BIAGINI, S. & CANNAS, M. (1970). *J. Chem. Soc.* (*A*), pp. 2398–2408.

CURTIS, N. F., MCCORMICK, I. R. N. & WATERS, T. N. (1973). *J. Chem. Soc. Dalton*, pp. 1537–1548.

CURTIS, N. F., SWANN, D. A. & WATERS, T. N. (1973). *J. Chem. Soc. Dalton*, pp. 1408–1413.

HAQUE, M., CAUGHLAN, C. N. & EMERSON, K. (1970). *Inorg. Chem.* **9**, 2421–2424.

*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.

IRVING, R. J., POST, M. L. & POVEY, D. C. (1973). *J. Chem. Soc. Dalton*, pp. 697–701.

IUPAC (1971). *Nomenclature of Inorganic Chemistry, Coordination Compounds*, pp. 39–83. London: Butterworths.

LOUIS, R., PÉLISSARD, D. & WEISS, R. (1974). *Acta Cryst.* A paraître.

MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

PÉLISSARD, D. & LOUIS, R. (1972). *Tetrahedron Lett.* pp. 4589–4592.

PREWITT, C. T. (1966). *SFLS*-5, ORNL-TM-306. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

RILEY, P. E. & SEFF, K. (1972). *Inorg. Chem.* **11**, 2993–2999.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMANN, G. (1959). *Acta Cryst.* **12**, 600–604.

WEI, C. H. & DAHL, L. F. (1970). *Inorg. Chem.* **9**, 1878–1887.

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*Acta Cryst.* (1974). B**30**, 780

# The Crystal and Molecular Structure of Iminodiacetic Acid Hydroiodide, $C_4H_7NO_4.HI$

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In a study of the geometry of the iminodiacetic acid group in the solid state, the crystal and molecular structure of $C_4H_7NO_4.HI$ has been determined from X-ray intensities collected with a four-circle diffractometer. The orthorhombic unit cell has $a=9{\cdot}610$ (2), $b=14{\cdot}499$ (2) and $c=11{\cdot}309$ (2) Å. The space group is *Pbca*, with $Z=8$. The structure has been refined to $R=0{\cdot}050$. Positively charged iminodiacetic acid ions, $[C_4H_8NO_4]^+$, are connected by hydrogen bonds of the type OH···I, NH···I, and NH···O forming layers that are stacked in the **b** direction. The forces between the layers are of van der Waals type.

## Introduction

In a systematic study of the geometry of the iminodiacetic acid group in different crystallographic surroundings, the structures of the isotypic iminodiacetic acid hydrochloride and hydrobromide (denoted IDAC and IDAB) have been described previously (Oskarsson, 1973). In these structures positively charged iminodiacetic acid ions, $[C_4H_8NO_4]^+$, with symmetry *mm*, are cross-linked by hydrogen bonds OH···X and NH···X. Because of the size of the iodide ion, one would expect differences in packing and hydrogen bonding in a related iodide compound, and these factors might affect the conformation of the organic ion.

This communication reports the crystal structure of iminodiacetic acid hydroiodide, denoted IDAI below.

## Crystal data

$C_4H_7NO_4.HI$. F.W. 261·03. Orthorhombic, *Pbca*, $a=9{\cdot}610$ (2),* $b=14{\cdot}499$ (2), $c=11{\cdot}309$ (2) Å, $V=1575{\cdot}8$ Å$^3$, $Z=8$, $\mu(\text{Cu } K\alpha)=324{\cdot}8$ cm$^{-1}$, $D_m=2{\cdot}2$, $D_x=2{\cdot}21$ g cm$^{-3}$.

## Experimental

Short prismatic colourless crystals of IDAI were obtained by evaporation of a solution of iminodiacetic acid in strong hydroiodic acid. The composition was checked by elemental analyses. The density was determined from the loss of weight in benzene.

Weissenberg photographs showed that IDAI has the diffraction symmetry *mmm*. The systematic absences $0kl$: $k\neq 2n$; $h0l$: $l\neq 2n$ and $hk0$: $h\neq 2n$ are consistent with the space group *Pbca*. The cell dimensions were improved by a least-squares refinement of a powder pattern obtained with Cu $K\alpha_1$ radiation ($\lambda=1{\cdot}54051$ Å) in a Guinier–Hägg focusing camera. Aluminum ($a=4{\cdot}0496$ Å) was used as an internal standard.

A single crystal with dimensions $0{\cdot}15\times0{\cdot}13\times0{\cdot}13$ mm was used for collecting intensities on a computer controlled four-circle diffractometer of type CAD-4. Experimental conditions and data reduction are described by Oskarsson (1973). Of the 1500 reflexions in the range $5°<\theta<70°$, 318 with $I\leq 3\sigma_c(I)$ were considered not significantly different from the background

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* Numbers in parentheses represent e.s.d.'s in the last significant digits.

and were excluded from the following calculations. The transmission factors evaluated by numerical integration varied from 0·049 to 0·174.

## Structure determination and refinement

The position of the iodide ion was deduced from a vector map. After five cycles of least-squares refinement of the atomic parameters of the iodide ion and a scale factor, a difference synthesis was calculated. The non-hydrogen atoms were found by geometrical considerations.

Full-matrix least-squares refinement minimizing $\sum w(|F_o|-|F_c|)^2$ was performed with weights $w=1/(\sigma_c^2+a|F_o|^2+b)$, where $a$ and $b$ were chosen so that the average value of $w(|F_o|-|F_c|)^2$ was fairly constant in different $|F_o|$ and $\sin\theta$ intervals. In the last cycles of refinement $a=0{\cdot}0013$ and $b=5{\cdot}5$ were used. The convergency was followed by the agreement indices $R$ and $R_w$ defined by $R=\sum(|F_o|-|F_c|)/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$. A refinement of the scale factor, the positional parameters and the anisotropic thermal parameters converged to $R=0{\cdot}066$ and $R_w=0{\cdot}091$. Probable positions of all hydrogen atoms were then located in a difference map using data with $\lambda^{-1}\sin\theta\leq 0{\cdot}4$ Å$^{-1}$. The hydrogen atoms of the methylene groups were included in the structure-factor calculation but were not refined. The positions of all other hydrogen atoms were refined with fixed isotropic temperature factors (3·0 Å$^2$). The coordinates of the hydrogen atoms in the methylene groups were adjusted every second cycle of the refinement by the program *HPLACE* (Nordin, 1973). The C–H distances were assumed to be 1·0 Å and the H–C–H angle 109·5°. The presence of extinction effects in the data was investigated by including an isotropic extinction parameter (Zachariasen, 1967) in the calculations. The refined value of this parameter, 0·28 (3) × 10$^{-4}$, corresponds to a mosaic spread of 20·7″ or a domain size of 0·43 × 10$^{-4}$ cm if the crystal is of type I or type II, respectively. Only 11 reflexions had extinction corrections larger than 10% in $|F_o|$. The final agreement

Table 3. *Observed and calculated structure factors*

The columns are $k$, $|F_o|$ and $F_c||$.

Table 1. *Atomic coordinates with e.s.d.'s*

The atoms H(1)–H(4) have not been refined.

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| I | 0·17514 (7) | 0·14598 (4) | 0·19670 (5) |
| N | 0·5090 (9) | 0·4295 (5) | 0·1830 (6) |
| O(1) | 0·3336 (11) | 0·3014 (5) | −0·0453 (6) |
| O(2) | 0·3507 (8) | 0·4524 (4) | −0·0096 (6) |
| O(3) | 0·4384 (11) | 0·3937 (7) | 0·4940 (6) |
| O(4) | 0·2953 (7) | 0·3968 (5) | 0·3389 (6) |
| C(1) | 0·3771 (11) | 0·3733 (5) | 0·0138 (7) |
| C(2) | 0·4629 (11) | 0·3447 (5) | 0·1183 (7) |
| C(3) | 0·5400 (10) | 0·4151 (6) | 0·3119 (7) |
| C(4) | 0·4101 (11) | 0·4011 (5) | 0·3809 (8) |
| H(1) | 0·407 | 0·305 | 0·172 |
| H(2) | 0·548 | 0·310 | 0·090 |
| H(3) | 0·600 | 0·358 | 0·319 |
| H(4) | 0·592 | 0·469 | 0·344 |
| H(5) | 0·441 (11) | 0·458 (7) | 0·182 (9) |
| H(6) | 0·600 (10) | 0·465 (6) | 0·137 (8) |
| H(7) | 0·411 (15) | 0·388 (10) | 0·526 (11) |
| H(8) | 0·303 (12) | 0·316 (9) | −0·085 (10) |

Table 2. *Thermal parameters $\beta_{ij}\times 10^4$ with e.s.d.'s, and r.m.s. components $R_i$ (Å) along the principal axes of the ellipsoids of thermal vibration*

The expression used is $\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$.

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|---|---|---|---|---|---|
| I | 138 (2) | 33 (1) | 50 (1) | −10 (1) | 0 (1) | −4 (1) | 0·177 | 0·189 | 0·255 |
| N | 97 (9) | 27 (3) | 49 (5) | 1 (4) | −4 (6) | 2 (3) | 0·169 | 0·178 | 0·213 |
| O(1) | 221 (15) | 36 (4) | 60 (6) | −17 (6) | −42 (7) | 8 (4) | 0·187 | 0·199 | 0·325 |
| O(2) | 166 (11) | 29 (3) | 64 (5) | 9 (4) | −24 (6) | 2 (3) | 0·175 | 0·201 | 0·821 |
| O(3) | 160 (14) | 60 (4) | 43 (6) | −31 (6) | 4 (6) | 0 (4) | 0·167 | 0·239 | 0·286 |
| O(4) | 90 (8) | 44 (3) | 76 (6) | −4 (4) | 4 (5) | −1 (4) | 0·204 | 0·217 | 0·223 |
| C(1) | 119 (12) | 30 (4) | 48 (6) | −4 (5) | 13 (7) | 0 (4) | 0·175 | 0·179 | 0·237 |
| C(2) | 148 (13) | 29 (4) | 47 (6) | 6 (6) | −5 (8) | −1 (4) | 0·174 | 0·176 | 0·263 |
| C(3) | 96 (10) | 38 (4) | 52 (6) | −3 (5) | 1 (7) | −3 (4) | 0·183 | 0·201 | 0·212 |
| C(4) | 132 (13) | 23 (3) | 56 (7) | −6 (5) | 7 (8) | −5 (4) | 0·155 | 0·191 | 0·249 |

indices obtained were $R=0{\cdot}050$ and $R_w=0{\cdot}062$. In the last cycle of refinement the shifts in the parameters were less than 1 % of the estimated standard deviations. A final difference map was featureless.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for the non-hydrogen atoms and from Stewart, Davidson & Simpson (1965) for the hydrogen atoms. The scattering factor for the iodide ion was corrected for anomalous dispersion. The positional and thermal parameters with the r.m.s. components along the principal axes of the thermal-motion ellipsoids are given in Tables 1 and 2. Observed and calculated structure factors are compared in Table 3. Selected interatomic distances and angles are shown in Table 4.

All computations were made on the UNIVAC 1108 computer in Lund, Sweden, and a list of the programs used is given by Oskarsson (1973).

### Description of the structure

The atoms of the organic molecule are designated in Fig. 1. The structure is built up of iodide ions and positively charged iminodiacetic acid ions, $[C_4H_8NO_4]^+$. The latter are connected by hydrogen bonds OH···I···HO forming chains running in the **c** direction. These chains are cross-linked *via* hydrogen bonds NH···I and NH···O(2) [and possibly NH···O(4)] forming layers that are stacked in the **b** direction. The layers have a thickness of *b*/2, as seen in Fig. 2. The closest contacts between the layers, I-H(1) and I-H(2), are 3·2 Å, indicating van der Waals contacts.

In contrast with the related chloride and bromide compounds (Oskarsson, 1973), where the iminodiacetic acid ion, $[C_4H_8NO_4]^+$, exhibits symmetry *mm*, this ion

Table 4. *Selected interatomic distances* (Å) *and angles* (°) *with estimated standard deviations*

(*a*) The iminodiacetic acid ion

| | | | |
|---|---|---|---|
| N—C(2) | 1·498 (11) | C(2)–N—C(3) | 114·7 (6) |
| N—C(3) | 1·503 (10) | N—C(2)–C(1) | 108·7 (6) |
| C(2)–C(1) | 1·499 (13) | N—C(3)–C(4) | 111·2 (8) |
| C(3)–C(4) | 1·486 (13) | C(2)–C(1)–O(1) | 111·0 (7) |
| C(1)–O(1) | 1·307 (11) | C(2)–C(1)–O(2) | 123·6 (8) |
| C(1)–O(2) | 1·204 (10) | O(1)–C(1)–O(2) | 125·4 (9) |
| C(4)–O(3) | 1·311 (11) | C(3)–C(4)–O(3) | 110·4 (9) |
| C(4)–O(4) | 1·203 (12) | C(3)–C(4)–O(4) | 124·8 (8) |
| N—H(5) | 0·77 (11) | O(3)–C(4)–O(4) | 124·8 (10) |
| N—H(6) | 1·14 (9) | C(1)–O(1)–H(8) | 105 (12) |
| O(1)–H(8) | 0·58 (12) | C(4)–O(3)–H(7) | 132 (18) |
| O(3)–H(7) | 0·46 (14) | H(5)–N—H(6) | 114 (9) |

(*b*) Dihedral angles

| | |
|---|---|
| N–C(2)–C(1)–O(1) | 180·0 (10) |
| N–C(2)–C(1)–O(2) | 180·0 (6) |
| N–C(3)–C(4)–O(3) | 177·5 (9) |
| N–C(3)–C(4)–O(4) | 177·4 (12) |

(*c*) The hydrogen bonds

| | | | |
|---|---|---|---|
| N·····I | 3·606 (7) | O(1)···I | 3·378 (8) |
| N——H(5) | 0·77 (11) | O(1)—H(8) | 0·58 (12) |
| I······H(5) | 2·95 (11) | I······H(8) | 2·81 (11) |
| ∠N——H(5)···I | 144 (9) | ∠O(1)—H(8)···I | 168 (15) |
| O(3)···I | 3·462 (9) | N·····O(2) | 2·932 (10) |
| O(3)—H(7) | 0·46 (14) | N——H(6) | 1·14 (9) |
| I······H(7) | 3·02 (14) | O(2)···H(6) | 1·93 (9) |
| ∠O(3)—H(7)···I | 167 (20) | ∠N—H(6)···O(2) | 144 (7) |

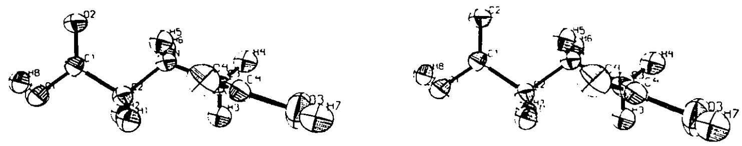

Fig. 1. A stereoscopic pair of drawings showing the positively charged iminodiacetic acid ion. The view is perpendicular to a least-squares plane through N, C(2), C(1), O(1) and O(2). Figs. 1-3 have been drawn by the program *ORTEP*.

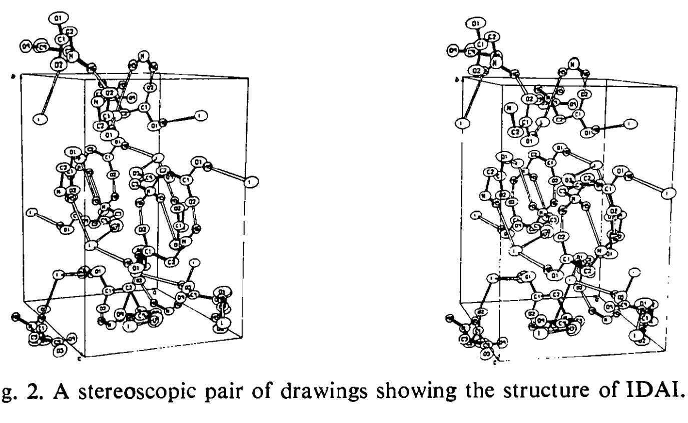

Fig. 2. A stereoscopic pair of drawings showing the structure of IDAI.

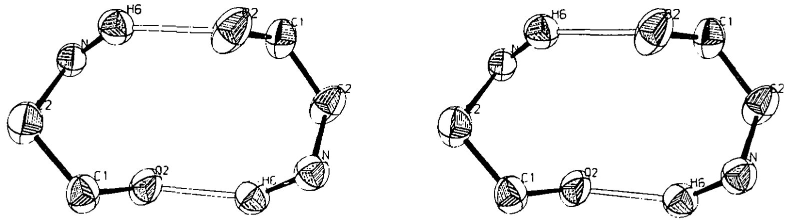

Fig. 3. A stereoscopic view of the 10-membered ring.

has no symmetry elements in the iodide. The non-hydrogen atoms form two planes (Table 5) that are twisted 83 (1)° at the nitrogen atom. Related inter-atomic distances and angles are not significantly different in the two halves of the molecule [Table 4(*a*)] and they agree well with those found in the chloride and bromide. The dihedral angles N–C–C–O are given in Table 4(*b*). A detailed discussion of the conformation of the iminodiacetic acid molecule in different crystallographic surroundings will be postponed to a following publication.

Table 5. *Deviations* (Å) *from the least-squares planes through the non-hydrogen atoms in the two halves of* $[C_4H_8NO_4]^+$

The atoms defining plane I are N, C(1), C(2), O(1), O(2), and the atoms defining plane II are N, C(3), C(4), O(3), O(4).

| Atom | I | Atom | II |
|---|---|---|---|
| N | 0·000 | N | 0·025 |
| C(1) | −0·002 | C(3) | −0·032 |
| C(2) | 0·007 | C(4) | −0·004 |
| O(1) | −0·002 | O(3) | 0·020 |
| O(2) | −0·003 | O(4) | −0·009 |

The hydrogen-bond system is shown in Fig. 2. Distances and angles involved are summarized in Table 4(*c*). From a geometrical point of view, a hydrogen bond is said to exist if a hydrogen-atom–heavy-atom distance is 0·2 Å or more shorter than the sum of the van der Waals radii (Hamilton & Ibers, 1968). In this structure the positions of the hydrogen atoms are not determined with the accuracy needed to use this criterion. As an additional condition one can use the rule that an A···B distance less than the van der Waals distance is sufficient but not necessary for hydrogen bonding. According to these criteria, the iodide ion is hydrogen bonded to two oxygen atoms and one nitrogen atom. The iodide ion is in van der Waals contact with O(2) in the same layer [3·659 (6) Å] and with H(1) and H(3) in the neighbouring layer. These hydrogen bond lengths are in agreement with those found in L-leucine hydroiodide (Chaney, Seely & Steinrauf, 1971), where the iodide ion also accepts three hydrogen bonds. Two of them are of the type NH···I with lengths 3·52 (2) and 3·54 (2) Å, and one is of the type OH···I with length 3·37 (2) Å.

The nitrogen atom is also hydrogen bonded to O(2) and a 10-membered ring is formed by H(6)–N–C(2)–C(1)–O(2) and an identical half molecule related by a centre of symmetry (Fig. 3). A similar ring is found in a monoclinic phase of iminodiacetic acid (Boman, Herbertsson & Oskarsson, 1974). According to the hydrogen-bond criteria mentioned above, a bifurcated hydrogen bond involving H(6) cannot be excluded since H(6)–O(4) is 2·14 (9) and N–O(4) 2·80 (1) Å. However, as the angle N–H(6)···O(4) is 114 (6)°, this is probably a short van der Waals contact rather than a hydrogen bond.

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## References

Boman, C.-E., Herbertsson, H. & Oskarsson, Å. (1974). *Acta Cryst.* **B30**, 378–382.
Chaney, M. O., Seely, O. & Steinrauf, L. K. (1971). *Acta Cryst.* **B27**, 544–548.
Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
*International Tables for X-ray Crystallography* (1962). Vol. III, 2nd ed., pp. 202–206. Birmingham: Kynoch Press.
Nordin, E. (1973). Private communication.
Oskarsson, Å. (1973). *Acta Cryst.* **B29**, 1747–1751.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.