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Crystal structures of isoquinoline–3-chloro-2-nitrobenzoic acid (1/1) and isoquinolinium 4-chloro-2-nitrobenzoate

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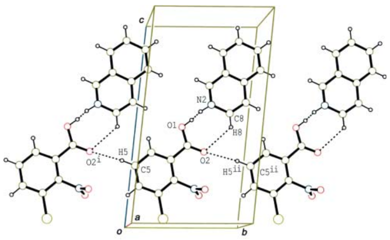
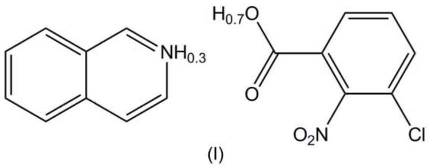


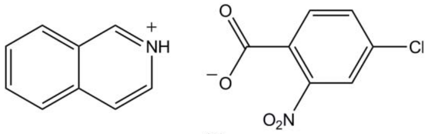
In each of the title isomeric compounds, $C_9H_{7.3}N\cdot C_7H_{3.7}ClNO_4$, (I), and $C_9H_8N\cdot C_7H_3ClNO_4$, (II), of isoquinoline with 3-chloro-2-nitrobenzoic acid and 4-chloro-2-nitrobenzoic acid, the two components are linked by a short hydrogen bond between a base N atom and a carboxy O atom. In the hydrogen-bonded unit of (I), the H atom is disordered over two positions with N and O site occupancies of 0.30 (3) and 0.70 (3), respectively, while in (II), an acid–base interaction involving H-atom transfer occurs and the H atom is located at the N site. In the crystal of (I), the acid–base units are connected through C—H$\cdots$O hydrogen bonds into a tape structure along the *b*-axis direction. Inversion-related adjacent tapes are further linked through π–π interactions [centroid–centroid distances = 3.6389 (7)–3.7501 (7) Å], forming a layer parallel to (001). In the crystal of (II), the acid–base units are connected through C—H$\cdots$O hydrogen bonds into a ladder structure along the *a*-axis direction. The ladders are further linked by another C—H$\cdots$O hydrogen bond into a layer parallel to (001).

1. Chemical context

The hydrogen bonds formed between organic acids and organic bases vary from an O—H$\cdots$N to an $O^-\cdots H—N^+$ type with increasing ΔpK_a [pK_a(base) − pK_a(acid)], and at an appropriate ΔpK_a value, a short strong hydrogen bond with a broad single minimum potential energy curve for the H atom or a double-minimum potential is observed (Jerzykiewicz *et al.*, 1998; Kalenik *et al.*, 1989; Steiner *et al.*, 2001; Schmidtmann & Wilson, 2008; Gilli & Gilli, 2009). For the system of pyridine derivative–chloro- and nitro-substituted benzoic acid (1/1), 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, and two compounds of phthalazine with 3-chloro-2-nitrobenzoic acid and 4-chloro-2-nitrobenzoic acid have a short double-well N$\cdots$H$\cdots$O hydrogen bond between the aromatic N atom and the carboxy O atom (Gotoh & Ishida, 2009, 2011*a*).



(I)



(II)

doi:10.1107/S2056989014026152

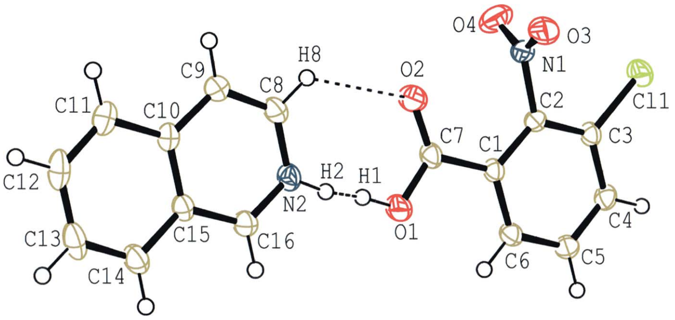


Figure 1
A molecular view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The disordered O—H···N/N—H···O hydrogen bond and the C—H···O interaction are indicated by dashed lines.

We report here two isomeric compounds of isoquinoline with chloro- and nitro-substituted benzoic acids, namely, isoquinoline–3-chloro-2-nitrobenzoic acid (1/1), (I), and 4-chloro-2-nitrobenzoate isoquinolinium, (II), in order to extend our studies of hydrogen bonding in the system of pyridine derivative–chloro- and nitro-substituted benzoic acid (Gotoh & Ishida, 2011*b*,*c*).

2. Structural commentary

The molecular structure of (I) is shown in Fig. 1. The base and acid molecules are held together by a short hydrogen bond between the N atom of the base and the carboxy O atom. The H atom in the hydrogen bond is disordered over two positions with the N and O sites occupancies refined to 0.30 (3) and 0.70 (3), respectively. In addition, a C—H···O hydrogen bond (C8—H8···O2; Table 1) is observed in the hydrogen-bonded acid–base unit. In the unit, the isoquinoline ring system, the carboxy group and the benzene ring of the acid molecule are almost coplanar with each other; the carboxy group makes dihedral angles of 5.35 (15) and 5.91 (15)°, respectively, with the isoquinoline ring system and the benzene ring, and the dihedral angle between the isoquinoline ring system and the benzene ring is 1.21 (4)°. On the other hand, the nitro group and the benzene ring are almost perpendicular with a dihedral angle of 83.71 (13)°.

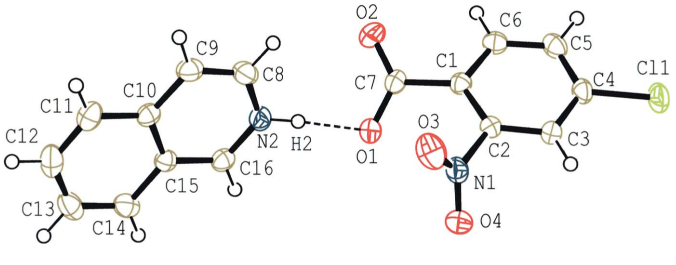


Figure 2
A molecular view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.84 (2)	1.74 (2)	2.5725 (12)	177 (2)
N2—H2···O1	0.88 (2)	1.69 (5)	2.5725 (12)	172 (5)
C5—H5···O2^{i}	0.95	2.49	3.3427 (14)	149
C8—H8···O2	0.95	2.53	3.1977 (14)	128

Symmetry code: (i) *x*, *y* − 1, *z*.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.91 (2)	1.67 (2)	2.5738 (14)	169 (2)
C3—H3···O2^{i}	0.95	2.21	3.1580 (15)	174
C13—H13···O3^{ii}	0.95	2.52	3.3405 (19)	145
C16—H16···O1^{iii}	0.95	2.43	3.3477 (15)	163

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

The molecular structure of (II) is shown in Fig. 2. An acid–base interaction involving H-atom transfer occurs and the base and acid molecules are linked by an N^{+}—H···O^{-} hydrogen bond. In the hydrogen-bonded unit, the isoquinoline ring system make dihedral angles of 54.12 (15) and 71.89 (5)°, respectively, with the carboxy group and the benzene ring of the acid. In the acid molecule, the benzene ring makes dihedral angles of 26.59 (15) and 67.69 (15)°, respectively, with the carboxy and nitro groups.

3. Supramolecular features

In the crystal of (I), the hydrogen-bonded acid-base units are linked by a C—H···O hydrogen bond (C5—H5···O2^{i}; Table 1), forming a tape structure along the *b*-axis direction (Fig. 3). Adjacent tapes, which are related by an inversion center, are further linked through π–π interactions between the benzene ring of the acid and the isoquinoline ring system

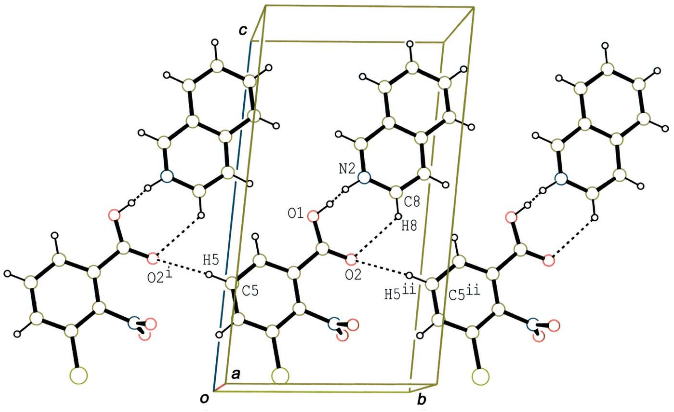


Figure 3
A packing diagram of (I), showing the hydrogen-bonded tape structure along the *b* axis. The dashed lines indicate disordered O—H···N/N—H···O hydrogen bonds and the C—H···O interactions. [Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) *x*, *y* + 1, *z*.]

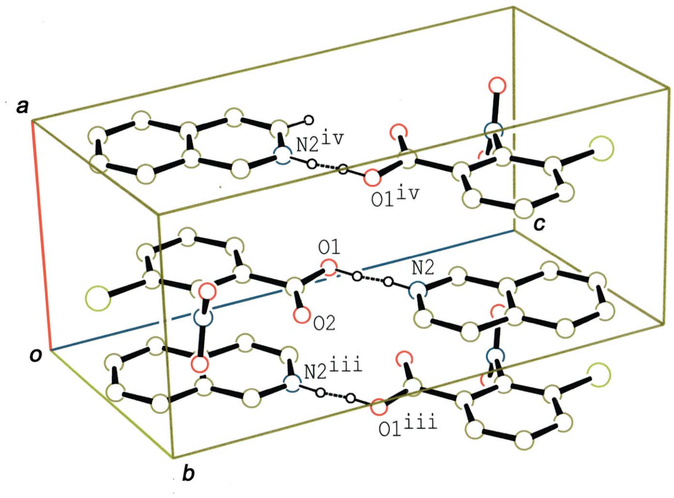


Figure 4
A packing diagram of (I), showing the π–π stacking structure along the *a* axis. The dashed lines indicate disordered O—H$\cdots$N/N—H$\cdots$O hydrogen bonds and H atoms not involved in the hydrogen bonds have been omitted. [Symmetry codes: (iii) $-x, -y+1, -z+1$; (iv) $-x+1, -y+1, -z+1$.]

(Fig. 4), forming a layer parallel to the (001) plane. The centroid–centroid distances are in the range 3.6389 (7)–3.7501 (7) Å [$Cg1\cdots Cg2^{iii}$ = 3.7501 (7), $Cg1\cdots Cg2^{iv}$ = 3.6674 (7), $Cg1\cdots Cg3^{iii}$ = 3.6637 (7) and $Cg1\cdots Cg3^{iv}$ = 3.6389 (7) Å, where *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6 benzene ring of the acid, and the N2/C8–C10/C15/C16 rings of the base, respectively. Symmetry codes: (iii) $-x, -y+1, -z+1$; (iv) $-x+1, -y+1, -z+1$.]

In the crystal of (II), the acid–base units are connected through C—H$\cdots$O hydrogen bonds (C3—H3$\cdots$O2^{i} and C13—H13$\cdots$O3^{ii}; Table 2) into a ladder structure along the *a*-axis direction (Fig. 5). Adjacent ladders are further linked by another C—H$\cdots$O hydrogen bond (C16—H16$\cdots$O1^{iii}; Table 2), forming a layer parallel to the (001) plane.

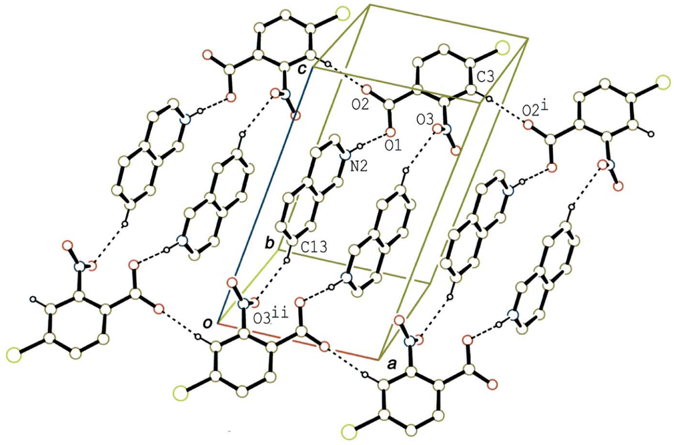


Figure 5
A packing diagram of (II), showing the hydrogen-bonded ladder structure along the *a* axis. The dashed lines indicate N—H$\cdots$O and C—H$\cdots$O hydrogen bonds. H atoms not involved in the hydrogen bonds have been omitted. [Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y, -z+1$.]

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, last update May 2014; Groom & Allen, 2014) showed 49 structures of co-crystals/salts of pyridine (or amine) derivative–chloro- and nitro-substituted benzoic acid: 16 structures containing 2-chloro-4-nitrobenzoic acid, nine for 2-chloro-5-nitrobenzoic acid, three for 3-chloro-2-nitrobenzoic acid, five for 3-chloro-6-nitrobenzoic acid, eight for 4-chloro-2-nitrobenzoic acid and eight for 4-chloro-3-nitrobenzoic acid. On the other hand, there were eight structures of co-crystals/salts of isoquinoline with organic acids. The N$\cdots$O distances of the N—H$\cdots$O/O—H$\cdots$N hydrogen bonds are in the range 2.578 (2)–2.8718 (17) Å. No disordered H atoms were observed in the hydrogen bonds.

5. Synthesis and crystallization

Crystals of compounds (I) and (II) were obtained by slow evaporation from acetonitrile solutions of isoquinoline with the corresponding chloro- and nitro-substituted benzoic acid in a 1:1 molar ratio at room temperature [50 ml acetonitrile solution of isoquinoline (0.202 g) and 3-chloro-2-nitrobenzoic acid (0.315 g) for (I), and 150 ml solution of isoquinoline (0.204 g) and 4-chloro-2-nitrobenzoic acid (0.318 g) for (II)].

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms in compounds (I) and (II) were found in difference Fourier maps. The H atom in (I), which is involved in the N$\cdots$H$\cdots$O hydrogen bonds, was found to be disordered over two positions in a difference Fourier map. Since the site-occupancy factors and isotropic displacement parameters were strongly correlated, the occupancy factors were refined, with $U_{iso}(H) = 1.5U_{eq}$(N or O). The positional parameters were refined with bond restraints of O—H = 0.84 (2) Å and N—H = 0.88 (2) Å. Atom H2 in (II) was refined freely [refined distance N2—H2 = 0.91 (2) Å]. Other H atoms of compounds (I) and (II) were positioned geometrically (C—H = 0.95 Å) and treated as riding, with $U_{iso}(H) = 1.2U_{eq}$(C).

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Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_9H_{7.3}N \cdot C_7H_{3.7}ClNO_4$	$C_9H_8N^+ \cdot C_7H_3ClNO_4^-$
M_r	330.73	330.73
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	190	190
a, b, c (Å)	6.93986 (15), 7.6629 (5), 13.9475 (5)	7.5916 (3), 7.7607 (3), 13.0456 (4)
α, β, γ (°)	83.945 (3), 87.6039 (16), 85.117 (4)	74.8360 (11), 80.1736 (10), 80.3642 (13)
V (Å^3)	734.50 (6)	724.84 (4)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.28	0.29
Crystal size (mm)	0.35 × 0.28 × 0.10	0.39 × 0.32 × 0.23
Data collection		
Diffractometer	Rigaku R-AXIS RAPIDII	Rigaku R-AXIS RAPIDII
Absorption correction	Numerical (*NUMABS*; Higashi, 1999)	Numerical (*NUMABS*; Higashi, 1999)
$T_{\min}, T_{\max}$	0.918, 0.972	0.903, 0.936
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15432, 4278, 3729	21510, 4224, 3559
R_{int}	0.022	0.024
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.704	0.704
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.098, 1.08	0.039, 0.117, 1.07
No. of reflections	4278	4224
No. of parameters	219	212
No. of restraints	2	0
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
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å^{-3})	0.41, −0.22	0.42, −0.16

Computer programs: *PROCESS-AUTO* (Rigaku/MSC, 2004), *SHELXS97* and *SHELXL2014* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *CrystalStructure* (Rigaku, 2010) and *PLATON* (Spek, 2009).

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supporting information

Acta Cryst. (2015). E**71**, 31-34   [https://doi.org/10.1107/S2056989014026152]

Crystal structures of isoquinoline–3-chloro-2-nitrobenzoic acid (1/1) and isoquinolinium 4-chloro-2-nitrobenzoate

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Computing details

For both compounds, data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO* (Rigaku/MSC, 2004); data reduction: *CrystalStructure* (Rigaku, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2010) and *PLATON* (Spek, 2009).

(I) Isoquinoline113-chloro-2-nitrobenzoic acid (1/1)

Crystal data

$C_9H_{7.3}N \cdot C_7H_{3.7}ClNO_4$
$M_r = 330.73$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.93986\ (15)$ Å
$b = 7.6629\ (5)$ Å
$c = 13.9475\ (5)$ Å
$\alpha = 83.945\ (3)°$
$\beta = 87.6039\ (16)°$
$\gamma = 85.117\ (4)°$
$V = 734.50\ (6)$ Å^3
$Z = 2$
$F(000) = 340.00$
$D_x = 1.495$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 13329 reflections
$\theta = 3.2–30.1°$
$\mu = 0.28$ mm^{-1}
$T = 190$ K
Prism, colorless
0.35 × 0.28 × 0.10 mm

Data collection

Rigaku R-AXIS RAPIDII diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: numerical (NUMABS; Higashi, 1999)
$T_{min} = 0.918$, $T_{max} = 0.972$
15432 measured reflections
4278 independent reflections
3729 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 30.0°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.098$
$S = 1.08$
4278 reflections
219 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.1994P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.41$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

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.

Refinement. Reflections were merged by *SHELXL* according to the crystal class for the calculation of statistics and refinement.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Cl1	0.34388 (4)	0.30344 (4)	0.03598 (2)	0.03254 (9)	
O1	0.27369 (15)	0.39376 (11)	0.48183 (6)	0.0351 (2)	
H1	0.250 (4)	0.474 (3)	0.5180 (18)	0.053*	0.70 (3)
O2	0.22586 (17)	0.61166 (11)	0.36405 (6)	0.0439 (2)	
O3	0.43819 (15)	0.63013 (11)	0.17433 (7)	0.0412 (2)	
O4	0.13125 (16)	0.61492 (13)	0.15530 (8)	0.0469 (3)	
N1	0.28995 (15)	0.55342 (12)	0.18246 (6)	0.0290 (2)	
N2	0.21395 (14)	0.63768 (12)	0.59551 (6)	0.02651 (19)	
H2	0.234 (8)	0.547 (5)	0.561 (4)	0.040*	0.30 (3)
C1	0.30225 (15)	0.32097 (13)	0.32234 (7)	0.02176 (19)	
C2	0.30705 (14)	0.36753 (12)	0.22318 (7)	0.02149 (18)	
C3	0.33329 (15)	0.24164 (13)	0.15844 (7)	0.02282 (19)	
C4	0.35608 (16)	0.06470 (13)	0.19197 (8)	0.0257 (2)	
H4	0.3727	−0.0222	0.1479	0.031*	
C5	0.35442 (17)	0.01595 (13)	0.29030 (8)	0.0276 (2)	
H5	0.3711	−0.1051	0.3139	0.033*	
C6	0.32847 (16)	0.14294 (13)	0.35468 (7)	0.0248 (2)	
H6	0.3286	0.1076	0.4220	0.030*	
C7	0.26468 (17)	0.45769 (14)	0.39226 (8)	0.0261 (2)	
C8	0.18964 (17)	0.80800 (15)	0.55602 (8)	0.0284 (2)	
H8	0.1919	0.8317	0.4878	0.034*	
C9	0.16227 (17)	0.94575 (15)	0.61069 (8)	0.0288 (2)	
H9	0.1455	1.0629	0.5806	0.035*	
C10	0.15886 (15)	0.91357 (14)	0.71228 (8)	0.0248 (2)	
C11	0.13139 (18)	1.04938 (16)	0.77399 (9)	0.0337 (2)	
H11	0.1108	1.1687	0.7477	0.040*	
C12	0.13459 (18)	1.00797 (19)	0.87164 (9)	0.0383 (3)	
H12	0.1176	1.0995	0.9129	0.046*	
C13	0.16253 (18)	0.8323 (2)	0.91205 (9)	0.0374 (3)	
H13	0.165 (3)	0.808 (2)	0.9796 (14)	0.051 (5)*	
C14	0.18547 (17)	0.69811 (17)	0.85431 (8)	0.0322 (2)	
H14	0.2017	0.5794	0.8822	0.039*	
C15	0.18491 (15)	0.73674 (14)	0.75304 (7)	0.02394 (19)	
C16	0.21142 (17)	0.60377 (14)	0.68986 (8)	0.0266 (2)	

H16	0.2282	0.4845	0.7167	0.032*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.04465 (17)	0.03447 (15)	0.01898 (12)	−0.00229 (11)	−0.00104 (10)	−0.00566 (9)
O1	0.0583 (6)	0.0276 (4)	0.0198 (4)	−0.0007 (4)	0.0001 (4)	−0.0063 (3)
O2	0.0840 (7)	0.0222 (4)	0.0253 (4)	−0.0024 (4)	0.0070 (4)	−0.0062 (3)
O3	0.0578 (6)	0.0236 (4)	0.0419 (5)	−0.0106 (4)	0.0128 (4)	−0.0012 (3)
O4	0.0582 (6)	0.0335 (5)	0.0460 (5)	0.0162 (4)	−0.0114 (5)	−0.0023 (4)
N1	0.0455 (5)	0.0197 (4)	0.0207 (4)	0.0021 (4)	0.0034 (4)	−0.0031 (3)
N2	0.0320 (5)	0.0275 (4)	0.0212 (4)	−0.0033 (3)	0.0002 (3)	−0.0076 (3)
C1	0.0250 (5)	0.0208 (4)	0.0202 (4)	−0.0041 (3)	0.0027 (3)	−0.0048 (3)
C2	0.0256 (5)	0.0177 (4)	0.0212 (4)	−0.0019 (3)	0.0010 (3)	−0.0029 (3)
C3	0.0262 (5)	0.0235 (4)	0.0195 (4)	−0.0033 (3)	0.0010 (3)	−0.0055 (3)
C4	0.0299 (5)	0.0207 (4)	0.0278 (5)	−0.0043 (4)	0.0028 (4)	−0.0082 (4)
C5	0.0347 (5)	0.0189 (4)	0.0293 (5)	−0.0041 (4)	0.0047 (4)	−0.0027 (4)
C6	0.0296 (5)	0.0224 (4)	0.0224 (4)	−0.0050 (4)	0.0037 (4)	−0.0015 (3)
C7	0.0342 (5)	0.0236 (4)	0.0215 (4)	−0.0060 (4)	0.0039 (4)	−0.0063 (4)
C8	0.0354 (6)	0.0310 (5)	0.0189 (4)	−0.0026 (4)	0.0004 (4)	−0.0027 (4)
C9	0.0350 (6)	0.0257 (5)	0.0251 (5)	−0.0005 (4)	0.0010 (4)	−0.0023 (4)
C10	0.0235 (5)	0.0281 (5)	0.0237 (5)	−0.0013 (4)	0.0008 (4)	−0.0081 (4)
C11	0.0348 (6)	0.0321 (6)	0.0361 (6)	−0.0004 (4)	0.0026 (5)	−0.0153 (5)
C12	0.0317 (6)	0.0526 (7)	0.0341 (6)	0.0009 (5)	0.0010 (5)	−0.0256 (6)
C13	0.0297 (6)	0.0622 (8)	0.0212 (5)	0.0028 (5)	−0.0004 (4)	−0.0141 (5)
C14	0.0320 (6)	0.0433 (6)	0.0204 (5)	0.0017 (5)	−0.0008 (4)	−0.0033 (4)
C15	0.0236 (5)	0.0294 (5)	0.0192 (4)	−0.0013 (4)	−0.0003 (3)	−0.0051 (4)
C16	0.0330 (5)	0.0246 (5)	0.0225 (5)	−0.0021 (4)	0.0000 (4)	−0.0041 (4)

Geometric parameters (Å, º)

Cl1—C3	1.7240 (10)	C5—H5	0.9500
O1—C7	1.2948 (13)	C6—H6	0.9500
O1—H1	0.840 (17)	C8—C9	1.3621 (15)
O2—C7	1.2150 (14)	C8—H8	0.9500
O3—N1	1.2230 (14)	C9—C10	1.4119 (15)
O4—N1	1.2196 (14)	C9—H9	0.9500
N1—C2	1.4738 (13)	C10—C15	1.4129 (15)
N2—C16	1.3138 (13)	C10—C11	1.4147 (14)
N2—C8	1.3616 (14)	C11—C12	1.3661 (18)
N2—H2	0.88 (2)	C11—H11	0.9500
C1—C6	1.3901 (14)	C12—C13	1.404 (2)
C1—C2	1.3911 (13)	C12—H12	0.9500
C1—C7	1.5048 (14)	C13—C14	1.3667 (17)
C2—C3	1.3853 (13)	C13—H13	0.941 (19)
C3—C4	1.3849 (14)	C14—C15	1.4124 (14)
C4—C5	1.3827 (15)	C14—H14	0.9500
C4—H4	0.9500	C15—C16	1.4116 (14)

C5—C6	1.3880 (14)	C16—H16	0.9500

C7—O1—H1	110.2 (19)	N2—C8—C9	122.49 (10)
O4—N1—O3	125.54 (10)	N2—C8—H8	118.8
O4—N1—C2	117.20 (10)	C9—C8—H8	118.8
O3—N1—C2	117.14 (9)	C8—C9—C10	119.69 (10)
C16—N2—C8	119.17 (9)	C8—C9—H9	120.2
C16—N2—H2	117 (4)	C10—C9—H9	120.2
C8—N2—H2	124 (4)	C9—C10—C15	117.69 (9)
C6—C1—C2	117.62 (9)	C9—C10—C11	123.08 (11)
C6—C1—C7	121.03 (9)	C15—C10—C11	119.23 (10)
C2—C1—C7	121.33 (9)	C12—C11—C10	119.63 (12)
C3—C2—C1	121.56 (9)	C12—C11—H11	120.2
C3—C2—N1	117.06 (9)	C10—C11—H11	120.2
C1—C2—N1	121.36 (8)	C11—C12—C13	121.09 (11)
C4—C3—C2	120.01 (9)	C11—C12—H12	119.5
C4—C3—Cl1	119.44 (8)	C13—C12—H12	119.5
C2—C3—Cl1	120.53 (8)	C14—C13—C12	120.59 (11)
C5—C4—C3	119.28 (9)	C14—C13—H13	120.3 (11)
C5—C4—H4	120.4	C12—C13—H13	119.1 (11)
C3—C4—H4	120.4	C13—C14—C15	119.68 (12)
C4—C5—C6	120.34 (9)	C13—C14—H14	120.2
C4—C5—H5	119.8	C15—C14—H14	120.2
C6—C5—H5	119.8	C16—C15—C14	122.15 (10)
C5—C6—C1	121.18 (10)	C16—C15—C10	118.08 (9)
C5—C6—H6	119.4	C14—C15—C10	119.77 (10)
C1—C6—H6	119.4	N2—C16—C15	122.89 (10)
O2—C7—O1	125.26 (10)	N2—C16—H16	118.6
O2—C7—C1	121.07 (10)	C15—C16—H16	118.6
O1—C7—C1	113.66 (9)		

C6—C1—C2—C3	1.20 (15)	C6—C1—C7—O1	4.66 (15)
C7—C1—C2—C3	−177.18 (9)	C2—C1—C7—O1	−177.02 (10)
C6—C1—C2—N1	−177.04 (9)	C16—N2—C8—C9	−0.12 (17)
C7—C1—C2—N1	4.58 (15)	N2—C8—C9—C10	0.13 (18)
O4—N1—C2—C3	82.77 (12)	C8—C9—C10—C15	0.13 (16)
O3—N1—C2—C3	−93.64 (12)	C8—C9—C10—C11	179.94 (11)
O4—N1—C2—C1	−98.92 (12)	C9—C10—C11—C12	−178.41 (11)
O3—N1—C2—C1	84.67 (12)	C15—C10—C11—C12	1.40 (17)
C1—C2—C3—C4	−0.19 (16)	C10—C11—C12—C13	−0.74 (19)
N1—C2—C3—C4	178.12 (10)	C11—C12—C13—C14	−0.6 (2)
C1—C2—C3—Cl1	−178.58 (8)	C12—C13—C14—C15	1.27 (18)
N1—C2—C3—Cl1	−0.28 (13)	C13—C14—C15—C16	178.85 (11)
C2—C3—C4—C5	−0.70 (16)	C13—C14—C15—C10	−0.58 (17)
Cl1—C3—C4—C5	177.70 (8)	C9—C10—C15—C16	−0.38 (15)
C3—C4—C5—C6	0.56 (17)	C11—C10—C15—C16	179.81 (10)
C4—C5—C6—C1	0.48 (17)	C9—C10—C15—C14	179.07 (10)
C2—C1—C6—C5	−1.33 (16)	C11—C10—C15—C14	−0.74 (16)

C7—C1—C6—C5	177.05 (10)	C8—N2—C16—C15	−0.16 (17)
C6—C1—C7—O2	−173.83 (12)	C14—C15—C16—N2	−179.03 (11)
C2—C1—C7—O2	4.49 (17)	C10—C15—C16—N2	0.41 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.84 (2)	1.74 (2)	2.5725 (12)	177 (2)
N2—H2···O1	0.88 (2)	1.69 (5)	2.5725 (12)	172 (5)
C5—H5···O2[i]	0.95	2.49	3.3427 (14)	149
C8—H8···O2	0.95	2.53	3.1977 (14)	128

Symmetry code: (i) *x*, *y*−1, *z*.

(II) Isoquinolinium 4-chloro-2-nitrobenzoate

Crystal data

$C_9H_8N^+\cdot C_7H_3ClNO_4^-$
M_r = 330.73
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.5916 (3) Å
b = 7.7607 (3) Å
c = 13.0456 (4) Å
α = 74.8360 (11)°
β = 80.1736 (10)°
γ = 80.3642 (13)°
V = 724.84 (4) Å^3
Z = 2
$F(000)$ = 340.00
D_x = 1.515 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 17960 reflections
θ = 3.0–30.1°
μ = 0.29 mm^{-1}
T = 190 K
Block, colorless
0.39 × 0.32 × 0.23 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} = 0.903, T_{max} = 0.936
21510 measured reflections
4224 independent reflections
3559 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 30.0°
$h = -10\rightarrow10$
$k = -10\rightarrow10$
$l = -18\rightarrow18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.117$
S = 1.07
4224 reflections
212 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0699P)^2 + 0.126P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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.

Refinement. Reflections were merged by *SHELXL* according to the crystal class for the calculation of statistics and refinement.

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.89304 (5)	0.83272 (5)	0.98941 (3)	0.04513 (12)
O1	0.49156 (12)	0.48077 (13)	0.69271 (7)	0.0359 (2)
O2	0.25649 (12)	0.50987 (15)	0.81971 (8)	0.0427 (2)
O3	0.78736 (17)	0.25408 (13)	0.80657 (10)	0.0503 (3)
O4	0.91034 (13)	0.46177 (16)	0.68317 (9)	0.0465 (3)
N1	0.81282 (13)	0.40954 (14)	0.76667 (9)	0.0328 (2)
N2	0.31990 (13)	0.26809 (14)	0.63693 (8)	0.0313 (2)
C1	0.53627 (14)	0.58384 (14)	0.83982 (8)	0.0253 (2)
C2	0.72336 (14)	0.54307 (14)	0.82731 (8)	0.0257 (2)
C3	0.83671 (15)	0.61582 (16)	0.87214 (9)	0.0293 (2)
H3	0.9639	0.5862	0.8608	0.035*
C4	0.75517 (17)	0.73430 (15)	0.93451 (9)	0.0310 (2)
C5	0.56930 (18)	0.77436 (16)	0.95367 (10)	0.0338 (2)
H5	0.5166	0.8522	0.9992	0.041*
C6	0.46123 (16)	0.69972 (15)	0.90582 (9)	0.0299 (2)
H6	0.3339	0.7281	0.9182	0.036*
C7	0.41584 (15)	0.51806 (15)	0.78102 (9)	0.0281 (2)
C8	0.24974 (17)	0.14032 (19)	0.71997 (10)	0.0357 (3)
H8	0.2368	0.1551	0.7910	0.043*
C9	0.19825 (16)	−0.00741 (18)	0.70253 (10)	0.0344 (2)
H9	0.1497	−0.0957	0.7610	0.041*
C10	0.21705 (14)	−0.02954 (15)	0.59708 (9)	0.0282 (2)
C11	0.17073 (17)	−0.18170 (17)	0.57248 (12)	0.0363 (3)
H11	0.1257	−0.2761	0.6282	0.044*
C12	0.19101 (18)	−0.19246 (19)	0.46842 (13)	0.0417 (3)
H12	0.1586	−0.2946	0.4524	0.050*
C13	0.25903 (18)	−0.0555 (2)	0.38392 (11)	0.0404 (3)
H13	0.2719	−0.0664	0.3121	0.048*
C14	0.30629 (16)	0.09202 (18)	0.40472 (9)	0.0339 (2)
H14	0.3528	0.1839	0.3478	0.041*
C15	0.28566 (14)	0.10747 (15)	0.51186 (9)	0.0264 (2)
C16	0.33645 (15)	0.25579 (16)	0.53682 (9)	0.0294 (2)
H16	0.3834	0.3486	0.4808	0.035*
H2	0.369 (3)	0.354 (3)	0.6545 (17)	0.060 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0583 (2)	0.0493 (2)	0.03860 (18)	−0.02822 (16)	−0.00558 (14)	−0.01675 (14)
O1	0.0312 (4)	0.0486 (5)	0.0341 (4)	−0.0119 (4)	−0.0042 (3)	−0.0166 (4)
O2	0.0260 (4)	0.0626 (6)	0.0428 (5)	−0.0125 (4)	−0.0022 (3)	−0.0155 (4)
O3	0.0648 (7)	0.0320 (5)	0.0575 (6)	0.0025 (4)	−0.0139 (5)	−0.0187 (4)
O4	0.0342 (5)	0.0670 (7)	0.0459 (5)	−0.0106 (4)	0.0058 (4)	−0.0311 (5)
N1	0.0273 (4)	0.0377 (5)	0.0386 (5)	0.0004 (4)	−0.0087 (4)	−0.0185 (4)
N2	0.0251 (4)	0.0361 (5)	0.0365 (5)	−0.0036 (4)	−0.0051 (4)	−0.0146 (4)
C1	0.0255 (5)	0.0250 (5)	0.0250 (5)	−0.0044 (4)	−0.0037 (4)	−0.0044 (4)
C2	0.0260 (5)	0.0265 (5)	0.0258 (5)	−0.0040 (4)	−0.0029 (4)	−0.0085 (4)
C3	0.0278 (5)	0.0340 (5)	0.0286 (5)	−0.0085 (4)	−0.0039 (4)	−0.0090 (4)
C4	0.0404 (6)	0.0285 (5)	0.0281 (5)	−0.0131 (4)	−0.0055 (4)	−0.0078 (4)
C5	0.0436 (6)	0.0274 (5)	0.0317 (5)	−0.0042 (4)	−0.0024 (5)	−0.0114 (4)
C6	0.0295 (5)	0.0287 (5)	0.0298 (5)	−0.0013 (4)	−0.0021 (4)	−0.0070 (4)
C7	0.0257 (5)	0.0289 (5)	0.0304 (5)	−0.0061 (4)	−0.0070 (4)	−0.0045 (4)
C8	0.0319 (6)	0.0482 (7)	0.0287 (5)	−0.0040 (5)	−0.0029 (4)	−0.0133 (5)
C9	0.0311 (5)	0.0417 (6)	0.0274 (5)	−0.0074 (5)	−0.0014 (4)	−0.0028 (4)
C10	0.0220 (5)	0.0308 (5)	0.0309 (5)	−0.0021 (4)	−0.0054 (4)	−0.0052 (4)
C11	0.0296 (5)	0.0312 (5)	0.0491 (7)	−0.0039 (4)	−0.0098 (5)	−0.0082 (5)
C12	0.0349 (6)	0.0391 (6)	0.0602 (8)	0.0020 (5)	−0.0175 (6)	−0.0247 (6)
C13	0.0360 (6)	0.0527 (8)	0.0381 (6)	0.0052 (5)	−0.0128 (5)	−0.0227 (6)
C14	0.0298 (5)	0.0430 (6)	0.0278 (5)	0.0002 (5)	−0.0062 (4)	−0.0080 (4)
C15	0.0207 (4)	0.0313 (5)	0.0267 (5)	−0.0012 (4)	−0.0048 (4)	−0.0063 (4)
C16	0.0228 (5)	0.0328 (5)	0.0323 (5)	−0.0035 (4)	−0.0044 (4)	−0.0068 (4)

Geometric parameters (Å, º)

Cl1—C4	1.7326 (12)	C6—H6	0.9500
O1—C7	1.2784 (15)	C8—C9	1.3550 (19)
O2—C7	1.2340 (14)	C8—H8	0.9500
O3—N1	1.2162 (15)	C9—C10	1.4108 (17)
O4—N1	1.2220 (15)	C9—H9	0.9500
N1—C2	1.4734 (14)	C10—C11	1.4131 (17)
N2—C16	1.3176 (16)	C10—C15	1.4168 (15)
N2—C8	1.3632 (17)	C11—C12	1.363 (2)
N2—H2	0.91 (2)	C11—H11	0.9500
C1—C6	1.3931 (15)	C12—C13	1.410 (2)
C1—C2	1.3933 (15)	C12—H12	0.9500
C1—C7	1.5118 (15)	C13—C14	1.3590 (19)
C2—C3	1.3814 (15)	C13—H13	0.9500
C3—C4	1.3855 (16)	C14—C15	1.4140 (16)
C3—H3	0.9500	C14—H14	0.9500
C4—C5	1.3869 (18)	C15—C16	1.4025 (16)
C5—C6	1.3862 (17)	C16—H16	0.9500
C5—H5	0.9500		

O3—N1—O4	125.41 (11)	C9—C8—N2	120.89 (11)
O3—N1—C2	116.47 (10)	C9—C8—H8	119.6
O4—N1—C2	118.08 (10)	N2—C8—H8	119.6
C16—N2—C8	121.77 (11)	C8—C9—C10	119.69 (11)
C16—N2—H2	121.1 (13)	C8—C9—H9	120.2
C8—N2—H2	116.6 (13)	C10—C9—H9	120.2
C6—C1—C2	116.80 (10)	C9—C10—C11	123.14 (11)
C6—C1—C7	119.68 (10)	C9—C10—C15	118.36 (11)
C2—C1—C7	123.42 (10)	C11—C10—C15	118.50 (11)
C3—C2—C1	124.21 (10)	C12—C11—C10	119.70 (12)
C3—C2—N1	115.37 (9)	C12—C11—H11	120.2
C1—C2—N1	120.38 (9)	C10—C11—H11	120.2
C2—C3—C4	116.52 (10)	C11—C12—C13	121.55 (12)
C2—C3—H3	121.7	C11—C12—H12	119.2
C4—C3—H3	121.7	C13—C12—H12	119.2
C3—C4—C5	121.97 (10)	C14—C13—C12	120.33 (12)
C3—C4—Cl1	117.91 (9)	C14—C13—H13	119.8
C5—C4—Cl1	120.12 (9)	C12—C13—H13	119.8
C6—C5—C4	119.35 (11)	C13—C14—C15	119.39 (12)
C6—C5—H5	120.3	C13—C14—H14	120.3
C4—C5—H5	120.3	C15—C14—H14	120.3
C5—C6—C1	121.06 (11)	C16—C15—C14	121.11 (11)
C5—C6—H6	119.5	C16—C15—C10	118.34 (10)
C1—C6—H6	119.5	C14—C15—C10	120.53 (11)
O2—C7—O1	126.47 (11)	N2—C16—C15	120.90 (11)
O2—C7—C1	118.47 (11)	N2—C16—H16	119.6
O1—C7—C1	115.02 (9)	C15—C16—H16	119.6

C6—C1—C2—C3	−2.85 (16)	C2—C1—C7—O1	−24.68 (15)
C7—C1—C2—C3	173.44 (10)	C16—N2—C8—C9	1.66 (18)
C6—C1—C2—N1	174.65 (10)	N2—C8—C9—C10	−0.10 (19)
C7—C1—C2—N1	−9.05 (16)	C8—C9—C10—C11	178.39 (11)
O3—N1—C2—C3	110.00 (12)	C8—C9—C10—C15	−1.62 (17)
O4—N1—C2—C3	−67.61 (14)	C9—C10—C11—C12	179.31 (11)
O3—N1—C2—C1	−67.71 (14)	C15—C10—C11—C12	−0.68 (17)
O4—N1—C2—C1	114.67 (12)	C10—C11—C12—C13	0.57 (19)
C1—C2—C3—C4	1.06 (17)	C11—C12—C13—C14	−0.04 (19)
N1—C2—C3—C4	−176.56 (10)	C12—C13—C14—C15	−0.36 (19)
C2—C3—C4—C5	1.76 (17)	C13—C14—C15—C16	178.64 (11)
C2—C3—C4—Cl1	−178.43 (8)	C13—C14—C15—C10	0.24 (17)
C3—C4—C5—C6	−2.62 (18)	C9—C10—C15—C16	1.85 (15)
Cl1—C4—C5—C6	177.57 (9)	C11—C10—C15—C16	−178.16 (10)
C4—C5—C6—C1	0.69 (18)	C9—C10—C15—C14	−179.71 (10)
C2—C1—C6—C5	1.91 (16)	C11—C10—C15—C14	0.28 (16)
C7—C1—C6—C5	−174.53 (10)	C8—N2—C16—C15	−1.40 (17)
C6—C1—C7—O2	−26.60 (16)	C14—C15—C16—N2	−178.81 (10)
C2—C1—C7—O2	157.21 (11)	C10—C15—C16—N2	−0.38 (16)
C6—C1—C7—O1	151.51 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.91 (2)	1.67 (2)	2.5738 (14)	169 (2)
C3—H3···O2^{i}	0.95	2.21	3.1580 (15)	174
C13—H13···O3^{ii}	0.95	2.52	3.3405 (19)	145
C16—H16···O1^{iii}	0.95	2.43	3.3477 (15)	163

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