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## Hydrogen bonding and C—H···X interactions in two triclinic phases of 4-carboxyquinolinium chloride monohydrate

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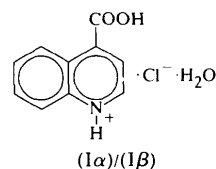
### Abstract

The title substance,  $C_{10}H_8NO_2^+ \cdot Cl^- \cdot H_2O$ , crystallized in the centrosymmetric space group  $P\bar{1}$  in two phases,  $\alpha$  and  $\beta$ , each with one organic cation, one  $Cl^-$  ion and one water molecule in the asymmetric unit. The principal structural difference in the two asymmetric units lies in the relative orientation of the water molecule. Three hydrogen bonds in the  $\alpha$  phase have donor–acceptor distances (N···Cl or O···Cl) ranging from 3.052 (1) to 3.189 (2) Å, while one has an O···O distance of 2.603 (3) Å. Three hydrogen bonds in the  $\beta$

phase have donor–acceptor distances (N···Cl or O···Cl) ranging from 3.044 (2) to 3.206 (2) Å, while two have O···O distances of 2.586 (2) and 3.147 (3) Å. The H atoms in all these hydrogen bonds are ordered. Each of these phases has five leading C—H···X interactions, for which the H···X distances are less than, or at most slightly greater than, the corresponding van der Waals radius sums. Taken together, these hydrogen bonds and C—H···X interactions form a three-dimensional network of interactions in each phase. The dihedral angle between the best-fit quinoline core plane and the carboxyl group plane is 25.9 (1)° for the  $\alpha$  phase and 20.0 (1)° for the  $\beta$  phase.

### Comment

Early compositional and crystallographic studies of solids obtained from aqueous solutions containing quinoline-4-carboxylic acid characterized a number of phases (Weidel, 1874; Claus & Kickelhayn, 1887; Muthmann & Nef, 1887; Muthmann, 1889; Skraup, 1880; Stuhlmann, 1888); these solids included both anhydrous and hydrated phases. We have previously reported structures of a monoclinic anhydrous phase (Dobson & Gerkin, 1998), a monoclinic dihydrate (Dobson & Gerkin, 1999a), and a triclinic trihydrate (Dobson & Gerkin, 1999b). Following addition of HCl to the parent solutions in attempts to crystallize the triclinic dihydrate phase of quinoline-4-carboxylic acid, two previously undescribed phases, ( $I\alpha$ ) and ( $I\beta$ ), were obtained and are characterized in this report.



The two phases of the title compound, ( $I\alpha$ ) and ( $I\beta$ ), crystallized in the centrosymmetric triclinic space group  $P\bar{1}$ , with one organic cation, one  $Cl^-$  ion and one water molecule in each of the asymmetric units. The refined asymmetric units and the atom-numbering schemes are shown in Fig. 1.

Four strong conventional hydrogen bonds are formed in the  $\alpha$  phase, while four strong bonds and one weaker bond are formed in the  $\beta$  phase. The H atoms in all these hydrogen bonds are ordered. Geometric details of these bonds are given in Tables 2 and 5. The rather modest differences in the two sets of strong conventional hydrogen bonds, as well as the presence of the fifth weaker one in the  $\beta$  phase, arise principally from the somewhat different relative orientation of the water molecule in the two asymmetric units.

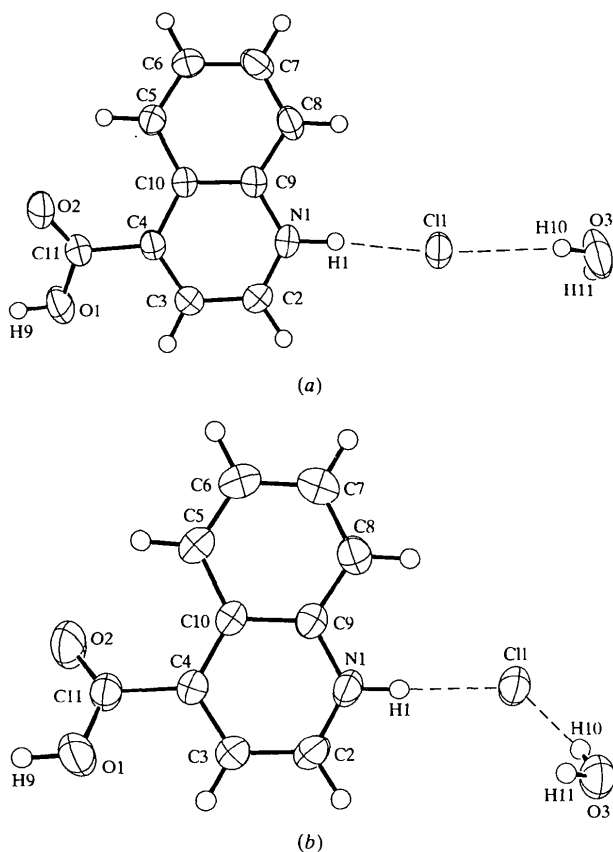


Fig. 1. ORTEPII (Johnson, 1976) drawings of (a) ( $\alpha$ ) and (b) ( $\beta$ ), showing our numbering schemes. Displacement ellipsoids are drawn at 50% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms. Dashed lines depict hydrogen bonds within the asymmetric units.

The results of hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) for basic first- and second-level sets involving these hydrogen bonds, labeled for this purpose *a-d* for ( $\alpha$ ) and *a-e* for ( $\beta$ ), are presented in Tables 3 and 6. The preponderance of finite graphs in these tables is consistent with the very substantial involvement of the  $Cl^-$  ion and the water molecule in the hydrogen bonding in these phases.

Proceeding to third-level graph sets, we find for the  $\alpha$  phase, for *abc*, a chain propagating along  $[110]$ , for *abd*, a ring pattern and for *acd* and *bcd*, finite patterns. Similarly, for the  $\beta$  phase, for *abc*, *abd*, *ace* and *ade*, chains propagating along  $[10\bar{1}]$ ,  $[20\bar{1}]$ ,  $[001]$  and  $[10\bar{1}]$ , respectively, and for *abe*, *acd*, *bcd*, *bce*, *bde* and *cde*, finite patterns. Packing diagrams of the  $\alpha$  and  $\beta$  phases, including each type of conventional hydrogen bond tabulated in Tables 2 and 5, are presented in Fig. 2. The most obvious overall hydrogen-bonding features are the  $R_4^2(8)$  ring pattern in the  $\alpha$  phase, and the [fourth-level (*bcde*)]  $R_3^3(8)$  ring pattern with (third-level) chains running through it in the  $\beta$  phase.

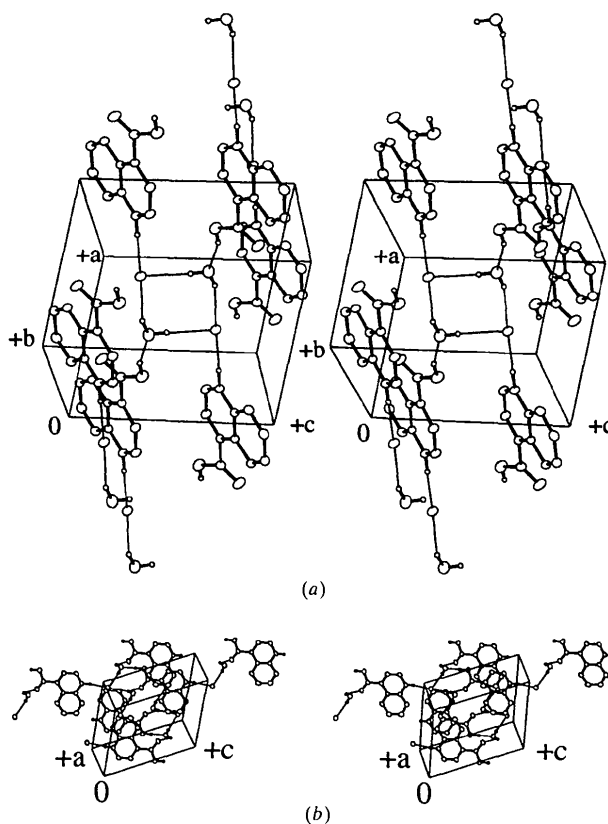


Fig. 2. ORTEPII (Johnson, 1976) packing diagrams of (a) ( $\alpha$ ) and (b) ( $\beta$ ). Displacement ellipsoids are drawn for 20% ( $\alpha$ ) or 30% ( $\beta$ ) probability for all non-H atoms; spheres of arbitrary small radius depict H atoms. For clarity, H atoms bonded to C have been omitted. Hydrogen bonds are depicted by the finer interatomic lines.

Geometric details of the leading intermolecular C—H $\cdots$ X interactions, whose H $\cdots$ X distances are less, or just greater than, the corresponding Bondi (1964) van der Waals radius sums, are also given in Tables 2 and 5. Including these interactions with the conventional hydrogen bonds leads, in both the  $\alpha$  and the  $\beta$  phase, to three-dimensional interaction networks, as is now shown. A basic method of demonstrating that a three-dimensional network of interactions is generated in a structure is to establish that a given structural unit interacts (by a combination of hydrogen bonding or C—H $\cdots$ X interactions or both) with identical structural units displaced from it by one unit along each of the principal axes in turn. Designating the organic cation as *M*, the water molecule as *W* and the  $Cl^-$  anion as *I*, and designating the interactions as *a-i* ( $\alpha$  phase) or *a-j* ( $\beta$  phase) in their order of appearance in Tables 2 or 5, respectively, compact explicit expressions for such connections are, for the  $\alpha$ -phase,  $MalcWdl'eM'al''cWbM''$  for a unit *a* translation,  $MalcWdl'eM'$  for a unit *b* translation and  $MileM'al''cWbM''$  for a unit *c* translation. Similarly, for the  $\beta$  phase,  $MaldWeM'al'cWeM''$  for a

unit **a** translation,  $MfIaM'hM'eWcI'aM''$  for a unit **b** translation and  $MalcWeM'$  for a unit **c** translation.

The heterocyclic and carbocyclic rings of the quinoline cores of ( $I\alpha$ ) and ( $I\beta$ ) are, separately, very nearly planar: the maximum deviations of an atom from the best-fit planes describing the rings are 0.005 (2) and 0.005 (2) Å, respectively, for the  $\alpha$  phase, and 0.011 (2) and 0.005 (2) Å, respectively, for the  $\beta$  phase. Since the dihedral angle between the planes of these rings is only 0.31 (6)° in the  $\alpha$  phase and 1.24 (7)° in the  $\beta$  phase, the quinoline cores as a whole are nearly planar. The maximum deviation of a core atom from the best-fit core plane is 0.007 (2) Å for the  $\alpha$  phase and 0.022 (2) Å for the  $\beta$  phase. The dihedral angle between the core plane and the plane of the carboxyl group is 25.9 (1)° in the  $\alpha$  phase and 20.0 (1)° in the  $\beta$  phase.

Corresponding (non-H) bond lengths for the quinoline cores of ( $I\alpha$ ) and ( $I\beta$ ) are in very good agreement. The greatest difference between members of 11 pairs of corresponding bond lengths, whose individual s.u.'s are 0.002–0.003 Å, is 0.005 Å, while the average difference is 0.002 Å. With respect to quinoline core angles, the agreement is also very good: for 12 corresponding core angles, whose s.u.'s are 0.1–0.2°, the greatest difference is 0.6°, while the average difference is 0.24°. The C—O bond distances in the carboxyl groups of ( $I\alpha$ ) and ( $I\beta$ ) are also in good agreement: 1.306 (2) and 1.192 (2) Å versus 1.296 (2) and 1.192 (2) Å, respectively.

Selected bond distances and angles of ( $I\alpha$ ) and ( $I\beta$ ) are given in Tables 1 and 4. All distances and angles fall within normal limits. The closest intermolecular approaches, excluding pairs of atoms involved in hydrogen-bonding groups or in groups involved in the tabulated C—H...X interactions, are between C6 and C6<sup>vi</sup> [symmetry code: (vi)  $-1-x, 1-y, -z$ ] in the  $\alpha$  phase, and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.06 Å; analogously, in the  $\beta$  phase, the closest approach is greater than the corresponding van der Waals radius sum.

## Experimental

Quinoline-4-carboxylic acid was obtained from the Aldrich Chemical Company as a tan powder of stated purity 97%. It was dissolved in water as received, and the solution was either just filtered or treated with decolorizing carbon and then filtered. Upon addition of small amounts of hydrochloric acid to such solutions and evaporation at room temperature, both phases of the title substance crystallized. The mineral acid was added to the organic acid solution in attempts to crystallize the triclinic dihydrate phase of the organic acid, following descriptions by earlier investigators, including Skraup (1880), Claus & Kickelhayn (1887) and Muthmann (1889). In an attempt to minimize gain or loss of water, the experimental samples were coated with Apiezon grease. They underwent no detectable deterioration during data collection.

## Compound ( $I\alpha$ )

### Crystal data

$C_{10}H_8NO_2 \cdot Cl^- \cdot H_2O$

$M_r = 227.65$

Triclinic

$P\bar{1}$

$a = 7.740$  (1) Å

$b = 7.948$  (2) Å

$c = 9.984$  (1) Å

$\alpha = 84.25$  (1)°

$\beta = 77.38$  (1)°

$\gamma = 61.02$  (1)°

$V = 524.3$  (1) Å<sup>3</sup>

$Z = 2$

$D_x = 1.442$  Mg m<sup>-3</sup>

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 14.3$ – $17.4$ °

$\mu = 0.35$  mm<sup>-1</sup>

$T = 296$  K

Irregular hexagonal column

$0.46 \times 0.38 \times 0.35$  mm

Colorless

### Data collection

Rigaku AFC-5S diffractometer

$\omega/2\theta$  scans

Absorption correction: none

2594 measured reflections

2420 independent reflections

1913 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.011$

$\theta_{max} = 27.56$ °

$h = -10 \rightarrow 8$

$k = -10 \rightarrow 0$

$l = -12 \rightarrow 12$

6 standard reflections

every 150 reflections

intensity decay:  $\pm 1.2\%$

(average maximum

relative intensity)

### Refinement

Refinement on  $F^2$

$R(F) = 0.039$

$wR(F^2) = 0.096$

$S = 1.93$

2420 reflections

152 parameters

H atoms: see below

$w = 1/[\sigma_{cs}^2 + (0.003I)^2]$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.43$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.33$  e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

Stewart *et al.* (1965) (H)

and Creagh & McAuley

(1992) (C, N, O, Cl)

Table 1. Selected geometric parameters (Å, °) for ( $I\alpha$ )

O1—C11	1.306 (2)	N1—C2	1.319 (2)
O2—C11	1.192 (2)	N1—C9	1.370 (2)
H10—O3—H11	107 (2)	O1—C11—O2	124.7 (2)
C2—N1—C9	123.2 (1)	O1—C11—C4	111.6 (1)
C3—C4—C11	118.0 (1)	O2—C11—C4	123.6 (2)
C10—C4—C11	121.7 (1)		

Table 2. Hydrogen bonds and leading intermolecular C—H...X interactions (Å, °) for ( $I\alpha$ )

Note that no s.u.'s are given for atoms H2–H7 since they were fixed.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1...C11	0.97 (2)	2.08 (2)	3.052 (1)	175 (2)
O1—H9...O3 <sup>i</sup>	0.86 (3)	1.78 (3)	2.603 (3)	158 (3)
O3—H10...C11	0.78 (3)	2.44 (3)	3.189 (2)	161 (2)
O3—H11...C11 <sup>ii</sup>	0.82 (3)	2.32 (3)	3.135 (2)	174 (2)
C2—H2...C11 <sup>iii</sup>	0.98	2.77	3.619 (2)	145
C3—H3...O3 <sup>iii</sup>	0.98	2.78	3.754 (2)	170
C5—H5...O2 <sup>iv</sup>	0.98	2.64	3.290 (2)	124
C6—H6...O2 <sup>iv</sup>	0.98	2.67	3.308 (2)	123
C7—H7...C11 <sup>v</sup>	0.98	2.91	3.828 (2)	157

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

Table 3. Basic first- and second-level graph-set descriptors involving hydrogen bonds which are designated a–d in the order given in Table 2

	a	b	c	d
a	D	D <sub>2</sub> <sup>2</sup> (10)	D <sub>2</sub> <sup>1</sup> (5)	D <sub>2</sub> <sup>1</sup> (5)
b		D	D <sub>2</sub> <sup>2</sup> (5)	D <sub>2</sub> <sup>2</sup> (5)
c			D	R <sub>4</sub> <sup>2</sup> (8)
d				D

### Compound (Iβ)

#### Crystal data

C<sub>10</sub>H<sub>8</sub>NO<sub>2</sub><sup>+</sup>·Cl<sup>-</sup>·H<sub>2</sub>O

M<sub>r</sub> = 227.65

Triclinic

P1

a = 4.2969 (6) Å

b = 10.785 (2) Å

c = 11.360 (1) Å

α = 85.00 (1)°

β = 82.99 (1)°

γ = 89.48 (1)°

V = 520.5 (1) Å<sup>3</sup>

Z = 2

D<sub>x</sub> = 1.452 Mg m<sup>-3</sup>

D<sub>m</sub> not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 15.0–17.5°

μ = 0.35 mm<sup>-1</sup>

T = 296 K

Prism

0.35 × 0.35 × 0.31 mm

Colorless

#### Data collection

Rigaku AFC-5S diffractometer

ω/2θ scans

Absorption correction: none

2541 measured reflections

2413 independent reflections

1860 reflections with

I > 2σ(I)

R<sub>int</sub> = 0.012

θ<sub>max</sub> = 27.56°

h = -5 → 5

k = -14 → 0

l = -14 → 14

6 standard reflections

every 150 reflections

intensity decay: ±1.3%  
(average maximum relative intensity)

#### Refinement

Refinement on F<sup>2</sup>

R(F) = 0.040

wR(F<sup>2</sup>) = 0.090

S = 1.95

2413 reflections

153 parameters

H atoms: see below

w = 1/[σ<sub>cs</sub><sup>2</sup> + (0.003I)<sup>2</sup>]

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.39 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.32 e Å<sup>-3</sup>

Extinction correction:

Zachariasen (1963, 1968)

Extinction coefficient:

1 (5) × 10<sup>-7</sup>

Scattering factors from

Stewart *et al.* (1965) (H)  
and Creagh & McAuley  
(1992) (C, N, O, Cl)

Table 5. Hydrogen bonds and leading intermolecular C—H···X interactions (Å, °) for (Iβ)

Note that no s.u.'s are given for atoms H2–H8 since they were fixed.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···C11	0.91 (2)	2.15 (2)	3.044 (2)	167 (2)
O1—H9···O3 <sup>i</sup>	0.95 (3)	1.63 (3)	2.586 (2)	178 (3)
O3—H10···C11	0.77 (3)	2.35 (3)	3.111 (2)	170 (2)
O3—H11···C11 <sup>ii</sup>	0.89 (3)	2.42 (3)	3.206 (2)	146 (2)
O3—H11···O2 <sup>iii</sup>	0.89 (3)	2.72 (3)	3.147 (3)	111 (2)
C2—H2···C11 <sup>iv</sup>	0.98	2.70	3.595 (2)	153
C3—H3···O3 <sup>v</sup>	0.98	2.52	3.395 (2)	149
C6—H6···O2 <sup>vi</sup>	0.98	2.75	3.589 (2)	143
C7—H7···C11 <sup>vii</sup>	0.98	2.82	3.763 (2)	163
C8—H8···C11	0.98	2.94	3.667 (2)	132

Symmetry codes: (i) 1 + x, y, z - 1; (ii) 1 + x, y, z; (iii) x, y, 1 + z; (iv) 1 - x, -y, -z; (v) 2 - x, -y, -z; (vi) 1 - x, -1 - y, -1 - z; (vii) -x, -1 - y, -z.

Table 6. Basic first- and second-level graph set descriptors involving hydrogen bonds which are designated a–e in the order given in Table 5

	a	b	c	d	e
a	D	D <sub>2</sub> <sup>2</sup> (10)	D <sub>2</sub> <sup>1</sup> (5)	D <sub>2</sub> <sup>1</sup> (5)	D <sub>2</sub> <sup>2</sup> (10)
b		D	D <sub>2</sub> <sup>2</sup> (5)	D <sub>2</sub> <sup>2</sup> (5)	C <sub>2</sub> <sup>2</sup> (6)
c			D	C <sub>2</sub> <sup>1</sup> (4)	D <sub>2</sub> <sup>2</sup> (5)
d				D	D <sub>2</sub> <sup>1</sup> (4)
e					D

The H atoms on ring C atoms were treated as riding atoms. H atoms on N and O were refined isotropically and refined distances are given in Tables 2 and 5.

For both compounds, data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSCIAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

We acknowledge with pleasure our use of the departmental X-ray crystallographic facility, which is supervised by staff crystallographer Dr J. C. Gallucci. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1208). Services for accessing these data are described at the back of the journal.

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Table 4. Selected geometric parameters (Å, °) for (Iβ)

O1—C11	1.296 (2)	N1—C2	1.318 (2)
O2—C11	1.192 (2)	N1—C9	1.370 (2)
H10—O3—H11	107 (2)	O1—C11—O2	123.7 (2)
C2—N1—C9	123.4 (1)	O1—C11—C4	112.5 (2)
C3—C4—C11	118.3 (2)	O2—C11—C4	123.7 (2)
C10—C4—C11	121.7 (1)		

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*Acta Cryst.* (1999). **C55**, 1503–1506

### Bis(1,10-phenanthroline-1-ium) chlorodiodide(1-) dichloriodide(1-)

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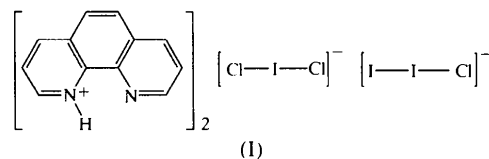
#### Abstract

The title compound,  $2C_{12}H_9N_2^+ \cdot I_2Cl^- \cdot ICl_2^-$ , consists of 1,10-phenanthroline-1-ium ( $phenH^+$ ) cations, trihalide anions ( $ICl_2^-$ ) and the polyanion  $[I_2Cl^-]_n$ . The  $phenH^+$  cations stack in columns and the  $[I_2Cl^-]_n$  polyanion forms chains, both running along the *a* direction. The packing of the  $phenH^+$  columns produces channels occupied by the  $[I_2Cl^-]_n$  chains and cavities occupied by the  $ICl_2^-$  anions. Hydrogen bonds between the N—H groups of  $phenH^+$  and Cl atoms of the  $I_2Cl^-$  chain, along with many weak C—H...X ( $X = Cl, I$ ) interactions, play important roles in the formation of the crystal structure.

#### Comment

Polyhalides display a variety of structures and belong to a class of long known but poorly understood ma-

terials (Poli *et al.*, 1992; Bailar *et al.*, 1973). During the last decade, various compounds with interesting structures were found when protonated aromatic nitrogen bases were combined with polyhalides. Many of these structures possess interesting hydrogen-bonding patterns. These aromatic nitrogen bases include pyridine (El-Kholy *et al.*, 1988; Hendrixson *et al.*, 1991), bipyridine (Tebbe & Bittner, 1995; Liu *et al.*, 1992) and quinoline (Liu *et al.*, 1991). Rich polyhalide chemistry is found in these simple systems with structures varying from discrete to extended. For example, in the 2,2'-bipyridine- $I_2$ -HI (Tebbe & Bittner, 1995) system, different polyiodides are produced simply by adjusting the molar ratio of the reactants. We have investigated recently the 1,10-phenanthroline-HCl-KI- $I_2$  system. At least three different types of crystals have been obtained. The title compound, (I), is one of them, and its crystal structure is reported here.



The asymmetric unit consists of two mono-protonated 1,10-phenanthroline cations ( $phenH^+$ ) and two different trihalide moieties,  $ICl_2^-$  and  $I_2Cl^-$  (Fig. 1). Both  $phenH^+$  cations are planar, with deviations of the non-H atoms from the least-squares plane of less than 0.020 (3) Å in the  $phenH^+$  cation (A) consisting of N1, N2, C1 to C12, and 0.039 (4) Å in the  $phenH^+$  cation (B) defined by N3, N4, C13 to C24. The angle between the two planar cations in the asymmetric unit is 53.68 (6)°. Compared with the neutral base, 1,10-phenanthroline (Nishigaki *et al.*, 1978), the bond distances in the  $phenH^+$  cations show no significant differences, but some internal bond angles vary slightly. The internal

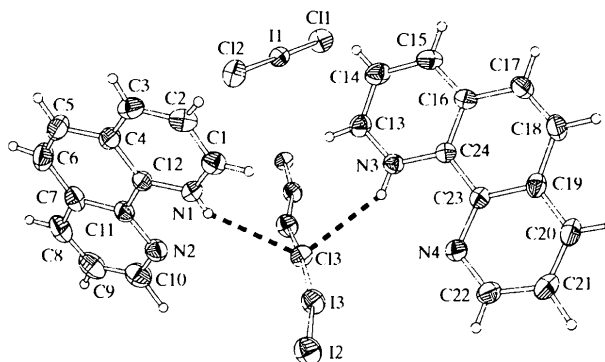


Fig. 1. The molecular structure of (I) drawn with 30% probability displacement ellipsoids.