10—C11—C16	0.97 (14)
Cl1—C2—C3—C4	−179.42 (7)	C10—C11—C12—C13	−179.69 (9)

C2—C3—C4—C5	−0.70 (14)	C16—C11—C12—C13	0.62 (14)
C2—C3—C4—N1	178.55 (8)	C11—C12—C13—C14	0.77 (15)
O3—N1—C4—C3	8.31 (13)	C11—C12—C13—C17	−179.57 (9)
O4—N1—C4—C3	−171.89 (9)	C12—C13—C14—C15	−1.57 (16)
O3—N1—C4—C5	−172.41 (9)	C17—C13—C14—C15	178.76 (10)
O4—N1—C4—C5	7.39 (13)	C13—C14—C15—C16	0.91 (15)
C3—C4—C5—C6	−0.78 (14)	C8—N2—C16—C15	−179.81 (9)
N1—C4—C5—C6	179.98 (8)	C8—N2—C16—C11	0.65 (14)
C4—C5—C6—C1	1.46 (14)	C14—C15—C16—N2	−179.02 (9)
C2—C1—C6—C5	−0.64 (14)	C14—C15—C16—C11	0.53 (14)
C7—C1—C6—C5	180.00 (8)	C10—C11—C16—N2	−1.45 (13)
C6—C1—C7—O2	−151.53 (10)	C12—C11—C16—N2	178.26 (9)
C2—C1—C7—O2	29.15 (15)	C10—C11—C16—C15	179.01 (9)
C6—C1—C7—O1	28.79 (12)	C12—C11—C16—C15	−1.28 (13)
C2—C1—C7—O1	−150.52 (9)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.85 (2)	1.70 (2)	2.5452 (12)	174 (3)
N2—H2···O1	0.88 (3)	1.66 (3)	2.5452 (12)	176 (3)
C8—H8···O4^{i}	0.95	2.59	3.2307 (13)	125

Symmetry code: (i) x, $-y$+3/2, z−1/2.

2-Chloro-5-nitrobenzoic acid–6-methylquinoline (1/1) (II)

Crystal data

$C_7H_4ClNO_4{\cdot}C_{10}H_9N$
M_r = 344.74
Triclinic, $P\overline{1}$
a = 6.8693 (3) Å
b = 7.6482 (4) Å
c = 15.1195 (4) Å
α = 78.218 (3)°
β = 81.1923 (18)°
γ = 77.754 (3)°
V = 754.89 (6) Å^3

Z = 2
F(000) = 356.00
D_x = 1.517 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 13517 reflections
θ = 3.1–30.1°
μ = 0.28 mm^{-1}
T = 186 K
Block, colorless
0.45 × 0.35 × 0.30 mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.891, T_{max} = 0.920
15404 measured reflections

4381 independent reflections
3868 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 30.0°, θ_{min} = 3.1°
h = −9→9
k = −10→10
l = −20→21

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.108$	$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 0.1585P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
4381 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
222 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.11678 (4)	0.98086 (4)	0.61864 (2)	0.03561 (10)
O1	0.21038 (15)	0.43541 (12)	0.54709 (6)	0.0366 (2)
O2	0.28610 (18)	0.71213 (14)	0.49895 (6)	0.0478 (3)
O3	0.18489 (15)	0.29378 (13)	0.96192 (6)	0.0392 (2)
O4	0.25163 (16)	0.14131 (12)	0.85221 (6)	0.0405 (2)
N1	0.20962 (14)	0.28451 (13)	0.88057 (6)	0.02681 (18)
N2	0.29763 (14)	0.34416 (12)	0.38322 (6)	0.02569 (18)
C1	0.19890 (14)	0.60827 (13)	0.65842 (7)	0.02253 (19)
C2	0.15118 (15)	0.77299 (14)	0.69035 (7)	0.02393 (19)
C3	0.12289 (16)	0.77660 (14)	0.78333 (7)	0.0264 (2)
H3	0.091426	0.890115	0.803551	0.032*
C4	0.14004 (15)	0.61713 (14)	0.84642 (7)	0.0254 (2)
H4	0.119312	0.619066	0.909822	0.030*
C5	0.18819 (14)	0.45521 (13)	0.81441 (6)	0.02191 (18)
C6	0.21638 (15)	0.44738 (13)	0.72259 (7)	0.02259 (19)
H6	0.247515	0.333038	0.703216	0.027*
C7	0.23535 (16)	0.59389 (15)	0.55899 (7)	0.0274 (2)
C8	0.34550 (16)	0.16678 (15)	0.38795 (7)	0.0279 (2)
H8	0.346849	0.091817	0.446377	0.033*
C9	0.39475 (17)	0.08253 (14)	0.31103 (8)	0.0284 (2)
H9	0.429397	−0.046122	0.317664	0.034*
C10	0.39200 (16)	0.18891 (14)	0.22624 (7)	0.0267 (2)
H10	0.424134	0.134301	0.173486	0.032*
C11	0.34115 (14)	0.38015 (13)	0.21768 (7)	0.02121 (18)
C12	0.33604 (15)	0.50006 (14)	0.13253 (7)	0.02423 (19)
H12	0.364652	0.451051	0.078062	0.029*
C13	0.29069 (15)	0.68496 (14)	0.12730 (7)	0.02410 (19)
C14	0.24533 (16)	0.75428 (14)	0.20953 (8)	0.0271 (2)

H14	0.212931	0.882237	0.206693	0.032*
C15	0.24652 (16)	0.64331 (14)	0.29307 (7)	0.0264 (2)
H15	0.214505	0.694420	0.346914	0.032*
C16	0.29544 (14)	0.45298 (13)	0.29885 (6)	0.02121 (18)
C17	0.28690 (19)	0.81553 (17)	0.03801 (8)	0.0341 (2)
H17A	0.323370	0.747133	−0.012173	0.051*
H17B	0.382979	0.895687	0.034211	0.051*
H17C	0.151890	0.888699	0.033913	0.051*
H1	0.243 (3)	0.420 (3)	0.4899 (15)	0.064 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.03973 (16)	0.02267 (14)	0.03659 (16)	−0.00175 (10)	−0.00100 (11)	0.00595 (10)
O1	0.0568 (6)	0.0320 (4)	0.0209 (4)	−0.0110 (4)	0.0014 (3)	−0.0059 (3)
O2	0.0815 (8)	0.0429 (5)	0.0220 (4)	−0.0271 (5)	−0.0024 (4)	0.0010 (4)
O3	0.0584 (6)	0.0364 (5)	0.0194 (4)	−0.0069 (4)	−0.0037 (3)	0.0005 (3)
O4	0.0648 (6)	0.0216 (4)	0.0315 (4)	−0.0031 (4)	−0.0064 (4)	−0.0010 (3)
N1	0.0315 (4)	0.0243 (4)	0.0227 (4)	−0.0046 (3)	−0.0038 (3)	0.0002 (3)
N2	0.0299 (4)	0.0250 (4)	0.0208 (4)	−0.0049 (3)	−0.0029 (3)	−0.0012 (3)
C1	0.0227 (4)	0.0234 (5)	0.0203 (4)	−0.0042 (3)	−0.0029 (3)	−0.0012 (3)
C2	0.0222 (4)	0.0215 (4)	0.0262 (5)	−0.0043 (3)	−0.0032 (3)	0.0007 (3)
C3	0.0291 (5)	0.0209 (4)	0.0292 (5)	−0.0040 (4)	−0.0023 (4)	−0.0061 (4)
C4	0.0278 (5)	0.0265 (5)	0.0221 (4)	−0.0054 (4)	−0.0022 (3)	−0.0050 (4)
C5	0.0233 (4)	0.0213 (4)	0.0202 (4)	−0.0048 (3)	−0.0034 (3)	−0.0001 (3)
C6	0.0250 (4)	0.0213 (4)	0.0208 (4)	−0.0038 (3)	−0.0027 (3)	−0.0028 (3)
C7	0.0303 (5)	0.0297 (5)	0.0212 (5)	−0.0052 (4)	−0.0042 (4)	−0.0016 (4)
C8	0.0298 (5)	0.0249 (5)	0.0269 (5)	−0.0066 (4)	−0.0042 (4)	0.0027 (4)
C9	0.0310 (5)	0.0183 (4)	0.0347 (5)	−0.0046 (4)	−0.0040 (4)	−0.0015 (4)
C10	0.0308 (5)	0.0201 (4)	0.0293 (5)	−0.0050 (4)	−0.0006 (4)	−0.0065 (4)
C11	0.0217 (4)	0.0193 (4)	0.0226 (4)	−0.0049 (3)	−0.0014 (3)	−0.0035 (3)
C12	0.0274 (5)	0.0250 (5)	0.0203 (4)	−0.0060 (4)	−0.0013 (3)	−0.0039 (3)
C13	0.0252 (4)	0.0234 (5)	0.0230 (5)	−0.0067 (4)	−0.0047 (3)	0.0010 (3)
C14	0.0326 (5)	0.0188 (4)	0.0298 (5)	−0.0035 (4)	−0.0067 (4)	−0.0033 (4)
C15	0.0335 (5)	0.0209 (5)	0.0249 (5)	−0.0023 (4)	−0.0043 (4)	−0.0064 (4)
C16	0.0223 (4)	0.0204 (4)	0.0206 (4)	−0.0042 (3)	−0.0024 (3)	−0.0028 (3)
C17	0.0424 (6)	0.0308 (5)	0.0268 (5)	−0.0099 (5)	−0.0071 (4)	0.0059 (4)

Geometric parameters (Å, º)

Cl1—C2	1.7245 (10)	C8—C9	1.4055 (16)
O1—C7	1.3106 (14)	C8—H8	0.9500
O1—H1	0.89 (2)	C9—C10	1.3713 (15)
O2—C7	1.2104 (14)	C9—H9	0.9500
O3—N1	1.2302 (12)	C10—C11	1.4134 (13)
O4—N1	1.2192 (13)	C10—H10	0.9500
N1—C5	1.4686 (13)	C11—C16	1.4149 (13)
N2—C8	1.3161 (14)	C11—C12	1.4205 (13)

N2—C16	1.3737 (12)	C12—C13	1.3705 (14)
C1—C2	1.3972 (14)	C12—H12	0.9500
C1—C6	1.3984 (13)	C13—C14	1.4157 (15)
C1—C7	1.5084 (14)	C13—C17	1.5066 (14)
C2—C3	1.3946 (15)	C14—C15	1.3706 (15)
C3—C4	1.3819 (15)	C14—H14	0.9500
C3—H3	0.9500	C15—C16	1.4103 (14)
C4—C5	1.3781 (14)	C15—H15	0.9500
C4—H4	0.9500	C17—H17A	0.9800
C5—C6	1.3838 (14)	C17—H17B	0.9800
C6—H6	0.9500	C17—H17C	0.9800

C7—O1—H1	112.6 (13)	C10—C9—H9	120.5
O4—N1—O3	123.42 (10)	C8—C9—H9	120.5
O4—N1—C5	118.51 (9)	C9—C10—C11	119.73 (10)
O3—N1—C5	118.07 (9)	C9—C10—H10	120.1
C8—N2—C16	118.47 (9)	C11—C10—H10	120.1
C2—C1—C6	117.92 (9)	C10—C11—C16	117.36 (9)
C2—C1—C7	123.90 (9)	C10—C11—C12	123.30 (9)
C6—C1—C7	118.17 (9)	C16—C11—C12	119.33 (9)
C3—C2—C1	120.97 (9)	C13—C12—C11	121.38 (9)
C3—C2—Cl1	116.41 (8)	C13—C12—H12	119.3
C1—C2—Cl1	122.59 (8)	C11—C12—H12	119.3
C4—C3—C2	120.83 (10)	C12—C13—C14	118.14 (9)
C4—C3—H3	119.6	C12—C13—C17	122.58 (10)
C2—C3—H3	119.6	C14—C13—C17	119.27 (10)
C5—C4—C3	117.86 (9)	C15—C14—C13	122.32 (9)
C5—C4—H4	121.1	C15—C14—H14	118.8
C3—C4—H4	121.1	C13—C14—H14	118.8
C4—C5—C6	122.59 (9)	C14—C15—C16	119.78 (9)
C4—C5—N1	118.54 (9)	C14—C15—H15	120.1
C6—C5—N1	118.86 (9)	C16—C15—H15	120.1
C5—C6—C1	119.81 (9)	N2—C16—C15	118.88 (9)
C5—C6—H6	120.1	N2—C16—C11	122.08 (9)
C1—C6—H6	120.1	C15—C16—C11	119.03 (9)
O2—C7—O1	124.98 (10)	C13—C17—H17A	109.5
O2—C7—C1	123.97 (10)	C13—C17—H17B	109.5
O1—C7—C1	111.02 (9)	H17A—C17—H17B	109.5
N2—C8—C9	123.38 (10)	C13—C17—H17C	109.5
N2—C8—H8	118.3	H17A—C17—H17C	109.5
C9—C8—H8	118.3	H17B—C17—H17C	109.5
C10—C9—C8	118.97 (10)		

C6—C1—C2—C3	0.31 (15)	C16—N2—C8—C9	0.03 (16)
C7—C1—C2—C3	−178.82 (10)	N2—C8—C9—C10	−0.48 (17)
C6—C1—C2—Cl1	−177.73 (7)	C8—C9—C10—C11	0.35 (16)
C7—C1—C2—Cl1	3.14 (14)	C9—C10—C11—C16	0.19 (15)
C1—C2—C3—C4	−0.43 (16)	C9—C10—C11—C12	179.57 (10)

Cl1—C2—C3—C4	177.73 (8)	C10—C11—C12—C13	−178.37 (10)
C2—C3—C4—C5	0.75 (16)	C16—C11—C12—C13	0.99 (15)
C3—C4—C5—C6	−1.02 (16)	C11—C12—C13—C14	−1.05 (15)
C3—C4—C5—N1	179.20 (9)	C11—C12—C13—C17	179.13 (9)
O4—N1—C5—C4	179.79 (10)	C12—C13—C14—C15	0.36 (16)
O3—N1—C5—C4	−0.50 (15)	C17—C13—C14—C15	−179.82 (10)
O4—N1—C5—C6	−0.01 (15)	C13—C14—C15—C16	0.40 (16)
O3—N1—C5—C6	179.71 (10)	C8—N2—C16—C15	−179.29 (10)
C4—C5—C6—C1	0.93 (16)	C8—N2—C16—C11	0.55 (15)
N1—C5—C6—C1	−179.29 (8)	C14—C15—C16—N2	179.39 (9)
C2—C1—C6—C5	−0.54 (15)	C14—C15—C16—C11	−0.45 (15)
C7—C1—C6—C5	178.64 (9)	C10—C11—C16—N2	−0.65 (14)
C2—C1—C7—O2	23.08 (17)	C12—C11—C16—N2	179.94 (9)
C6—C1—C7—O2	−156.05 (12)	C10—C11—C16—C15	179.19 (9)
C2—C1—C7—O1	−158.73 (10)	C12—C11—C16—C15	−0.22 (14)
C6—C1—C7—O1	22.14 (13)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.89 (2)	1.78 (2)	2.6569 (13)	169 (2)
C15—H15···O2	0.95	2.46	3.3211 (14)	151

3-Chloro-2-nitrobenzoic acid–6-methylquinoline (1/1) (III)

Crystal data

$C_7H_{3.59}ClNO_4 \cdot C_{10}H_{9.41}N$
$M_r = 344.75$
Orthorhombic, $P2_12_12_1$
$a = 7.1156\ (4)$ Å
$b = 7.5854\ (4)$ Å
$c = 28.8599\ (14)$ Å
$V = 1557.70\ (14)$ Å^3
$Z = 4$
$F(000) = 712.00$

$D_x = 1.470$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 28109 reflections
$\theta = 3.0$–$30.0°$
$\mu = 0.27$ mm^{-1}
$T = 190$ K
Block, colorless
0.30 × 0.30 × 0.17 mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
$T_{min} = 0.938$, $T_{max} = 0.955$
30061 measured reflections

4532 independent reflections
4365 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 30.0°$, $\theta_{min} = 3.0°$
$h = -10 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -39 \rightarrow 40$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.079$
$S = 1.06$

4532 reflections
225 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.1455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Absolute structure: Flack *x* determined using 1821 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.014 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Cl1	0.53139 (7)	0.88067 (5)	0.01741 (2)	0.03788 (11)	
O1	0.27295 (18)	0.75649 (15)	0.22566 (4)	0.0324 (2)	
H1	0.236 (6)	0.671 (4)	0.2421 (12)	0.049*	0.59 (4)
O2	0.3168 (2)	0.54391 (16)	0.17307 (4)	0.0419 (3)	
O3	0.2617 (2)	0.56590 (17)	0.07241 (4)	0.0410 (3)	
O4	0.55968 (19)	0.53587 (15)	0.08592 (5)	0.0385 (3)	
N1	0.41299 (18)	0.61877 (16)	0.08702 (4)	0.0263 (2)	
N2	0.18381 (18)	0.49896 (17)	0.27884 (4)	0.0260 (2)	
H2	0.203 (8)	0.585 (5)	0.2590 (16)	0.039*	0.41 (4)
C1	0.37616 (18)	0.84027 (16)	0.15112 (4)	0.0210 (2)	
C2	0.42073 (19)	0.80125 (17)	0.10505 (4)	0.0216 (2)	
C3	0.4747 (2)	0.93226 (17)	0.07416 (4)	0.0240 (2)	
C4	0.4842 (2)	1.10660 (18)	0.08878 (5)	0.0265 (3)	
H4	0.520281	1.196857	0.067766	0.032*	
C5	0.4404 (2)	1.14758 (18)	0.13447 (5)	0.0272 (3)	
H5	0.446936	1.266384	0.144760	0.033*	
C6	0.38715 (19)	1.01549 (18)	0.16517 (5)	0.0246 (2)	
H6	0.357703	1.045362	0.196302	0.030*	
C7	0.3188 (2)	0.69810 (18)	0.18471 (5)	0.0245 (3)	
C8	0.2211 (2)	0.3372 (2)	0.26449 (5)	0.0297 (3)	
H8	0.261320	0.320660	0.233404	0.036*	
C9	0.2039 (2)	0.18918 (19)	0.29319 (5)	0.0307 (3)	
H9	0.229500	0.074532	0.281546	0.037*	
C10	0.1493 (2)	0.21234 (19)	0.33840 (5)	0.0282 (3)	
H10	0.138409	0.113530	0.358444	0.034*	
C11	0.10940 (18)	0.38383 (19)	0.35510 (4)	0.0234 (2)	
C12	0.0566 (2)	0.4191 (2)	0.40170 (5)	0.0269 (3)	
H12	0.046576	0.324225	0.423028	0.032*	
C13	0.0200 (2)	0.5876 (2)	0.41648 (5)	0.0283 (3)	
C14	0.0319 (2)	0.7280 (2)	0.38397 (5)	0.0311 (3)	
H14	0.003183	0.844465	0.393774	0.037*	

C15	0.0841 (2)	0.69943 (19)	0.33867 (5)	0.0292 (3)
H15	0.091762	0.795472	0.317624	0.035*
C16	0.12609 (19)	0.52672 (18)	0.32360 (5)	0.0233 (2)
C17	−0.0287 (3)	0.6272 (3)	0.46621 (5)	0.0399 (4)
H17A	−0.128360	0.716224	0.467272	0.060*
H17B	0.082912	0.671801	0.482279	0.060*
H17C	−0.072283	0.519138	0.481428	0.060*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0610 (2)	0.03165 (18)	0.02096 (15)	−0.00237 (17)	0.01009 (15)	0.00035 (13)
O1	0.0498 (7)	0.0250 (5)	0.0223 (5)	−0.0041 (5)	0.0099 (5)	−0.0005 (4)
O2	0.0751 (9)	0.0223 (5)	0.0282 (5)	−0.0037 (5)	0.0160 (6)	0.0008 (4)
O3	0.0507 (7)	0.0332 (6)	0.0390 (6)	−0.0137 (5)	−0.0115 (5)	−0.0032 (5)
O4	0.0478 (6)	0.0249 (5)	0.0427 (6)	0.0058 (5)	0.0072 (5)	−0.0060 (5)
N1	0.0391 (6)	0.0201 (5)	0.0197 (5)	−0.0037 (5)	0.0015 (4)	−0.0007 (4)
N2	0.0325 (6)	0.0245 (5)	0.0209 (5)	−0.0020 (5)	0.0034 (4)	0.0025 (4)
C1	0.0240 (5)	0.0193 (5)	0.0199 (5)	−0.0003 (4)	0.0020 (4)	0.0011 (4)
C2	0.0258 (5)	0.0173 (5)	0.0215 (5)	−0.0005 (4)	0.0004 (4)	−0.0006 (4)
C3	0.0298 (6)	0.0222 (5)	0.0198 (5)	0.0002 (5)	0.0032 (5)	0.0012 (4)
C4	0.0324 (6)	0.0197 (5)	0.0274 (6)	−0.0006 (5)	0.0027 (5)	0.0033 (5)
C5	0.0341 (7)	0.0187 (5)	0.0289 (6)	0.0012 (5)	0.0029 (5)	−0.0017 (5)
C6	0.0300 (6)	0.0210 (5)	0.0228 (6)	0.0017 (5)	0.0037 (5)	−0.0021 (5)
C7	0.0302 (6)	0.0226 (6)	0.0209 (6)	−0.0012 (5)	0.0038 (5)	0.0029 (5)
C8	0.0375 (7)	0.0289 (7)	0.0227 (6)	−0.0030 (6)	0.0033 (5)	−0.0012 (5)
C9	0.0409 (8)	0.0219 (6)	0.0292 (7)	−0.0017 (6)	0.0016 (6)	−0.0021 (5)
C10	0.0349 (7)	0.0229 (6)	0.0268 (6)	−0.0034 (5)	0.0005 (5)	0.0030 (5)
C11	0.0247 (5)	0.0238 (5)	0.0218 (5)	−0.0027 (5)	−0.0009 (4)	0.0023 (5)
C12	0.0293 (6)	0.0307 (7)	0.0207 (6)	−0.0033 (5)	0.0006 (5)	0.0043 (5)
C13	0.0275 (6)	0.0346 (7)	0.0228 (6)	−0.0013 (5)	0.0025 (5)	−0.0005 (5)
C14	0.0346 (7)	0.0273 (6)	0.0313 (7)	0.0020 (6)	0.0062 (6)	−0.0014 (5)
C15	0.0356 (7)	0.0229 (6)	0.0291 (6)	0.0008 (5)	0.0051 (6)	0.0034 (5)
C16	0.0246 (5)	0.0234 (6)	0.0220 (6)	−0.0013 (4)	0.0012 (5)	0.0022 (5)
C17	0.0464 (9)	0.0483 (9)	0.0251 (7)	0.0006 (8)	0.0071 (6)	−0.0055 (7)

Geometric parameters (Å, º)

Cl1—C3	1.7316 (13)	C8—C9	1.401 (2)
O1—C7	1.3035 (17)	C8—H8	0.9500
O1—H1	0.847 (13)	C9—C10	1.372 (2)
O2—C7	1.2170 (18)	C9—H9	0.9500
O3—N1	1.2238 (18)	C10—C11	1.416 (2)
O4—N1	1.2189 (18)	C10—H10	0.9500
N1—C2	1.4797 (17)	C11—C16	1.4197 (18)
N2—C8	1.322 (2)	C11—C12	1.4217 (18)
N2—C16	1.3717 (17)	C12—C13	1.372 (2)
N2—H2	0.879 (14)	C12—H12	0.9500

C1—C6	1.3918 (18)	C13—C14	1.421 (2)
C1—C2	1.3986 (17)	C13—C17	1.507 (2)
C1—C7	1.5065 (18)	C14—C15	1.376 (2)
C2—C3	1.3890 (17)	C14—H14	0.9500
C3—C4	1.3899 (19)	C15—C16	1.4124 (19)
C4—C5	1.3900 (19)	C15—H15	0.9500
C4—H4	0.9500	C17—H17A	0.9800
C5—C6	1.3902 (19)	C17—H17B	0.9800
C5—H5	0.9500	C17—H17C	0.9800
C6—H6	0.9500		

C7—O1—H1	109 (3)	C10—C9—C8	118.97 (14)
O4—N1—O3	125.11 (13)	C10—C9—H9	120.5
O4—N1—C2	117.38 (12)	C8—C9—H9	120.5
O3—N1—C2	117.42 (13)	C9—C10—C11	119.86 (13)
C8—N2—C16	119.84 (12)	C9—C10—H10	120.1
C8—N2—H2	117 (4)	C11—C10—H10	120.1
C16—N2—H2	123 (4)	C10—C11—C16	117.81 (12)
C6—C1—C2	117.80 (11)	C10—C11—C12	123.23 (13)
C6—C1—C7	120.75 (11)	C16—C11—C12	118.95 (13)
C2—C1—C7	121.45 (11)	C13—C12—C11	121.31 (13)
C3—C2—C1	121.42 (12)	C13—C12—H12	119.3
C3—C2—N1	117.00 (11)	C11—C12—H12	119.3
C1—C2—N1	121.58 (11)	C12—C13—C14	118.75 (13)
C2—C3—C4	119.96 (12)	C12—C13—C17	121.67 (14)
C2—C3—Cl1	120.65 (10)	C14—C13—C17	119.56 (15)
C4—C3—Cl1	119.39 (10)	C15—C14—C13	121.68 (14)
C3—C4—C5	119.33 (12)	C15—C14—H14	119.2
C3—C4—H4	120.3	C13—C14—H14	119.2
C5—C4—H4	120.3	C14—C15—C16	119.71 (13)
C4—C5—C6	120.30 (12)	C14—C15—H15	120.1
C4—C5—H5	119.9	C16—C15—H15	120.1
C6—C5—H5	119.9	N2—C16—C15	119.72 (12)
C5—C6—C1	121.19 (12)	N2—C16—C11	120.72 (12)
C5—C6—H6	119.4	C15—C16—C11	119.55 (12)
C1—C6—H6	119.4	C13—C17—H17A	109.5
O2—C7—O1	125.02 (13)	C13—C17—H17B	109.5
O2—C7—C1	120.90 (12)	H17A—C17—H17B	109.5
O1—C7—C1	114.08 (12)	C13—C17—H17C	109.5
N2—C8—C9	122.77 (13)	H17A—C17—H17C	109.5
N2—C8—H8	118.6	H17B—C17—H17C	109.5
C9—C8—H8	118.6		

C6—C1—C2—C3	0.1 (2)	C2—C1—C7—O1	−176.81 (13)
C7—C1—C2—C3	−179.62 (13)	C16—N2—C8—C9	0.2 (2)
C6—C1—C2—N1	180.00 (13)	N2—C8—C9—C10	−1.2 (3)
C7—C1—C2—N1	0.25 (19)	C8—C9—C10—C11	0.8 (2)
O4—N1—C2—C3	83.25 (16)	C9—C10—C11—C16	0.6 (2)

O3—N1—C2—C3	−93.42 (16)	C9—C10—C11—C12	−178.41 (14)
O4—N1—C2—C1	−96.63 (16)	C10—C11—C12—C13	179.70 (14)
O3—N1—C2—C1	86.70 (17)	C16—C11—C12—C13	0.7 (2)
C1—C2—C3—C4	−0.4 (2)	C11—C12—C13—C14	1.2 (2)
N1—C2—C3—C4	179.77 (13)	C11—C12—C13—C17	−177.59 (14)
C1—C2—C3—Cl1	179.38 (10)	C12—C13—C14—C15	−1.8 (2)
N1—C2—C3—Cl1	−0.49 (18)	C17—C13—C14—C15	177.06 (15)
C2—C3—C4—C5	0.4 (2)	C13—C14—C15—C16	0.4 (2)
Cl1—C3—C4—C5	−179.37 (11)	C8—N2—C16—C15	−179.21 (15)
C3—C4—C5—C6	−0.2 (2)	C8—N2—C16—C11	1.3 (2)
C4—C5—C6—C1	0.0 (2)	C14—C15—C16—N2	−177.94 (14)
C2—C1—C6—C5	0.1 (2)	C14—C15—C16—C11	1.6 (2)
C7—C1—C6—C5	179.82 (13)	C10—C11—C16—N2	−1.7 (2)
C6—C1—C7—O2	−176.84 (16)	C12—C11—C16—N2	177.42 (13)
C2—C1—C7—O2	2.9 (2)	C10—C11—C16—C15	178.81 (14)
C6—C1—C7—O1	3.4 (2)	C12—C11—C16—C15	−2.1 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.85 (3)	1.72 (3)	2.5640 (17)	174 (3)
N2—H2···O1	0.88 (4)	1.69 (4)	2.5640 (17)	170 (4)
C5—H5···.O2^{i}	0.95	2.44	3.3245 (19)	155
C8—H8···.O2	0.95	2.46	3.1438 (19)	129

Symmetry code: (i) *x*, *y*+1, *z*.

4-Chloro-2-nitrobenzoic acid–6-methylquinoline (1/1) (IV)

Crystal data

$C_7H_{3.48}ClNO_4\cdot C_{10}H_{9.52}N$
M_r = 344.75
Monoclinic, *Cc*
a = 7.4271 (6) Å
b = 14.4348 (6) Å
c = 16.2208 (7) Å
β = 113.203 (3)°
V = 1598.35 (16) Å^3
Z = 4
$F(000)$ = 712.00
D_x = 1.433 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 14736 reflections
θ = 3.1–30.2°
μ = 0.26 mm^{-1}
T = 185 K
Block, colorless
0.28 × 0.25 × 0.20 mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.931, T_{max} = 0.949
16695 measured reflections
4645 independent reflections
4158 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 30.0°, θ_{min} = 3.1°
h = −10→10
k = −19→20
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.081$
$S = 1.09$
4645 reflections
225 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.1089P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Absolute structure: Flack x determined using 1899 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.023 (9)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.60068 (7)	0.04982 (4)	0.11442 (3)	0.04410 (14)	
O1	0.5629 (2)	0.26210 (10)	0.47141 (9)	0.0398 (3)	
H1	0.543 (10)	0.290 (4)	0.512 (3)	0.060*	0.48 (5)
O2	0.5224 (3)	0.38723 (10)	0.38416 (11)	0.0448 (4)	
O3	0.8822 (3)	0.13730 (13)	0.49214 (11)	0.0557 (5)	
O4	0.6225 (5)	0.05352 (14)	0.45694 (15)	0.0794 (8)	
N1	0.7212 (3)	0.11139 (11)	0.44056 (12)	0.0423 (4)	
N2	0.5616 (2)	0.36395 (11)	0.59693 (10)	0.0297 (3)	
H2	0.543 (8)	0.336 (3)	0.546 (2)	0.044*	0.52 (5)
C1	0.5733 (3)	0.23966 (12)	0.33064 (11)	0.0274 (3)	
C2	0.6451 (3)	0.14958 (13)	0.34899 (12)	0.0292 (3)	
C3	0.6568 (3)	0.09002 (13)	0.28407 (13)	0.0325 (4)	
H3	0.708220	0.029174	0.298910	0.039*	
C4	0.5909 (3)	0.12266 (15)	0.19705 (12)	0.0322 (4)	
C5	0.5203 (3)	0.21248 (15)	0.17566 (12)	0.0339 (4)	
H5	0.478690	0.234289	0.115740	0.041*	
C6	0.5111 (3)	0.26997 (13)	0.24225 (12)	0.0311 (4)	
H6	0.461428	0.331090	0.227361	0.037*	
C7	0.5518 (3)	0.30391 (14)	0.39964 (12)	0.0306 (4)	
C8	0.5951 (3)	0.45366 (13)	0.59630 (12)	0.0317 (4)	
H8	0.593525	0.481201	0.542828	0.038*	
C9	0.6328 (3)	0.50947 (13)	0.67162 (14)	0.0353 (4)	
H9	0.653792	0.574126	0.669007	0.042*	
C10	0.6390 (3)	0.46968 (13)	0.74905 (13)	0.0337 (4)	
H10	0.666629	0.506454	0.801199	0.040*	
C11	0.6041 (3)	0.37319 (12)	0.75145 (12)	0.0282 (3)	
C12	0.6091 (3)	0.32621 (16)	0.82941 (12)	0.0350 (4)	

H12	0.637854	0.360018	0.883369	0.042*
C13	0.5730 (3)	0.23282 (16)	0.82796 (15)	0.0391 (4)
C14	0.5312 (3)	0.18307 (15)	0.74760 (17)	0.0401 (4)
H14	0.506395	0.118429	0.746653	0.048*
C15	0.5253 (3)	0.22500 (13)	0.67141 (14)	0.0354 (4)
H15	0.496495	0.189993	0.618127	0.042*
C16	0.5625 (2)	0.32146 (13)	0.67232 (12)	0.0277 (3)
C17	0.5805 (4)	0.1813 (2)	0.9099 (2)	0.0549 (6)
H17A	0.456380	0.148651	0.896253	0.082*
H17B	0.601873	0.225362	0.958894	0.082*
H17C	0.688173	0.136438	0.928067	0.082*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0500 (3)	0.0567 (3)	0.0311 (2)	−0.0080 (2)	0.02182 (19)	−0.0170 (2)
O1	0.0611 (9)	0.0370 (7)	0.0260 (6)	0.0069 (7)	0.0223 (6)	−0.0011 (5)
O2	0.0707 (11)	0.0298 (7)	0.0430 (8)	−0.0030 (7)	0.0322 (8)	−0.0026 (6)
O3	0.0667 (11)	0.0593 (10)	0.0284 (7)	0.0180 (9)	0.0052 (7)	0.0040 (7)
O4	0.149 (2)	0.0547 (11)	0.0454 (10)	−0.0336 (13)	0.0493 (13)	0.0042 (9)
N1	0.0760 (13)	0.0273 (8)	0.0260 (7)	0.0026 (8)	0.0226 (8)	0.0006 (6)
N2	0.0320 (8)	0.0326 (7)	0.0246 (7)	0.0054 (6)	0.0113 (6)	−0.0020 (6)
C1	0.0325 (8)	0.0297 (8)	0.0230 (7)	−0.0069 (7)	0.0140 (6)	−0.0037 (6)
C2	0.0370 (9)	0.0307 (9)	0.0214 (7)	−0.0053 (7)	0.0133 (6)	−0.0006 (6)
C3	0.0390 (9)	0.0319 (9)	0.0300 (8)	−0.0065 (7)	0.0172 (7)	−0.0048 (7)
C4	0.0333 (9)	0.0428 (10)	0.0243 (8)	−0.0098 (7)	0.0154 (7)	−0.0110 (7)
C5	0.0347 (9)	0.0468 (10)	0.0216 (7)	−0.0056 (8)	0.0124 (7)	−0.0003 (7)
C6	0.0314 (9)	0.0365 (9)	0.0261 (8)	−0.0038 (7)	0.0122 (7)	0.0016 (7)
C7	0.0332 (9)	0.0344 (9)	0.0268 (8)	−0.0046 (7)	0.0145 (7)	−0.0047 (7)
C8	0.0341 (8)	0.0350 (9)	0.0271 (9)	0.0064 (7)	0.0133 (8)	0.0056 (7)
C9	0.0411 (10)	0.0260 (8)	0.0386 (9)	0.0021 (7)	0.0153 (8)	0.0004 (8)
C10	0.0389 (9)	0.0304 (8)	0.0304 (9)	0.0030 (7)	0.0120 (7)	−0.0064 (7)
C11	0.0293 (8)	0.0309 (8)	0.0249 (7)	0.0040 (6)	0.0113 (6)	−0.0001 (6)
C12	0.0363 (10)	0.0443 (10)	0.0258 (8)	0.0066 (8)	0.0137 (7)	0.0039 (8)
C13	0.0313 (9)	0.0474 (11)	0.0418 (10)	0.0093 (8)	0.0177 (8)	0.0178 (9)
C14	0.0342 (10)	0.0320 (9)	0.0546 (12)	0.0012 (8)	0.0180 (9)	0.0083 (9)
C15	0.0365 (10)	0.0286 (8)	0.0395 (10)	0.0007 (7)	0.0133 (8)	−0.0044 (7)
C16	0.0269 (8)	0.0289 (8)	0.0273 (8)	0.0037 (6)	0.0108 (6)	−0.0006 (7)
C17	0.0506 (13)	0.0653 (15)	0.0552 (14)	0.0110 (11)	0.0276 (11)	0.0320 (12)

Geometric parameters (Å, º)

Cl1—C4	1.7273 (18)	C8—C9	1.397 (3)
O1—C7	1.285 (2)	C8—H8	0.9500
O1—H1	0.836 (15)	C9—C10	1.365 (3)
O2—C7	1.230 (3)	C9—H9	0.9500
O3—N1	1.217 (3)	C10—C11	1.420 (3)
O4—N1	1.208 (3)	C10—H10	0.9500

N1—C2	1.472 (2)	C11—C16	1.410 (2)
N2—C8	1.319 (2)	C11—C12	1.423 (3)
N2—C16	1.365 (2)	C12—C13	1.373 (3)
N2—H2	0.873 (14)	C12—H12	0.9500
C1—C6	1.392 (2)	C13—C14	1.411 (3)
C1—C2	1.392 (3)	C13—C17	1.505 (3)
C1—C7	1.510 (2)	C14—C15	1.361 (3)
C2—C3	1.389 (3)	C14—H14	0.9500
C3—C4	1.382 (3)	C15—C16	1.418 (3)
C3—H3	0.9500	C15—H15	0.9500
C4—C5	1.390 (3)	C17—H17A	0.9800
C5—C6	1.385 (3)	C17—H17B	0.9800
C5—H5	0.9500	C17—H17C	0.9800
C6—H6	0.9500		

C7—O1—H1	122 (5)	C10—C9—C8	118.99 (17)
O4—N1—O3	125.3 (2)	C10—C9—H9	120.5
O4—N1—C2	117.1 (2)	C8—C9—H9	120.5
O3—N1—C2	117.46 (18)	C9—C10—C11	119.82 (17)
C8—N2—C16	120.89 (15)	C9—C10—H10	120.1
C8—N2—H2	113 (4)	C11—C10—H10	120.1
C16—N2—H2	126 (4)	C16—C11—C10	118.13 (16)
C6—C1—C2	117.21 (16)	C16—C11—C12	118.45 (17)
C6—C1—C7	118.77 (16)	C10—C11—C12	123.42 (17)
C2—C1—C7	123.97 (16)	C13—C12—C11	121.08 (18)
C3—C2—C1	123.32 (17)	C13—C12—H12	119.5
C3—C2—N1	114.79 (16)	C11—C12—H12	119.5
C1—C2—N1	121.85 (16)	C12—C13—C14	119.07 (18)
C4—C3—C2	117.43 (18)	C12—C13—C17	122.1 (2)
C4—C3—H3	121.3	C14—C13—C17	118.9 (2)
C2—C3—H3	121.3	C15—C14—C13	121.93 (19)
C3—C4—C5	121.32 (17)	C15—C14—H14	119.0
C3—C4—Cl1	118.61 (16)	C13—C14—H14	119.0
C5—C4—Cl1	120.06 (14)	C14—C15—C16	119.38 (19)
C6—C5—C4	119.59 (16)	C14—C15—H15	120.3
C6—C5—H5	120.2	C16—C15—H15	120.3
C4—C5—H5	120.2	N2—C16—C11	119.95 (16)
C5—C6—C1	121.10 (18)	N2—C16—C15	119.96 (16)
C5—C6—H6	119.4	C11—C16—C15	120.08 (17)
C1—C6—H6	119.4	C13—C17—H17A	109.5
O2—C7—O1	125.94 (17)	C13—C17—H17B	109.5
O2—C7—C1	120.75 (16)	H17A—C17—H17B	109.5
O1—C7—C1	113.29 (16)	C13—C17—H17C	109.5
N2—C8—C9	122.19 (16)	H17A—C17—H17C	109.5
N2—C8—H8	118.9	H17B—C17—H17C	109.5
C9—C8—H8	118.9		

C6—C1—C2—C3	0.0 (3)	C16—N2—C8—C9	0.0 (3)

C7—C1—C2—C3	177.39 (18)	N2—C8—C9—C10	1.3 (3)
C6—C1—C2—N1	177.83 (18)	C8—C9—C10—C11	−1.0 (3)
C7—C1—C2—N1	−4.8 (3)	C9—C10—C11—C16	−0.4 (3)
O4—N1—C2—C3	−73.6 (3)	C9—C10—C11—C12	179.57 (18)
O3—N1—C2—C3	102.9 (2)	C16—C11—C12—C13	−0.5 (3)
O4—N1—C2—C1	108.3 (2)	C10—C11—C12—C13	179.59 (19)
O3—N1—C2—C1	−75.1 (3)	C11—C12—C13—C14	0.3 (3)
C1—C2—C3—C4	−0.9 (3)	C11—C12—C13—C17	179.03 (19)
N1—C2—C3—C4	−178.83 (17)	C12—C13—C14—C15	−0.1 (3)
C2—C3—C4—C5	1.6 (3)	C17—C13—C14—C15	−178.90 (19)
C2—C3—C4—Cl1	−179.20 (14)	C13—C14—C15—C16	0.1 (3)
C3—C4—C5—C6	−1.6 (3)	C8—N2—C16—C11	−1.4 (3)
Cl1—C4—C5—C6	179.26 (14)	C8—N2—C16—C15	179.73 (18)
C4—C5—C6—C1	0.7 (3)	C10—C11—C16—N2	1.6 (3)
C2—C1—C6—C5	0.1 (3)	C12—C11—C16—N2	−178.32 (16)
C7—C1—C6—C5	−177.44 (17)	C10—C11—C16—C15	−179.54 (18)
C6—C1—C7—O2	−16.2 (3)	C12—C11—C16—C15	0.5 (3)
C2—C1—C7—O2	166.48 (19)	C14—C15—C16—N2	178.48 (17)
C6—C1—C7—O1	162.34 (17)	C14—C15—C16—C11	−0.4 (3)
C2—C1—C7—O1	−15.0 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.84 (7)	1.70 (6)	2.514 (2)	163 (7)
N2—H2···O1	0.87 (4)	1.67 (5)	2.514 (2)	162 (4)
C10—H10···O2^{i}	0.95	2.54	3.364 (3)	145

Symmetry code: (i) *x*, −*y*+1, *z*+1/2.