3. Crystal Structure of Tetrakis(phenacetin) Dihydrogentetraiodide Dihydrate $\{[H_5C_2OC_6H_4N(H)C(CH_3){=}O]_4 \cdot H_2I_4 \cdot 2\,H_2O\}$[1])

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Dedicated to Prof. *Jack D. Dunitz* on the occasion of his 60th birthday

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Summary

(Phenacetin)$_4 \cdot H_2I_4 \cdot 2\,H_2O$ is triclinic, $a = 13.641\,(7)$, $b = 12.807\,(6)$, $c = 7.201\,(3)$ Å, $\alpha = 99.8\,(4)$, $\beta = 86.5\,(4)$, $\gamma = 104.0\,(5)$°, $P\bar{1}$, $Z = 1$. The ordered crystal structure has been refined to $R_F = 0.050$, using 4173 independent reflections measured on a four-circle diffractometer with Mo*Kα* (graphite monochromator) radiation. The crystals are composed of alternating positively and negatively charged slices; each positive slice contains a double layer of stacks of hemi-protonated phenacetin molecules which are H-bonded through their carbonyl groups (d(O - - - O) = 2.432 (4) Å) while each negative slice contains a single layer of I_4^{2-}-ions linked in chains along [100] through H-bonds to pairs of water molecules. The axes of the phenacetin stacks are parallel to the planes of the ($I_4^{2-} \cdot 2\,H_2O$)-layers. The I_4^{2-}-ion is centrosymmetric and can be approximately represented as I^- - - - I–I - - - I^- (d(I^- - - - I) = 3.404 (1) Å; d(I–I) = 2.774 (1) Å). The compound is a pseudo-type A basic salt.

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1. Introduction. - The title compound was obtained during a study of the crystal structure of (phenacetin)$_2 \cdot HI_5$ (phenacetin = *N*-(4-ethoxyphenyl)-acetamide) [2]. IR. spectra suggested the presence of phenacetin 'dimers' H-bonded through their carbonyl groups, but it was not clear whether the iodine moieties were I^- and I_3^- or I_4^{2-} (both possibilities were compatible with the preliminary crystallographic results), nor was the role of the water molecules apparent. The crystal structure, determined to clarify these questions, shows that phenacetin 'dimers' are present and that I_4^{2-}-ions and water molecules are H-bonded together in sheets. The interatomic distances in I_4^{2-}-suggest that this moiety can be approximately represented as I^- - - - I–I - - - I^-, in accordance with previous results.

2. Experimental. - Diffraction-quality single crystals were obtained by the following procedure: 0.5 g phenacetin, dissolved in 15 ml $CHCl_3$, was vigorously stirred for 30 min with 3 ml conc. HI containing traces of I_2. Strongly dichroic ruby-red needles (elongated along [001] and showing (100), (010) and $(1\bar{1}0)$) formed within 2-3 days. The crystals were all macroscopically twinned (see *Sect. 3.3*) and a single crystal, suitable for intensity measurements, had to be cut off a twinned fragment. The single crystal was sealed into a capillary before starting the intensity measurements. Crystal data are given in *Table 1*.

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[1]) Part VI of 'Crystal Structures of Polyiodide Salts and Molecular Complexes'. Part V: [1].

Table 1. *Crystal data, determined on four-circle diffractometer,* of Tetrakis(phenacetin) dihydrogentetraiodide dihydrate $[H_5C_2OC_6H_4N(H)C(CH_3)=O]_4 \cdot H_2I_4 \cdot 2\,H_2O$

Triclinic[a])		
$a = 13.641$ (7) Å	$b = 12.807$ (6)	$c = 7.201$ (3)
$\alpha = 99.8$ (4)°	$\beta = 86.5$ (4)	$\gamma = 104.0$ (5)
$V = 1202.8$ Å^3	$D_{meas} = 1.72$ g cm^{-3} [b])	
$D_{calc} = 1.69$ g cm^{-3} for $Z = 1$	$\mu(MoK\alpha) = 24.5$ cm^{-1}	
F.Wt. = 1246.53	F(000) = 618	

[a]) The cell given is the triacute *Dirichlet*-reduced cell but with origin shifted. The *Delaunay*-reduced cell is:

$a = 13.641$ Å	$b = 13.576$	$c = 7.196$
$\alpha = 111.7°$	$\beta = 96.7$	$\gamma = 101.2$

[b]) See [2].

The intensities of 4231 independent reflections were measured on a *Philips PW 1100/20* four-circle diffractometer (graphite-monochromated Mo$K\alpha$; $\omega/2\theta$-method; $2.5 \leq \theta \leq 25°$; scan width and speed (in ω) 1.2° and 0.05° s^{-1}; background counted for 10 s at scan extremities; 3 standard reflections measured every 120 min, with no significant change during the measurement period). *Lorentz* and polarization corrections were made, but absorption was not taken into account. The positions of the two I-atoms in the asymmetric unit were found from a *Patterson* synthesis, showing that I_4^{2-}-ions were

Table 2. *Atomic parameters* (in brackets e.s.d., in units of the last significant figure; × 10^4 for non-H- and × 10^3 for H-atoms; $U_{eq} = \frac{1}{3}$ trace $\tilde{U}$)

Atom	x	y	z	U_{eq}
I(1)	1523 (0)	4560 (0)	3595 (1)	630
I(2)	3990 (0)	4871 (0)	4616 (1)	669
C(1)	4572 (4)	1478 (5)	4039 (9)	651
C(2)	5691 (3)	1937 (4)	4131 (7)	477
O(3)	−3848 (2)	1023 (2)	3531 (5)	486
C(4)	−2824 (3)	1237 (4)	3532 (7)	416
C(5)	−2198 (3)	2250 (3)	4135 (7)	427
C(6)	−1161 (3)	2356 (3)	4074 (7)	440
C(7)	−742 (3)	1490 (4)	3418 (6)	392
C(8)	−1375 (4)	472 (4)	2820 (8)	494
C(9)	−2412 (3)	359 (4)	2886 (7)	471
N(10)	334 (3)	1694 (3)	3419 (6)	482
C(11)	925 (3)	1008 (4)	3054 (7)	466
O(12)	579 (3)	5 (3)	2699 (6)	651
C(13)	2036 (4)	1463 (5)	3120 (9)	606
C(1)A	7615 (4)	7178 (5)	1419 (9)	683
C(2)A	6534 (4)	6787 (5)	847 (8)	573
O(3)A	6146 (2)	7731 (3)	836 (5)	523
C(4)A	5127 (3)	7566 (4)	718 (7)	438
C(5)A	4755 (4)	8501 (4)	1072 (8)	531
C(6)A	3731 (4)	8423 (4)	999 (8)	498
C(7)A	3060 (3)	7413 (4)	618 (6)	424
C(8)A	3443 (4)	6495 (4)	236 (7)	498
C(9)A	4465 (4)	6559 (4)	265 (7)	492
N(10)A	1992 (3)	7232 (3)	573 (6)	467
C(11)A	1414 (3)	7906 (4)	1174 (6)	453
O(12)A	1808 (2)	8893 (3)	1911 (5)	540
C(13)A	302 (4)	7512 (5)	1033 (8)	603
O(H_2O)	865 (4)	5256 (3)	8409 (7)	833

Table 2 (continued)

Atom	x	y	z	U_{iso}
H(11)	437 (6)	90 (7)	470 (12)	100
H(12)	441 (6)	113 (7)	291 (12)	87
H(13)	424 (6)	201 (7)	446 (12)	130
H(21)	596 (6)	214 (6)	523 (11)	147
H(22)	583 (7)	196 (8)	311 (14)	239
H(51)	−251 (3)	291 (4)	473 (6)	36
H(61)	−74 (4)	294 (4)	456 (8)	51
H(81)	−111 (6)	−15 (6)	259 (10)	100
H(91)	−285 (5)	−22 (5)	216 (9)	69
H(101)	58 (5)	238 (5)	368 (9)	56
H(131)	219 (5)	219 (5)	339 (8)	68
H(132)	240 (4)	128 (4)	182 (7)	51
H(133)	241 (5)	112 (6)	381 (10)	92
H(11)A	808 (11)	646 (12)	176 (20)	252
H(12)A	754 (9)	735 (10)	264 (18)	173
H(13)A	801 (6)	772 (6)	89 (11)	73
H(21)A	608 (5)	632 (6)	160 (10)	91
H(22)A	662 (6)	646 (7)	−100 (12)	102
H(51)A	532 (4)	921 (4)	136 (8)	69
H(61)A	354 (5)	914 (5)	120 (9)	74
H(81)A	295 (3)	583 (3)	−32 (6)	12
H(91)A	480 (4)	588 (5)	7 (8)	56
H(101)A	159 (4)	654 (5)	14 (8)	56
H(131)A	14 (6)	677 (7)	41 (12)	127
H(132)A	22 (6)	792 (7)	51 (12)	118
H(133)A	−4 (4)	764 (5)	242 (8)	68
H(1)(H_2O)	103 (5)	508 (6)	911 (11)	90
H(2)(H_2O)	60 (6)	559 (7)	836 (12)	73

present. The positions of the light atoms were found from successive difference syntheses and the structure refined to $R_F = 0.050$ ($R_W = 0.060$). The *SHELX-76* programme package [3] was used for these calculations. Atomic coordinates are given in *Table 2* and temperature factors (anisotropic for I, C, N, O and isotropic for H) are available from the authors. In the final refinement cycle 4173 reflections were used and 375 parameters refined (in two blocks, one for I, C, N, O and the second for H).

Representative values of the estimated standard deviations (e.s.d.) are: σ(I-I) 0.001 Å, σ(I-I--I) 0.02°, σ(I---O) 0.006 Å, σ(I--O---I) 0.1°, σ(C–C) 0.009 Å, σ(C–C–C) 0.2-0.5°.

3. Results. – 3.1. *Crystal Structure.* A projection of the structure down [001] *(Fig. 1)* and an accompanying *ORTEP* [4] stereoview *(Fig. 2)* show that the structure can be described in terms of alternating slices of phenacetin molecules and $H_2O \cdot I_4^{2-} \cdot OH_2$ groups lying about successive (020)-planes. The phenacetin slice contains two sheets, related to each other by crystallographic centres of symmetry. Each sheet contains stacks of phenacetin molecules; the stack axis is along [001] and the long axes of the phenacetin molecules are parallel to [100]. Each stack has a repetition of translationally equivalent pairs of phenacetin molecules; the two phenacetin molecules in such a pair are crystallographically independent but are parallel and mutually displaced by ≈ 2.4 Å along [100] and ≈ 1.2 Å along [010] *(Fig. 3)*. Crystallographically independent phenacetin molecules in adjacent stacks have a short separation of 2.432 (5) Å between their carbonyl O-atoms. Considering

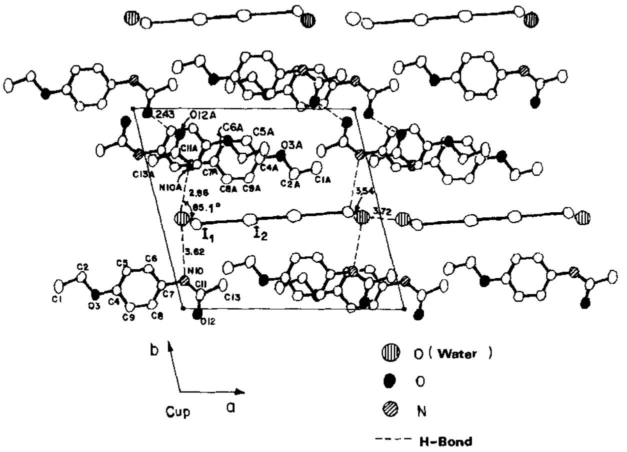


Fig. 1. *Projection down [001], showing numbering of reference atoms and some inter-moiety distances*

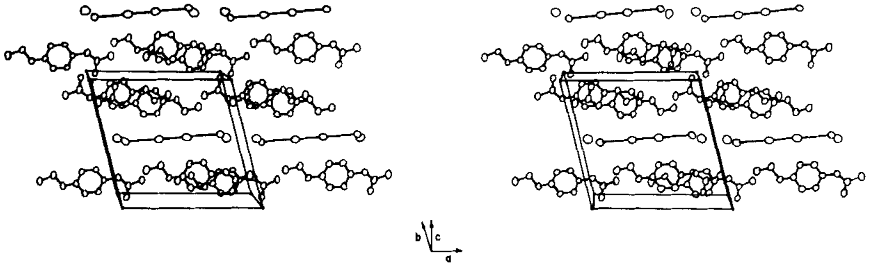


Fig. 2. ORTEP *stereoview, seen in approximately the same direction as* Figure 1 (The thermal ellipsoids are 50%-probability ellipsoids)

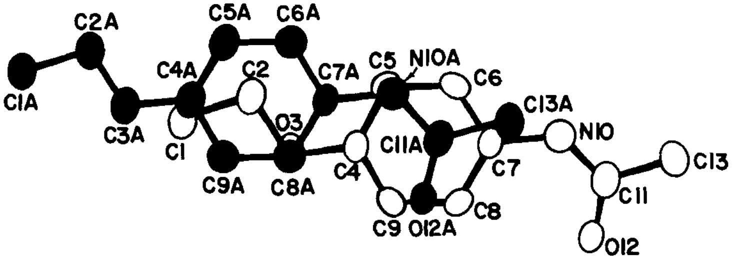


Fig. 3. *Projection of one phenacetin molecule in a stack onto the best plane of the adjacent* (crystallographically independent) *molecule* (Such a pair of molecules is repeated by translation along [001] to form the stack)

earlier works [2] [5] we interpret this separation as indicating a strong H-bonded between the carbonyl O-atoms, with the acid proton located in this bond. The C,O-distances in the two carbonyl groups are significantly different (see *Fig. 5c*; $\Delta/\sigma = 0.039/0.008 = 4.9$), and this suggests that the proton is located unsymmetrically. Some support for this view is given by a small peak (height 0.4 e $Å^{-3}$) appearing in the bond, closer to the longer of the C,O-bonds.

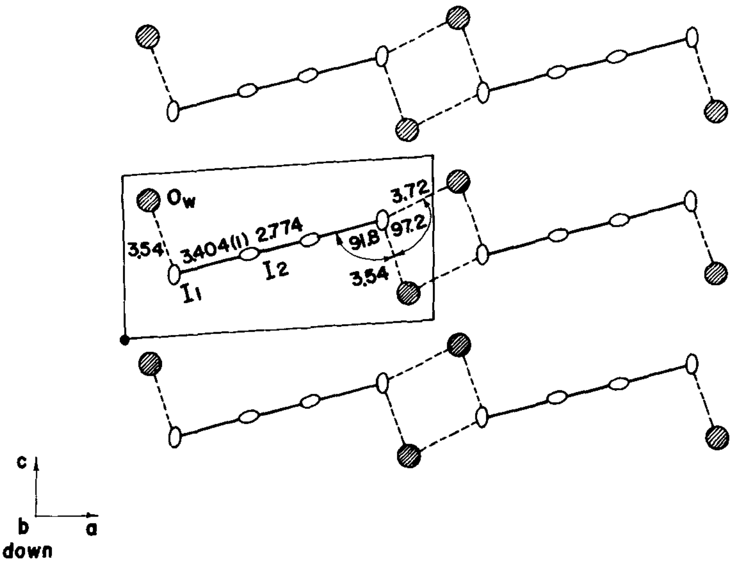
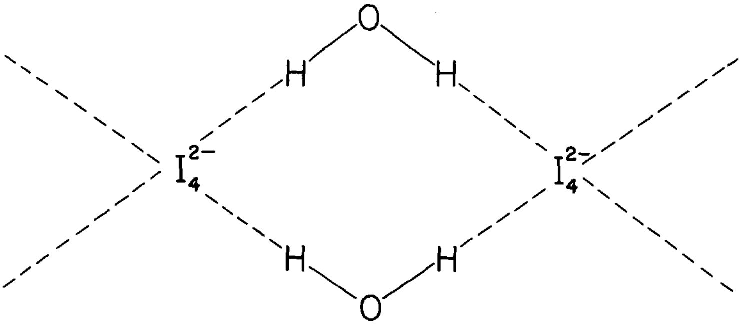


Fig. 4. *Arrangement of I_4^{2-}-ions and water molecules in (020)-planes* (The H-bonds are shown as broken lines)

The negatively charged slice contains a coplanar array of I_4^{2-}-ions and water molecules *(Fig. 4)*. Each terminal I-atom acts as an acceptor to H-bonds from two different water molecules (which are related by a centre of symmetry), with d(I---HO) = 3.54 and 3.72 Å, respectively. Thus chains of composition **A** extending in the [100]-direction are formed. There are no close contacts in the [001]-direction; in particular, the two centrosymmetrically related water O-atoms are not bonded to each other, their separation being 3.26 Å. In addition to the electrostatic and dispersion interactions between the layers, there are two H-bonds – one has N(10)H as donor to I(1) (d(N---I) = 3.62 Å) and the other has N(10A)H as donor to the water molecule (d(N---O) = 2.86 (1) Å). The inter-moiety links from I(1) are approximately orthogonal and in-plane ($\sphericalangle$I(2)–I(1)–O_W = 91.8 (1)°; $\sphericalangle O_{W'}$–I(1)–O_W = 97.2 (1)°; $\sphericalangle$N(10)–I(1)–O_W = 85.1 (1)°) and those about the water molecule approximately pyramidal ($\sphericalangle$I(1)–O_W–N(10) A = 120.2 (2)°; $\sphericalangle$I(1)–O_W–I(1′) = 82.8 (1)°; $\sphericalangle$I(1′)–O_W–N(10) A = 115.9 (2)°). At the two N-atoms



A

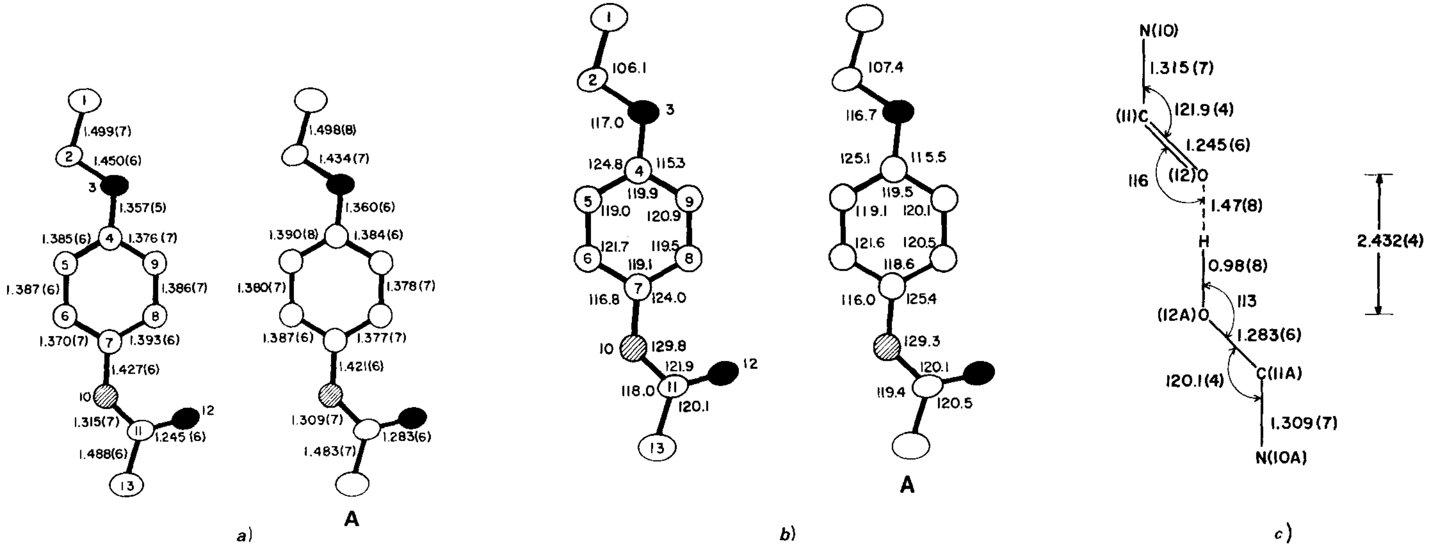


Fig. 5. *Dimensions of the two crystallographically independent phenacetin molecules: a)* bond lengths, *b)* bond angles, *c)* region of the strong H-bond. No attempt has been made to specify the bonding in the lower part of this figure.

involved in H-bonding the relevant angles are C(7)–N(10)---I(1) = 112.3 (1)° and C(7)A–N(10)A---O_W = 118.5 (5)°.

3.2. *Dimensions of the phenacetin molecules.* The two crystallographically independent phenacetin molecules do not differ significantly *(Fig. 5)*, except for the region of the H-bonded carbonyl groups as discussed above; the mean dimensions are similar to those reported earlier [2] but are appreciably more accurate.

Best planes were calculated through the ethoxy O-atom, the six C-atoms of the benzene ring and the N-atom of the amide group for each of the independent molecules. No significant deviations were found. The angle between the two planes is 9°. The acetyl groups deviate from the planes defined above, principally due to rotation about the N, C(ring)-bonds. The torsion angles C(11)–N(10)–C(7)–C(8) and C(11)A–N(10)A–C(7)A–C(8)A are –6.9 (9)° and –13.5 (9)°, respectively.

3.3. *Twinning.* Oscillation and *Weissenberg* photographs about [001] of a twinned crystal showed that c_1 and c_2 (subscripts represent individuals 1 and 2 of the twin) were parallel (*i.e.* the oscillation photograph did *not* have a (spurious) mirror plane) and that a_1^*, a_2^* and b_1^*, b_2^* were pairwise either parallel or antiparallel (*i.e.* the hk0-*Weissenberg* photograph showed only one reciprocal lattice section whereas the higher-layer *Weissenberg* photographs showed two reciprocal lattice sections). Distinction between parallelism and antiparallelism is conveniently made on the four-circle diffractometer, following *Krauss et al.* [6]. The *UB* matrices for the two individuals were found to be

$$UB1 = \begin{bmatrix} -0.0316 & -0.1252 & -0.0237 \\ 0.1117 & -0.0048 & -0.0109 \\ -0.0002 & 0.0061 & 0.2149 \end{bmatrix}$$

$$UB2 = \begin{bmatrix} 0.0304 & 0.1251 & 0.0452 \\ -0.1121 & 0.0034 & 0.0162 \\ -0.0002 & -0.0066 & 0.2112 \end{bmatrix}$$

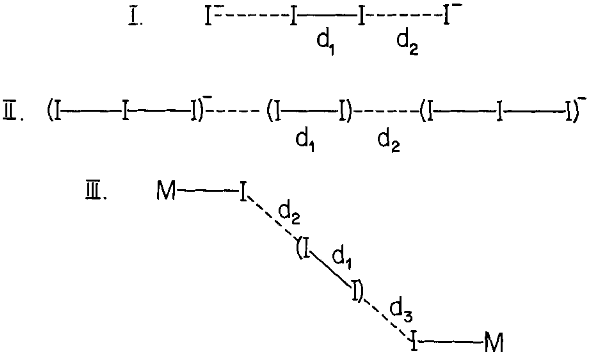
These *UB* matrices describe the reciprocal lattice vectors in the coordinate system of the diffractometer. The columns of the *UB*-matrices represent the projections of a^*, b^*, c^* on the axes of the diffractometer coordinate system.

Comparison of *UB1* and *UB2* shows that $a_1^* = -a_2^*$, $b_1^* = -b_2^*$ (it will also be noticed that c_1^* and c_2^* are approximately related by a two-fold rotation about the *z*-axis of the diffractometer; this is a coincidence resulting from the accidentally close alignment of the common *c*-axis with the ϕ-axis of the diffractometer). Both these *UB*-matrices give, within the limits of error, the unit cell of *Table 1.* The relation between the two individuals of the twin is given by $a_1^* = -a_2^*$, $b_1^* = -b_2^*$, $c_1 = c_2$.

Thus the operation which describes the relationship between the twins is a two-fold rotation about *c*. The twinning is by pseudo-merohedry and the twin law is analogous to the *Pericline Law* of mineralogy [6]. The obliquity (the angle between *c* and c^*) is 9.8°.

4. Discussion. – This crystal structure resembles that of other polyiodides in many respects, but there are some interesting differences. The arrangement of alternating cationic and anionic sheets has been found in (phenacetin)$_2 \cdot HI_5$, (theobromine)$_2 \cdot H_2I_8$ [2] and in (glycine)$_4 \cdot KI_3$ [8]). The angle of ≈90° between the planes of phenacetin molecules and the polyiodide layer found here (and in (phenacetin)$_2 \cdot HI_5$) allows N–H---I H-bonding to contribute to the cohesion between cationic and anionic layers. In (glycine)$_4 \cdot KI_3$ the anionic layers contain only triiodide ions, but mixed layers are found in CsI_3 [9], $KIBr_2 \cdot H_2O$ [10] and protonated 1-methylcytosine triiodide [11]. In the latter salt there are bifurcated I---N H-bonds, of lengths 3.610 (3) and 3.597 (3) Å, respectively, to the vertex iodines in a zigzag $--I_3^- --- I_3^- --$ chain. These distances are very similar to the N---I distances found in the present structure. The bonding geometries about the terminal I-atoms are different in the two compounds. In the present compound the terminal I-atom forms three in-plane bonds (*Fig. 4*) and another H-bond, approximately normal to this plane, to NH of phenacetin. In protonated (1-methyl-

Table 3. *Dimensions of essentially isolated I_4^{2-}-ions and of I_2-molecules interacting with two I_3^--ions* (E.s.d. are cited where available)



Compound	d_1 (Å)	d_2 (Å)	Reference
I. Essentially-isolated I_4^{2-}-ions			
1. $[UO_2(OH) \cdot 3\,CO(NH_2)_2] \cdot I_4$	2.81	3.40	[12]
2. $[Co(NH_3)_6] \cdot I_7$	2.761 (4)	3.318 (4)	[13]
3. $[Cu(NH_3)_4] \cdot I_4$	2.802 (1)	3.342 (1)	[14]
4. (phenacetin)$_4 \cdot H_2I_4 \cdot 2\,H_2O$	2.774 (1)	3.404 (1)	present work
II. I_2 interacting with two I_3^--ions			
1. Cu(en)$_2 \cdot I_6$	2.779	3.376	[13]
2. Cs_2I_8	2.83	3.42	[15]
3. (theobromine)$_2 \cdot H_2I_8$	2.761 (2)	3.424 (2)	
		3.347 (2)	[2]
4. $[(C_2H_5)_4N] \cdot I_7$	2.735 (3)	3.435 (3)	[16]
5. $[(Py)_2I] \cdot I_7$	2.74	3.44	[17]
III. I_2 interacting with two I-M moieties	d_1	d_2/d_3 (Å)	
1. $\{Ir(C_5Me_5)_2\}I_6$	2.787 (2)	3.241 (2)	
		3.557 (2)	[18]
2. Pt(phen)I_5	2.739 (3)	3.289 (3)	
		3.457 (3)	[19]
3. Pt(phen)I_6	2.750 (3)	3.481 (3)	
		3.452 (3)	[19]

cytosine). I_3 there are only in-plane bonds, one covalent to iodine and one secondary to a neighbouring I_3^- (these are approximately mutually orthogonal), and two H-bonds to NH-groups of the protonated 1-methylcytosine moiety, their disposition being dictated by the dimensions of this cation.

Essentially isolated[2]) I_4^{2-}-ions have been found in a number of crystals *(Table 3)*; their dimensions are concordant and fit a model of two I-ions interacting with an I_2-molecule. The same situation is found when an I_2-molecule is located between two I_3-ions or between two coordinatively-bonded iodines, and similar $I^- - - - I_2$ distances are found in all three situations.

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[2]) 'Isolated I_4^{2-}-ions', in the present context, implies that there is no direct interaction between these ions, although they do, of course, interact directly with other moieties in the crystal (by H-bonding to O(water) and N(phenacetin)).