The Crystal Structures of the Polyiodide Salts (phenacetin) $_{2}\cdot HI_{5}$ and (theobromine) $_{2}\cdot H_{2}I_{8}$

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THE CRYSTAL STRUCTURES OF THE POLYIODIDE SALTS (PHENACETIN)$_2$·HI$_5$ AND (THEOBROMINE)$_2$·H$_2$I$_8$

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CONTENTS

The crystal structures of (phenacetin)$_2$·HI$_5$ (triclinic, $a = 12.44$ Å,† $b = 10.67$, $c = 5.81$, $\alpha = 103.3°$, $\beta = 103.7$, $\gamma = 87.3$, $P\overline{1}$, $Z = 1$) and (theobromine)$_2$·H$_2$I$_8$ (triclinic, $a = 14.38$ Å, $b = 14.07$, $c = 7.75$, $\alpha = 91.2°$, $\beta = 100.8$, $\gamma = 91.0$, $P\overline{1}$, $Z = 2$) have been solved by Patterson methods, using intensities measured by Weissenberg diffractometer with graphite-monochromated Mo Kα radiation (2815 and 2827 intensities, $R = 8.3$ % and 11.1 % respectively). Both structures are polyiodide salts, with alternating cationic (organic) and anionic (polyiodide) layers. In (phenacetin)$_2$·HI$_5$ the organic layers consist of hydrogen-bonded phenacetin 'dimers', with the proton bridging the oxygens of the carbonyl bonds in a short hydrogen bond (d(O...O) = 2.46 (2) Å); the polyiodide layers contain zigzag chains of alternating iodine molecules and triiodide ions, with secondary bonds (d(I...I) = 3.55 Å) between these moieties. There is only van der Waals bonding between parallel chains. This substance, bis(phenacetin)hydrogen iodine triiodide, is a type A *basic* salt. In (theobromine)$_2$·H$_2$I$_8$ the organic layer consists of hydrogen-bonded theobrominium cations and the polyiodide layer of centrosymmetric S-shaped (I_{16}^{4-}) ions, with the arrangement

$$I_3^- \cdot I_2 \cdot I_3^- \cdot I_3^- \cdot I_2 \cdot I_3^-;$$

there is secondary bonding between triiodide and iodine moieties within the hexadecaiodide ions. There are tertiary bonds (d(I...I) = 3.84 Å) between adjacent I_{16}^{4-} ions.

1. Introduction

Crystalline (phenacetin)$_2$·HI$_5$ was prepared by Emery (1914, 1916) during an investigation of methods of separating phenacetin, with its desirable medicinal properties, from mixtures which included acetanilide. (Theobromine)$_2$·H$_2$I$_8$ was first prepared by Jörgensen (1869) and studied by Shaw (1896). Both substances can be formulated as molecular complexes containing formally

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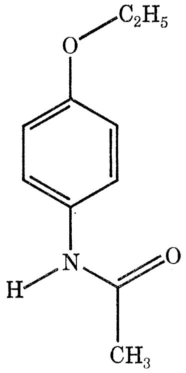
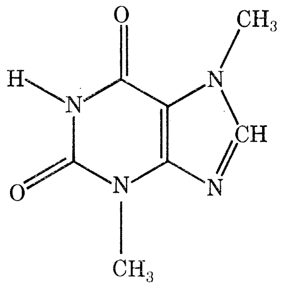
† 1 Å = 0.1 nm = 10^{-10} m.

neutral organic molecules, cations (here protons) and polyiodide anions. However, the mode of interaction between the moieties is not clear from the formula, nor are the structures of the polyiodide anions predictable. Our crystal structure analyses show that there are considerable resemblances between the two compounds – both are polyiodide salts and both are made up of alternating cationic and anionic layers, the former containing the protonated organic moiety and the latter the polyiodide anion. Neither layer is planar. Both polyiodide anions are made up of interacting iodine molecules and tri-iodide anions, but with different arrangements. The penta-iodide has zigzag chains $\ldots I_2 \cdot I_3^- \cdot I_2 \cdot I_3^- \ldots$ while the octa-iodide is better described as a hexadeca-iodide, the centrosymmetric S-shaped I_{16}^{4-} ions having the arrangement $I_3^- \cdot I_2 \cdot I_3^- \cdot I_3^- \cdot I_2 \cdot I_3^-$. This alternating layer arrangement can be contrasted with structures based on linear polyiodide anions enclosed in channels in an organic matrix, such as $(\text{benzamide})_2 \cdot HI_3$ (Reddy *et al.* 1964).

Brief reports of our work have appeared (Herbstein & Kapon 1972, 1975).



phenacetin



theobromine (3,7-dimethylxanthine)

2. CRYSTAL STRUCTURE OF $(\text{PHENACETIN})_2 \cdot HI_5$

(*a*) *Experimental*

Deep blue triclinic rhombs, with a metallic hue, were obtained from mixtures of appropriate quantities of an ethanolic solution of phenacetin and an aqueous solution of $HI + I_2$. The air-stable rhombs were slightly elongated along [001] and showed $\{110\}$ and $\{010\}$ faces. Crystallographic data (table 1) and intensities were obtained by standard techniques (table 2). Assuming space group $P\bar{1}$, there are one phenacetin molecule and two iodine atoms in general positions, and one iodine and one hydrogen at independent centres of symmetry. This choice of space group was confirmed by the structure analysis. The structure problem was solved in straightforward manner via Patterson methods. Standard refinement methods (table 2) gave the atomic coordinates of table 3 (hydrogen coordinates were not included; numbering of atoms is shown in figure 4); lists of observed and calculated structure factors (and the anisotropic temperature factors for $(\text{theobromine})_2 \cdot H_2I_8$) have been deposited in the archives of the Royal Society and in the British Library, Lending Division.†

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† Copies of the material deposited may be purchased from the British Library, Lending Division, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, U.K. (reference SUP 10029).

(*b*) *Results*

The crystal structure consists of alternating layers of organic moieties and polyiodide anions (figure 1). It is convenient to first describe the individual layers and then the crystal structure as a whole.

TABLE 1. CRYSTAL DATA FOR (PHENACETIN)$_2$·HI$_5$

$(C_{10}H_{13}O_2N)_2HI_5$	f.w. 993.95
triclinic	m. pt. 132°
space group $P\bar{1}$ (No. 2)	
$a = 12.44$ (1) Å	$\alpha = 103.3$ (1)°
$b = 10.67$ (1)	$\beta = 103.7$ (1)
$c = 5.81$ (1)	$\gamma = 87.3$ (1)

cell volume 730 Å^3
$\rho_{\text{meas}} = 2.26$ g cm^{-3} (flotation, sym-tetrabromoethane-toluene solution)
$\rho_{\text{calc}} = 2.26$ g cm^{-3} for $Z = 1$
F(000) = 458
λ(Mo K$\bar{\alpha}$) = 0.7107 Å
$\mu = 54.1$ cm^{-1} (for Mo K$\bar{\alpha}$)

TABLE 2. DETAILS OF EXPERIMENTAL TECHNIQUES FOR (PHENACETIN)$_2$·HI$_5$ (i) AND (THEOBROMINE)$_2$·H$_2$I$_8$ (ii)

2-circle Stoe Weissenberg diffractometer; graphite monochromated Mo Kα; $\omega/2\theta$ scan-mode, 1° 2θ min^{-1}, 20 s background at scan extremities, $\Delta\omega = 1°$; rotation axis [001]; absorption corrections following Busing & Levy 1957; atomic scattering factors from Hanson *et al.* 1964; dispersion corrections from *International tables for X-ray crystallography* 1962; refinement ORFLS (full matrix on F).

	i	ii
1. crystal size and shape	prism ≈ 0.2 mm × 0.4 mm × 0.5 mm	needle ≈ 0.06 mm × 0.08 mm × 0.32 mm
2. number of reflexions	2815 (135 unobserved)	2827 (225 unobserved)
3. *R*-factor (%)	8.3	11.1
4. goodness of fit	1.28	0.96

TABLE 3. (PHENACETIN)$_2$·HI$_5$: FINAL FRACTIONAL COORDINATES

(E.s.ds in parameters are in units of the least significant digit.)

atom	*x*	*y*	*z*
I(1)	0	0	0
I(2)	−0.07634 (9)	0.18912 (10)	−0.29015 (22)
I(3)	−0.02486 (11)	0.41540 (14)	0.27679 (26)
C(1)	0.335 (2)	0.589 (2)	0.489 (3)
C(2)	0.289 (1)	0.474 (2)	0.285 (4)
O(3)	0.371 (1)	0.446 (1)	0.137 (2)
C(4)	0.350 (1)	0.346 (2)	−0.062 (3)
C(5)	0.436 (1)	0.316 (2)	−0.186 (4)
C(6)	0.422 (1)	0.216 (2)	−0.392 (3)
C(7)	0.325 (1)	0.143 (2)	−0.478 (3)
C(8)	0.242 (1)	0.171 (2)	−0.350 (3)
C(9)	0.254 (1)	0.273 (2)	−0.150 (4)
N(10)	0.306 (1)	0.035 (1)	−0.684 (3)
C(11)	0.365 (1)	−0.008 (2)	−0.843 (3)
O(12)	0.453 (1)	0.047 (1)	−0.836 (3)
C(13)	0.320 (2)	−0.123 (2)	−1.055 (4)

TABLE 3A. (PHENACETIN)$_2$·HI$_5$: FINAL ANISOTROPIC DEBYE–WALLER FACTORS* IN UNITS OF Å^2 AND THEIR E.S.DS

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
I(1)	0.0218 (6)	0.0443 (8)	0.0367 (8)	−0.0012 (5)	0.0037 (6)	0.0043 (5)
I(2)	0.0378 (6)	0.0465 (6)	0.0483 (7)	−0.0023 (5)	0.0168 (5)	0.0032 (5)
I(3)	0.0516 (7)	0.0630 (8)	0.0577 (8)	−0.0052 (6)	0.0256 (6)	0.0151 (6)
C(1)	0.042 (10)	0.055 (11)	0.058 (10)	−0.000 (8)	−0.022 (8)	0.004 (8)
C(2)	0.038 (9)	0.054 (10)	0.056 (13)	0.001 (7)	−0.010 (9)	0.014 (8)
O(3)	0.034 (6)	0.061 (8)	0.049 (8)	−0.012 (6)	−0.013 (6)	0.017 (5)
C(4)	0.028 (8)	0.038 (8)	0.048 (10)	−0.000 (6)	−0.005 (7)	0.006 (6)
C(5)	0.029 (8)	0.048 (10)	0.056 (12)	−0.007 (7)	−0.006 (8)	0.018 (7)
C(6)	0.023 (7)	0.044 (9)	0.058 (10)	−0.007 (6)	−0.004 (7)	0.015 (6)
C(7)	0.025 (7)	0.042 (9)	0.047 (10)	−0.003 (6)	−0.001 (7)	0.008 (6)
C(8)	0.024 (7)	0.050 (9)	0.050 (11)	−0.005 (6)	−0.005 (7)	0.011 (6)
C(9)	0.024 (8)	0.047 (11)	0.079 (14)	−0.008 (7)	−0.017 (9)	0.017 (8)
N(10)	0.019 (6)	0.057 (9)	0.040(8)	−0.005 (5)	−0.004 (6)	0.010 (5)
C(11)	0.036 (8)	0.038 (9)	0.045 (10)	0.000 (7)	−0.003 (7)	0.011 (6)
O(12)	0.034 (6)	0.057 (7)	0.071 (9)	−0.008 (5)	−0.013 (6)	0.032 (6)
C(13)	0.037 (10)	0.063 (12)	0.064 (13)	−0.007 (9)	−0.018 (10)	0.021 (9)

* Form of the Debye–Waller factor: $T = \exp\left[-2\pi^2 \sum_{i,j=1}^{3} h_i h_j a_i^* a_j^* U_{ij}\right]$.

(i) *The polyiodide layer.* This consists of zigzag chains of alternating I_2 molecules (centred at 000 and equivalent positions) and I_3^- ions (centred at $0\frac{1}{2}\frac{1}{2}$ etc); the mean chain propagation vector is in the [011] direction (figure 2). The layer as a whole is corrugated, with iodine atoms displaced above and below the (100) plane, which is the mean plane of the layer. However, the atoms of a particular zigzag chain do not deviate by more than 0.035 Å from the plane

$$0.9867x + 0.1857y - 0.3434z = 0.$$

(All planes in this paper are referred to the *crystal* axes and were calculated, by using the CRYM program system (D. J. Duchamp, B. L. Trus & J. Westphal 1969, unpublished results), by the methods of Schomaker *et al.* (1959) and Waser *et al.* (1973)).

The distances between iodine atoms of adjacent chains are all greater than 4 Å (figure 2).

(ii) *The organic layer.* The phenacetin molecules are all parallel and arranged in pairs about the crystallographic centres of symmetry (figures 1 and 3). The phenacetin moiety, as a whole, is approximately planar while the individual parts (the benzene ring, the ethoxy group (C, O only) and the methylamide group (C, N, O only)) are each essentially planar (table 4). The mean plane of the phenacetin moiety is inclined at *ca.* 74° to (100); there is only a small amount of direct overlap between phenacetin molecules related by translation along [001] (figure 3).

The dimensions of the phenacetin moiety (figure 4) do not differ significantly from those found in analogous molecules such as acetanilide (Brown & Corbridge 1954; Brown 1966), *p*-chloroacetanilide (Subramanian 1966), *p*-bromoacetanilide (Andreetti *et al.* 1968) and *p*-methylacetanilide (Haisa *et al.* 1977). All these molecules have a *transoid* conformation (phenyl and methyl groups on opposite sides of the C–N bond). In all four molecules the C(ring)–N–C (carbonyl) angles are significantly greater than 120° (130 (1)° in phenacetin and ≈ 129 (1)° in the acetanilides). On the other hand the major intermolecular interaction in the acetanilides is via N–H---O=C hydrogen bonds, while these do not occur in (phenacetin)$_2$·HI$_5$; instead there

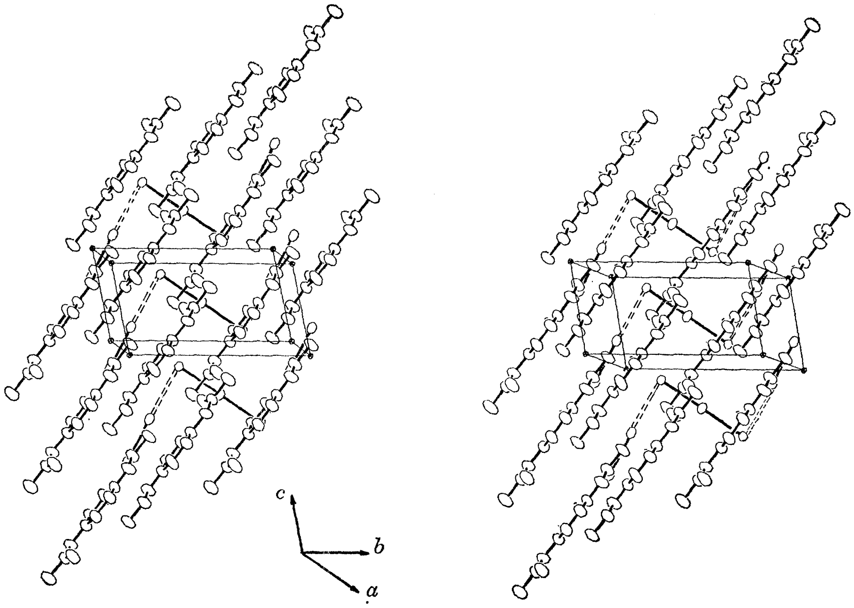


FIGURE 1. (Phenacetin)$_2$·HI$_5$: stereoview of structure viewed normal to the plane containing I(1), I(2), I(3) (ORTEP diagram, Johnson 1965). The origin of the coordinate system is at the *centre* of the parallelepiped shown which has its corners at $a/2$, $b/2$, $c/2$ etc.

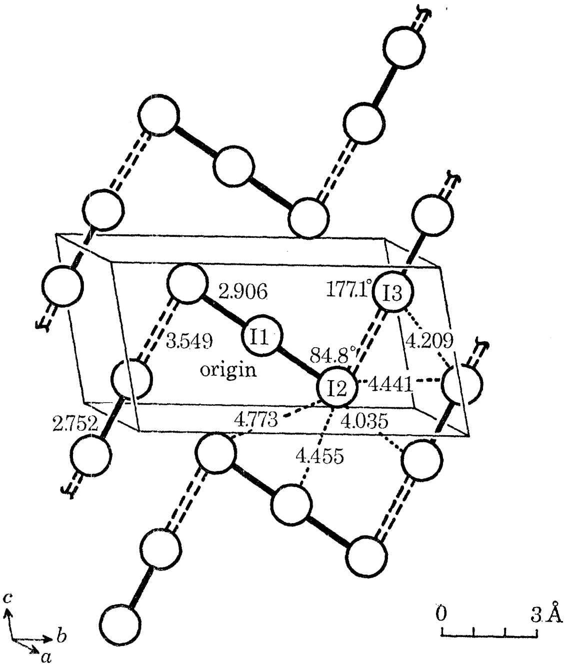


FIGURE 2. (Phenacetin)$_2$·HI$_5$: the polyiodide layer seen in projection on to the plane through atoms I(1), I(2), I(3). The origin is at the *centre* of the diagram and the box shown has its corners at $a/2$, $b/2$, $c/2$ etc. The reference iodine atoms (coordinates in table 3) are numbered. The interatomic distances have e.s.ds ≈ 0.002 Å.

TABLE 4. (PHENACETIN)$_2$·HI$_5$: PLANARITY OF THE PHENACETIN MOIETY

(All atoms were weighted equally in determining the various planes.)

atom	deviations in Å from the planes† through the atoms 1–13	4–9	10–13
C(1)	0.00	—	—
C(2)	−0.02	—	—
O(3)	0.02	—	—
C(4)	0.02	0.00	—
C(5)	−0.05	−0.01	—
C(6)	−0.06	0.00	—
C(7)	−0.01	0.01	—
C(8)	0.02	−0.02	—
C(9)	0.07	0.01	—
N(10)	−0.06	—	0.01
C(11)	−0.02	—	−0.02
O(12)	0.11	—	0.01
C(13)	−0.02	—	0.01

plane through atoms	l	m	n	d/Å
1–13	−0.2692	0.7667	−0.6416	1.872
4–9	−0.2278	0.7713	−0.6656	2.094
10–13	−0.3450	0.7418	−0.6074	1.369

† Planes are defined in the crystal system as $lx+my+nz-d = 0$.

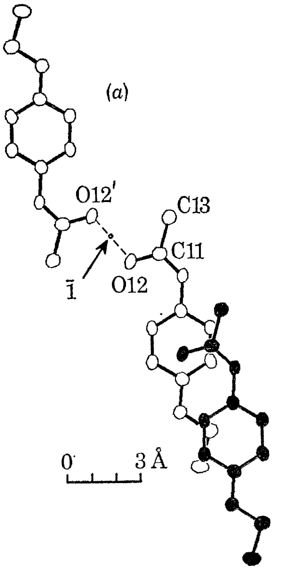


FIGURE 3

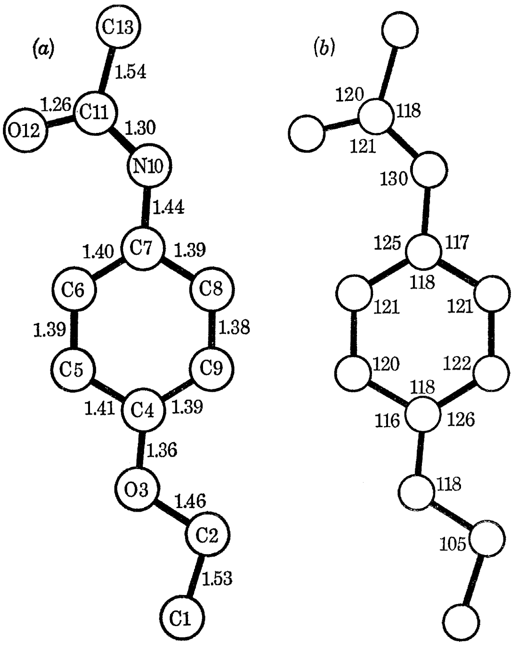


FIGURE 4

FIGURE 3. (Phenacetin)$_2$·HI$_5$: diagram shows (*a*) two molecules (open ellipses) related by centre of symmetry at $\frac{1}{2}$, 0, 0; d(O(12)---O(12′)) = 2.46 Å; (*b*) two overlapping molecules (open and filled ellipses), related by translation along [001].

FIGURE 4. Dimensions of the phenacetin moiety; (*a*) bond lengths (e.s.ds. ≈ 0.02 Å); (*b*) bond angles (e.s.ds. ≈ 1°). The torsion angles C(6), C(7)–C(11), O(12) and C(2), O(3)–C(4), C(9) are −8.0° and 5.1° respectively.

appear to be short symmetrical hydrogen bonds between carbonyl groups, as described in the next paragraph, and N–H---I hydrogen bonds between layers, as described in § 2 *b* (iii).

The most striking feature of the organic layer is the short distance of 2.46 (2) Å found between two oxygen atoms of centrosymmetrically related carbonyl groups (figure 3). This distance is too short to be a van der Waals contact (the van der Waals diameter of oxygen is generally taken to be 2.8 Å (Pauling 1963)) but is the right length for an approximately symmetrical hydrogen bond, the proton being taken to lie at the centre of symmetry $\frac{1}{2}00$ (we have already noted that the proton must lie at a centre of symmetry but there are six possibilities left after locating the I_3^- ion and I_2

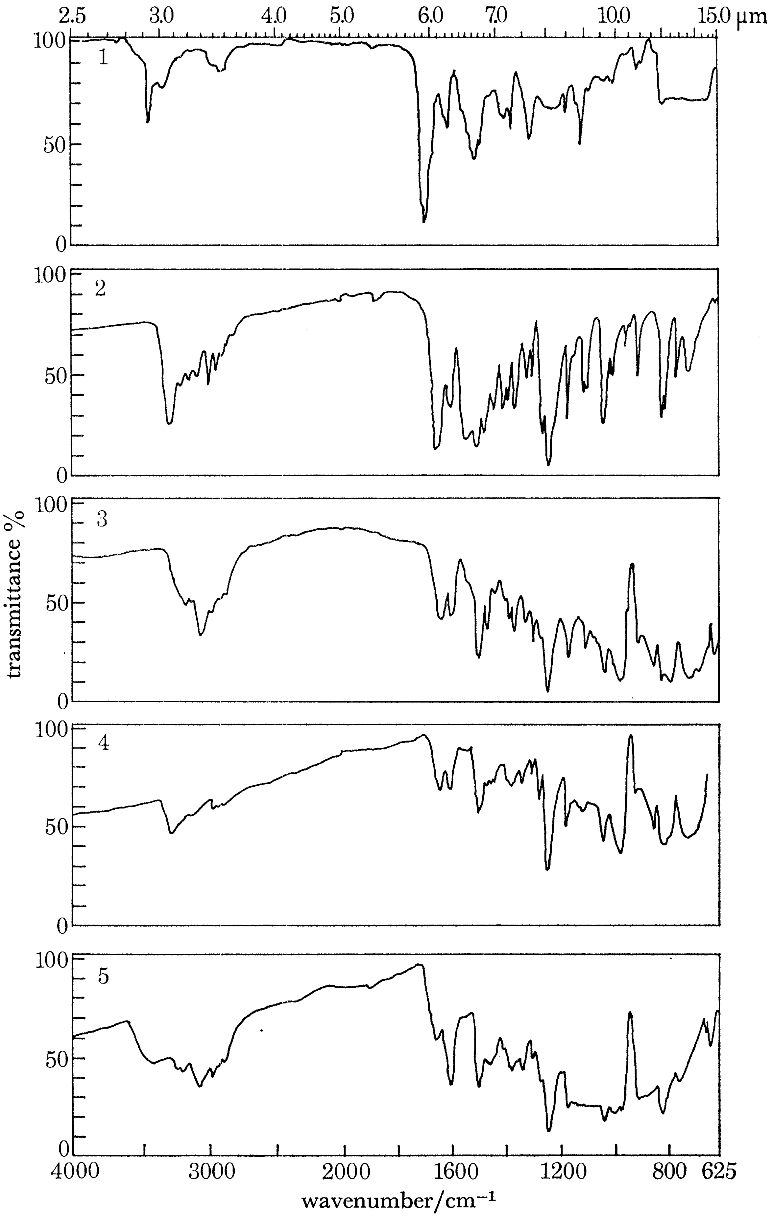
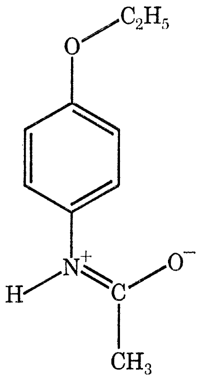
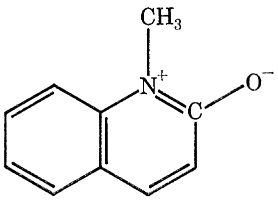


FIGURE 5. Infrared spectra of phenacetin in various chemical environments: (1), phenacetin dissolved in CHCl$_3$; (2), phenacetin in KBr pellet; (3), (phenacetin)$_2$·HI in KBr pellet; (4) (phenacetin)$_2$·HI$_5$ in KBr pellet; (5), (phenacetin)$_4$·HI·HI$_3$·2H$_2$O in KBr pellet.

molecule about the centres at 000 and $0\frac{1}{2}\frac{1}{2}$ respectively). Although a small peak (≈ 0.9 e Å^{-3} in height) was found at $\frac{1}{2}00$ in the difference synthesis, this is not considered conclusive because the map did not show the other hydrogens clearly, while spurious peaks of *ca* 1.7 e Å^{-3} remained around the iodines. There is, however, strong supporting evidence for the presence of a symmetrical hydrogen bond from infra-red spectroscopy (figure 5). The spectra of (phenacetin)$_2\cdot$HI and of (phenacetin)$_2\cdot$HI$_5$ are very similar and differ appreciably from those of phenacetin itself in solution and in the solid state; that of (phenacetin)$_4\cdot$HI$\cdot$HI$_3\cdot$2H$_2$O (appendix) also differs from the phenacetin spectra. The differences are particularly striking in the region of the carbonyl absorption band (≈ 6 µm) and in the region beyond 10 µm. The new features are typical of those found for strong, symmetrical hydrogen bonds between oxygen atoms (Speakman 1972).

The bond lengths N(10)–C(11) and C(11)–O(12) suggest an appreciable contribution of the resonance form shown below to the structure of the phenacetin moiety; a similar pattern of bond lengths led Calleri & Speakman (1969) to make an analogous proposal for 1-methyl-2-quinolone in its basic salt with HAsF$_6$:





We conclude, from both the structural and infrared evidence, that the phenacetin moiety exists, in both (phenacetin)$_2\cdot$HI and (phenacetin)$_2\cdot$HI$_5$, as the dimeric cation

$$(\text{phenacetin}\cdot\text{H}^+\cdot\text{phenacetin})$$

and not as molecular units (it seems probable that such dimeric cations are also present in (phenacetin)$_4\cdot$HI$\cdot$HI$_3\cdot$2H$_2$O).

(iii) *The overall crystal structure.* The crystal is made up of parallel layers of organic cations and polyiodide anions, the mean plane of the layers being (100). In addition to the ionic interaction between the oppositely charged layers there is some indication of N–H---I hydrogen bonding. The distances N(10)–H---I are rather similar for I(1)$^{-c}$ and I(2)$^{-c}$ (where the superscript refers to the I_3^- ion translated by $-c$ with respect to the reference ion), and the angles C(11)–N(10)---I are also rather similar (figure 6). Thus we are not able to distinguish between the two possible hydrogen bonds on dimensional grounds and it is feasible that there is a bifurcated hydrogen bond. The distance between the proton assumed to be at $\frac{1}{2}00$ and the nearest iodine atom (I(1) at the origin) is 6.22 Å ($\frac{1}{2}a$), too large for any direct interaction.

An appropriate formulation for (phenacetin)$_2\cdot$HI$_5$ on the basis of these results is:

$$(\text{C}_{10}\text{H}_{13}\text{NO}_2\cdot\text{H}^+\cdot\text{O}_2\text{NH}_{13}\text{C}_{10})\cdot\text{I}_2\cdot\text{I}_3^-$$

and an appropriate name would be bis (phenacetin) hydrogen iodine tri-iodide.

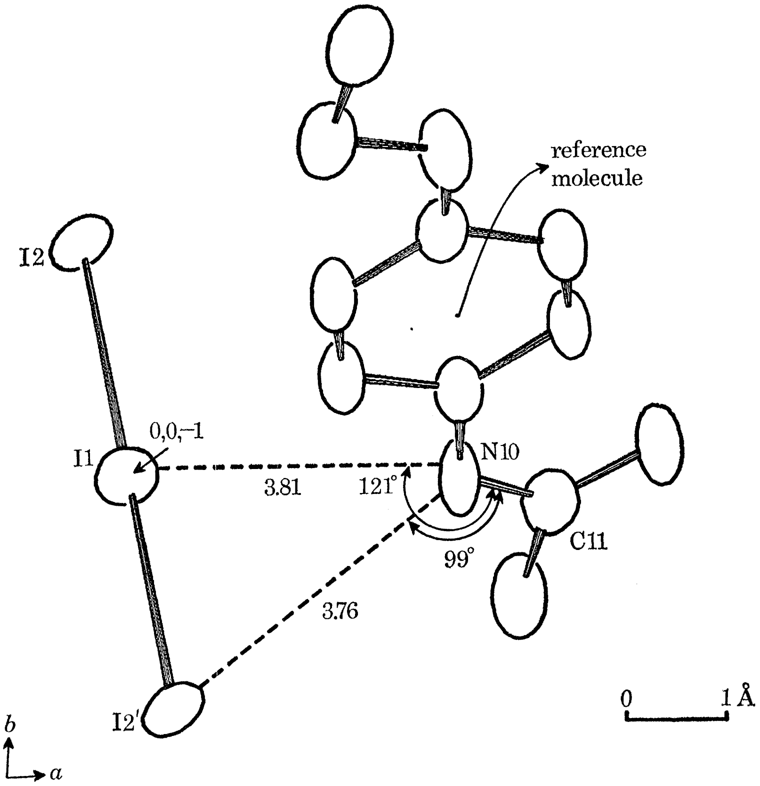


FIGURE 6. (Phenacetin)$_2\cdot$HI$_5$: possible N–H---I hydrogen bonds between the reference phenacetin molecule and the I_3^- group centred at 00 −1. The moieties are projected on to (001).

3. CRYSTAL STRUCTURE OF (THEOBROMINE)$_2\cdot$H$_2$I$_8$

(*a*) *Experimental*

Crystals were prepared as follows: theobromine was dissolved in concentrated HI (containing a small amount of I_2) until a clear red solution was obtained; on standing overnight a dark green precipitate formed. This was filtered off and dissolved in hot water. Well-formed dark blue needles, stable in air, were obtained on slow cooling. The needles are elongated along [001] and show {100}, {010}, {110} and sometimes {210} faces. Chemical analysis confirmed the formula given above. Cell dimensions, space group and intensities were determined by standard methods (tables 5 and 2). There are two crystallographically independent theobromine molecules at general positions in the unit cell, and also two protons and eight iodine atoms in the asymmetric unit. Although location of these latter atoms at or about centres of symmetry is possible in principle, firm predictions cannot be made and it turns out that all atoms are at general positions in the unit cell. An attempt to solve the structure by MULTAN (Germain *et al.* 1971) was unsuccessful and recourse was had to the Patterson method; after considerable effort all eight iodine atoms in the asymmetric unit were located and a first set of structure factor calculations (1407 reflections, $(\sin\theta)/\lambda \leqslant 0.15$) gave a discrepancy value $R = 0.39$. The remaining atoms were found from difference syntheses; refinement was by standard methods (table 2). Atomic coordinates are in table 6 while the lists of anisotropic temperature factors and structure factors have been deposited (see footnote on p. 200).

TABLE 5. CRYSTAL DATA FOR (THEOBROMINE)$_2$·H$_2$I$_8$

$(C_7H_8N_4O_2)_2 \cdot H_2I_8$ f.w. 1377.6
triclinic m.pt. 168°
space group P $\bar{1}$ (No. 2)
$a = 14.38$ (1) Å $\alpha = 91.2$ (1)°
$b = 14.07$ (1) $\beta = 100.8$ (1)
$c = 7.75$ (1) $\gamma = 91.0$ (1)

Cell volume 1539 Å^3
$\rho_{\text{meas}} = 2.92$ g cm^{-3} (flotation, di-iodomethane-toluene solution)
$\rho_{\text{calc}} = 2.97$ g cm^{-3} for $Z = 2$
F (000) = 1228
λ(Mo K$\bar{\alpha}$) = 0.7107 Å
$\mu = 81.3$ cm^{-1} (for Mo Kα).

TABLE 6. (THEOBROMINE)$_2$·H$_2$I$_8$: ATOMIC COORDINATES

(E.s.ds in parentheses are in units of the least significant digit; hydrogen atoms were not included in the analysis. The numbering of the atoms is given in figures 9 and 10.)

atom	x	y	z
I(1)	0.5955 (2)	−0.1496 (2)	−0.2246 (5)
I(2)	0.4138 (2)	−0.2365 (2)	−0.1997 (5)
I(3)	0.2248 (2)	−0.3138 (2)	−0.1854 (5)
I(4)	0.1778 (2)	−0.0872 (2)	−0.0636 (5)
I(5)	0.1205 (2)	0.0872 (2)	0.0413 (5)
I(6)	0.0370 (2)	0.2925 (2)	0.1657 (5)
I(7)	0.2204 (2)	0.3775 (2)	0.0962 (4)
I(8)	0.3944 (2)	0.4598 (2)	0.0472 (5)
N(1) A	0.470 (2)	0.380 (2)	0.578 (5)
C(2) A	0.385 (2)	0.424 (2)	0.555 (5)
N(3) A	0.308 (2)	0.377 (2)	0.594 (5)
C(4) A	0.319 (2)	0.286 (2)	0.645 (5)
C(5) A	0.407 (3)	0.242 (3)	0.685 (6)
C(6) A	0.489 (2)	0.290 (2)	0.650 (5)
N(7) A	0.388 (2)	0.151 (2)	0.725 (4)
C(8) A	0.296 (3)	0.140 (3)	0.373 (6)
N(9) A	0.253 (3)	0.220 (2)	0.682 (4)
C(10) A	0.217 (2)	0.427 (2)	0.592 (5)
C(11) A	0.456 (3)	0.079 (3)	0.769 (6)
O(1) A	0.382 (2)	0.507 (2)	0.511 (4)
O(2) A	0.567 (2)	0.255 (2)	0.670 (4)
N(1) B	−0.029 (2)	0.121 (2)	0.575 (4)
C(2) B	−0.116 (2)	0.070 (2)	0.555 (5)
N(3) B	−0.190 (2)	0.120 (2)	0.578 (4)
C(4) B	−0.182 (3)	0.213 (3)	0.637 (6)
C(5) B	−0.096 (3)	0.264 (3)	0.654 (6)
C(6) B	−0.013 (3)	0.215 (3)	0.636 (6)
N(7) B	−0.113 (2)	0.351 (2)	0.704 (4)
C(8) B	−0.203 (3)	0.351 (3)	0.708 (5)
N(9) B	−0.250 (2)	0.275 (2)	0.670 (5)
C(10) B	−0.284 (4)	0.067 (4)	0.570 (7)
C(11) B	−0.045 (3)	0.434 (3)	0.735 (7)
O(1) B	−0.123 (2)	−0.012 (2)	0.498 (4)
O(2) B	0.064 (1)	0.252 (1)	0.649 (3)

(*b*) *Results*

(i) *Overall description of crystal structure.* The crystal consists of alternating parallel organic and polyiodide layers stacked along [001] (figure 7). The organic layer consists of hydrogen-bonded theobrominium (protonated theobromine) cations; the anionic layers can be described as consisting of S-shaped I_{16}^{4-} ions, each located about an inversion centre at $\frac{1}{2}\frac{1}{2}0$ and equivalent positions. The theobrominium cation is essentially planar but the I_{16}^{4-} anion is not; neither layer as a whole is planar but portions of the organic layer are parallel to portions of the I_{16}^{4-} ions, as described in more detail below.

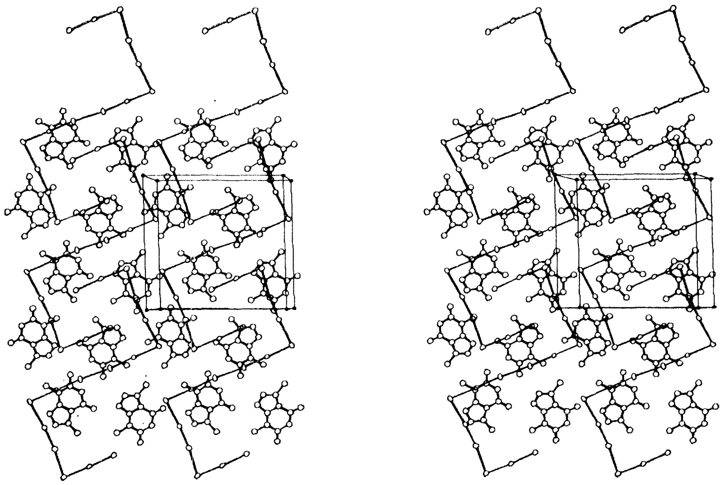


FIGURE 7. (Theobromine)$_2$·H$_2$I$_8$: ORTEP stereoview approximately down [001], i.e. approximately normal to organic and polyiodide sheets. The origin is at the lower left-hand corner of the cell, with [100] to the right and [010] towards the top of the page.

(ii) *The polyiodide layer.* The asymmetric unit of the polyiodide layer consists of two crystallographically independent I_3^- ions (I(1)–I(2)–I(3); I(6)–I(7)–I(8)) and one I_2 molecule (figure 8). There are secondary interactions between I_3^- and I_2 with distances of 3.42 and 3.35 Å respectively, and between two I_3^- ions, across a centre of symmetry, of 3.45 Å. All other distances are greater than 4.15 Å, and thus derive from van der Waals approaches, except for a distance of 3.84 Å between iodines of two I_3^- ions. We consider this to be a tertiary interaction and discuss it later. We thus *describe* the two I_3^- ions and one I_2 molecule of the reference asymmetric unit, together with their counterparts related by the centre of symmetry at $\frac{1}{2}\frac{1}{2}0$ as agglomerated into an essentially isolated S-shaped I_{16}^{4-} ion, the geometry of which is now discussed in more detail.

The dimensions of the centrosymmetric S-shaped I_{16}^{4-} ion (figure 8) indicate that it should be formulated as $I_3^- \cdot I_2 \cdot I_3^- \cdot I_3^- \cdot I_2 \cdot I_3^-$. The two crystallographically independent I_3^- ions within the I_{16}^{4-} moiety are asymmetric, nonlinear and have significantly different dimensions (see § 4 (*b*)). The I_{16}^{4-} ion is not planar but the central portion (I(4)...I(8)...I(8′)...I(4′)) lies close to the plane

$$0.2497x - 0.1967y + 0.8901z - 0.457 \text{ Å} = 0.$$

Thus the two outer I_3^- ions (I(1)–I(2)–I(3), I(3′)–I(2′)–I(1′)) are inclined symmetrically to the plane through the central portion of the ion at angles of ± 6.0°. All the I_{16}^{4-} ions are parallel and are symmetrically disposed with respect to the (001) planes; the central portion (I(4)...I(4′)) makes an angle of 27.1° with (001).

Each I_{16}^{4-} ion is linked to neighbouring ions on each side by four tertiary interactions

$$(d(\mathrm{I}...\mathrm{I}) = 3.84\,\text{Å}).$$

Although these close approaches are almost parallel to [100], the overall arrangement of the ions is such that the strongest inter-ionic cohesion in the crystal (due to the tertiary interactions) is in the [110] direction (figure 9).

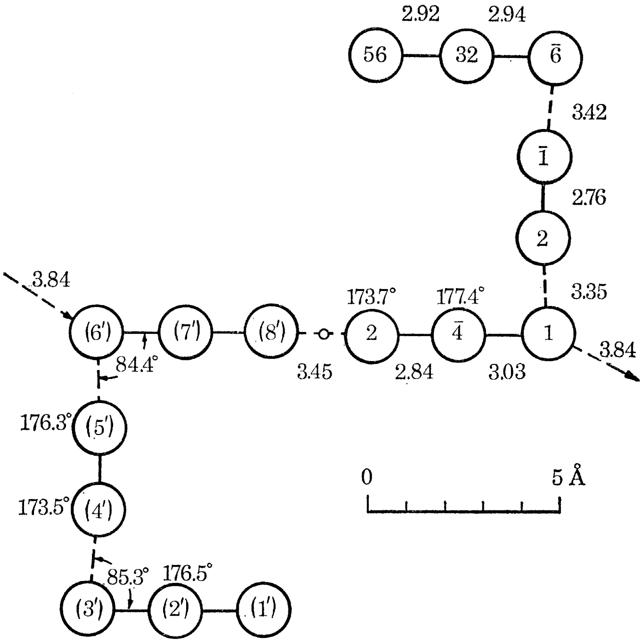


FIGURE 8. (Theobromine)$_2$·H_2I_8: the centrosymmetric S-shaped I_{16}^{4-} ion, showing atomic numbering (for atoms related to the reference atoms of table 6 by the centre of symmetry of the ion), bond lengths and angles, and deviations (10^{-2} Å) from the mean plane of the central portion of the ion (I(4')---I(4)).

(iii) *The organic layer.* The two crystallographically independent theobromine molecules, A and B, and those related to them by translation along [100] form infinite twisted A...B...A...B chains extending in the [100] direction (figure 10); the angle between the planes of A and B molecules is 37.8°. Since N(9) lacks a hydrogen in the neutral molecule, we infer that it is protonated in the organic layer, which is positively charged in consequence. No attempt was made to locate hydrogens directly.

Adjacent chains are linked by A...A and B...B hydrogen bonds; these centrosymmetric pairs are essentially coplanar. Thus each theobrominium cation uses its hydrogen-bonding capacity to the full, two carbonyl groups of each cation acting as acceptors and one N–H and one N^+–H acting as donors. The organic layer has additional pseudo-symmetry and its arrangement approximates to that of the partially periodic layer group $1P2_1/g$ (No. 17 of the list of G_1^2 groups given in the Pilot Issue of *International tables for X-ray Crystallography* (1973)) – the 2_1 axis here lies along [010] at $c/2$ and the glide plane is an *a* glide (figure 10).

Comparison of the dimensions of the two crystallographically independent theobrominium cations (figure 11) suggests that the e.s.d. of the bond lengths is ≈ 0.02 Å and of the bond angles ≈ 1.5°, in accordance with the values obtained from the least-squares analysis.

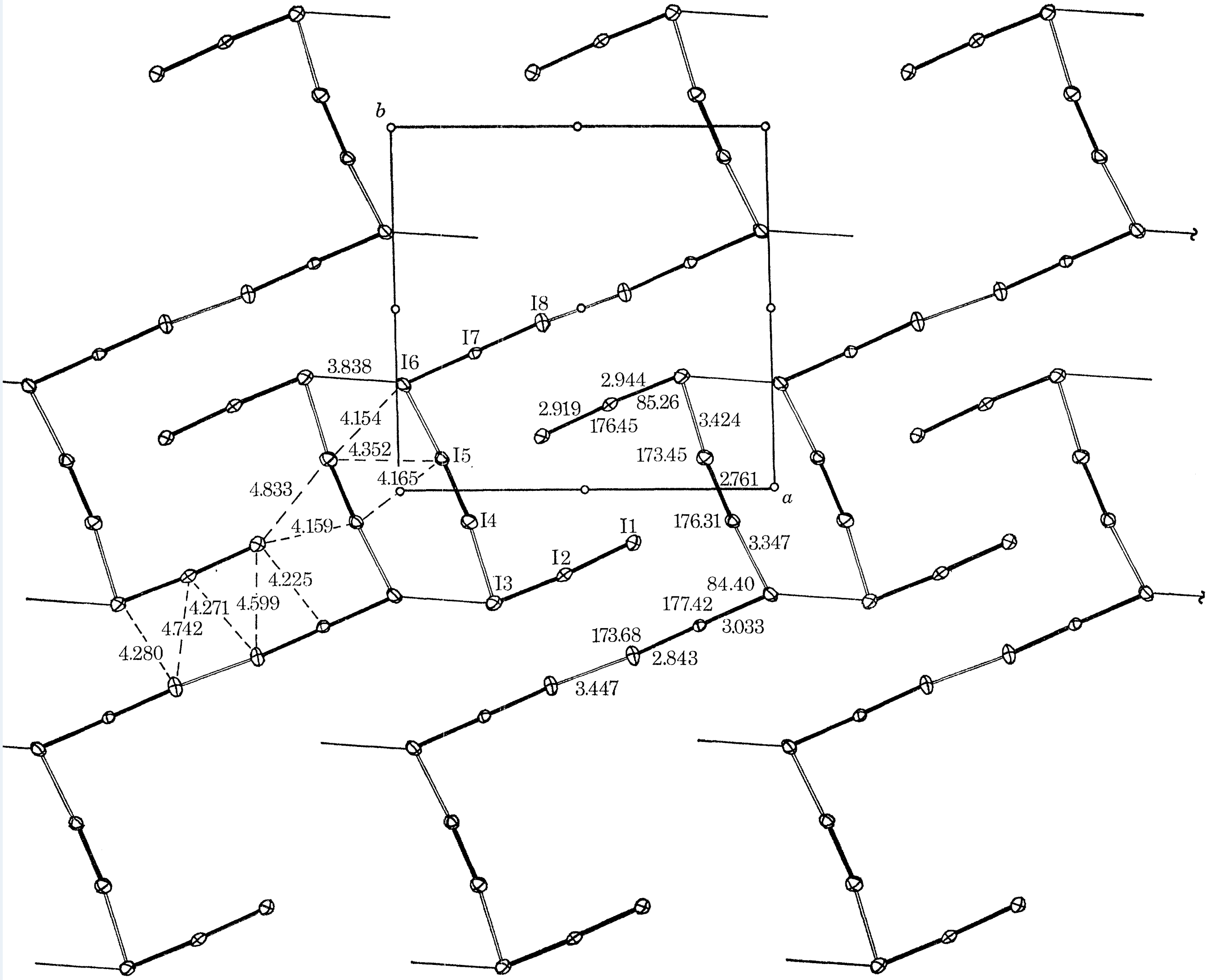


FIGURE 9. $(\mathrm{Theobromine})_2\cdot\mathrm{H}_2\mathrm{I}_8$: the polyiodide layer, showing the atoms of the reference moiety, the interatomic distances and angles. The primary bonds within I_3^- ions and I_2 molecules are shown as full lines, the secondary bonds among I_3^- and I_2 units within the I_{16}^{4-} anions are shown as open lines, the tertiary bond (3.838 Å) as a thin line, and the van der Waals interactions as broken lines. The thermal ellipsoids are the 50% probability ellipsoids. Some moieties have been omitted for clarity in the upper and lower portions of the diagram but the tertiary bonds have been inserted.

(iv) *The interactions between the charged layers.* Although both organic and polyiodide layers are corrugated, there are certain portions of each which are mutually approximately parallel. The (coplanar) pair of A molecules related by the inversion centre at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ lies above the atoms

$$-\mathrm{I}(7)-\mathrm{I}(8)\ldots\mathrm{I}(8')-\mathrm{I}(7')-$$

of the I_{16}^{4-} ion centred at $\frac{1}{2}\frac{1}{2}0$, above the atoms I(1)–I(2)–I(3)– of the I_{16}^{4-} ion centred at $\frac{1}{2}\frac{1}{2}0$ and above the atoms I(1′)–I(2′)–I(3′) of the I_{16}^{4-} ion centred at $\frac{1}{2}\frac{1}{2}1$. It should be noted that these last three iodine atoms belong to a polyiodide layer different from that in which the first (seven) iodines are found. The two planes are:

A...A pair $\quad 0.0374x + 0.3220y + 0.9140z - 6.078\ \text{Å} = 0$

iodine atoms as defined above

$$-0.0110x+0.3762y+0.9030z-2.567\,\text{Å} = 0.$$

The B–B pair centred at $00\frac{1}{2}$ is parallel to a region defined by the iodine atoms

$$\mathrm{I(6')–I(5')–I(4')–I(3')}$$

of the I_{16}^{4-} ion centred at $\frac{1}{2}\frac{1}{2}0$ and the iodine atoms related to these four iodines by the centre of symmetry at 000. The two planes are:

B...B pair $\quad 0.0387x-0.2900y+0.9391z-3.639\,\text{Å} = 0$

iodine atoms as defined above

$$0.0279x-0.2919y+0.9409z = 0.$$

For the first pair of planes, the interplanar angle is 18.9° and the perpendicular distance of the centre of symmetry between the A...A pair and the plane of the iodines is 3.66 Å; the corresponding values for the second pair of planes are 14.2° and 3.65 Å. Using Pauling's van der Waals

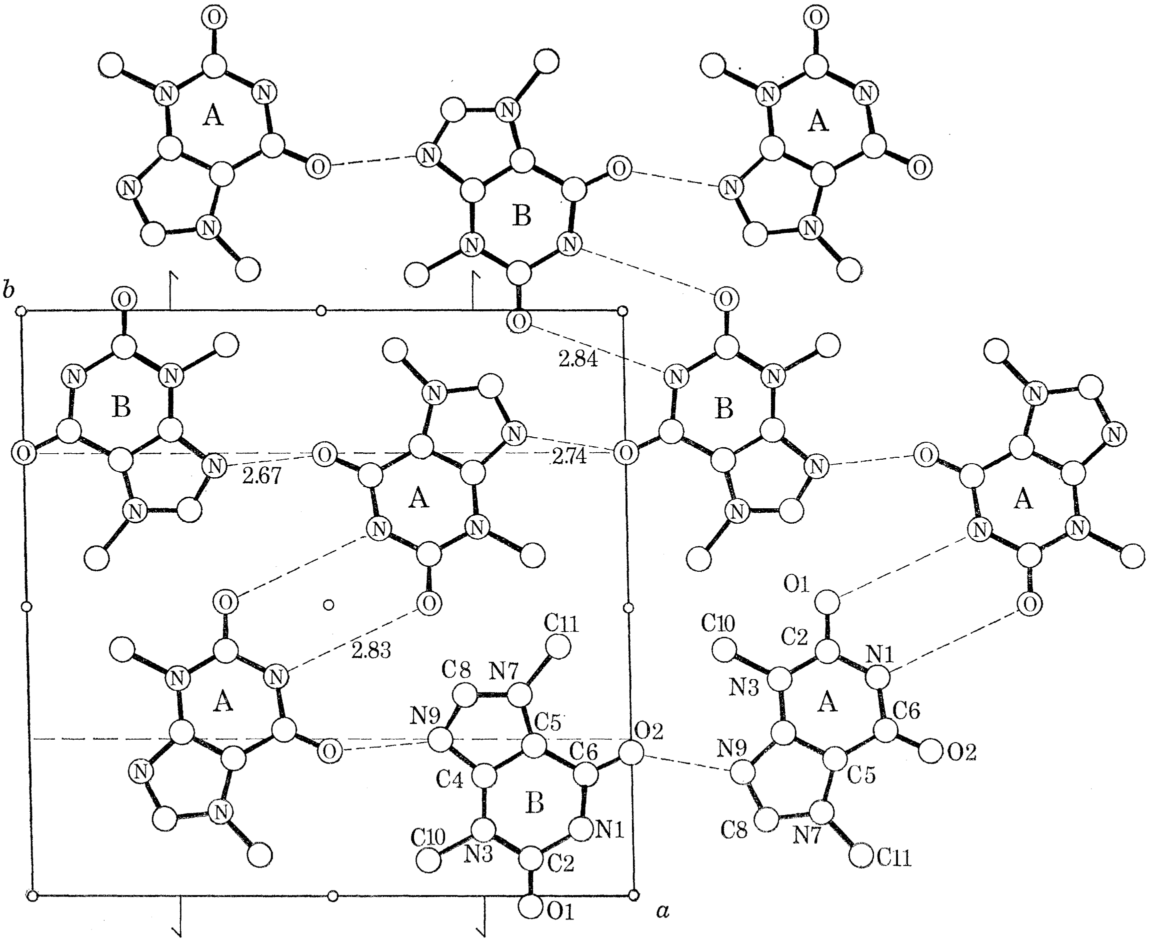


FIGURE 10. $(\text{Theobromine})_2\cdot H_2I_8$: arrangement of hydrogen-bonded theobrominium cations projected on to (001). The layer as a whole has partially periodic symmetry 1P $2_1/g$ and the cations A and B, although crystallographically independent, are approximately related by the symmetry elements shown (*a* glide, 2_1 axis parallel to [010]). The centres of symmetry are, of course, exact. The hydrogen bonds between cations are also shown by broken lines. The reference moieties are in the lower half of the unit cell frame: both reference moieties have been shifted by $+a$ with respect to the coordinates given in table 6.

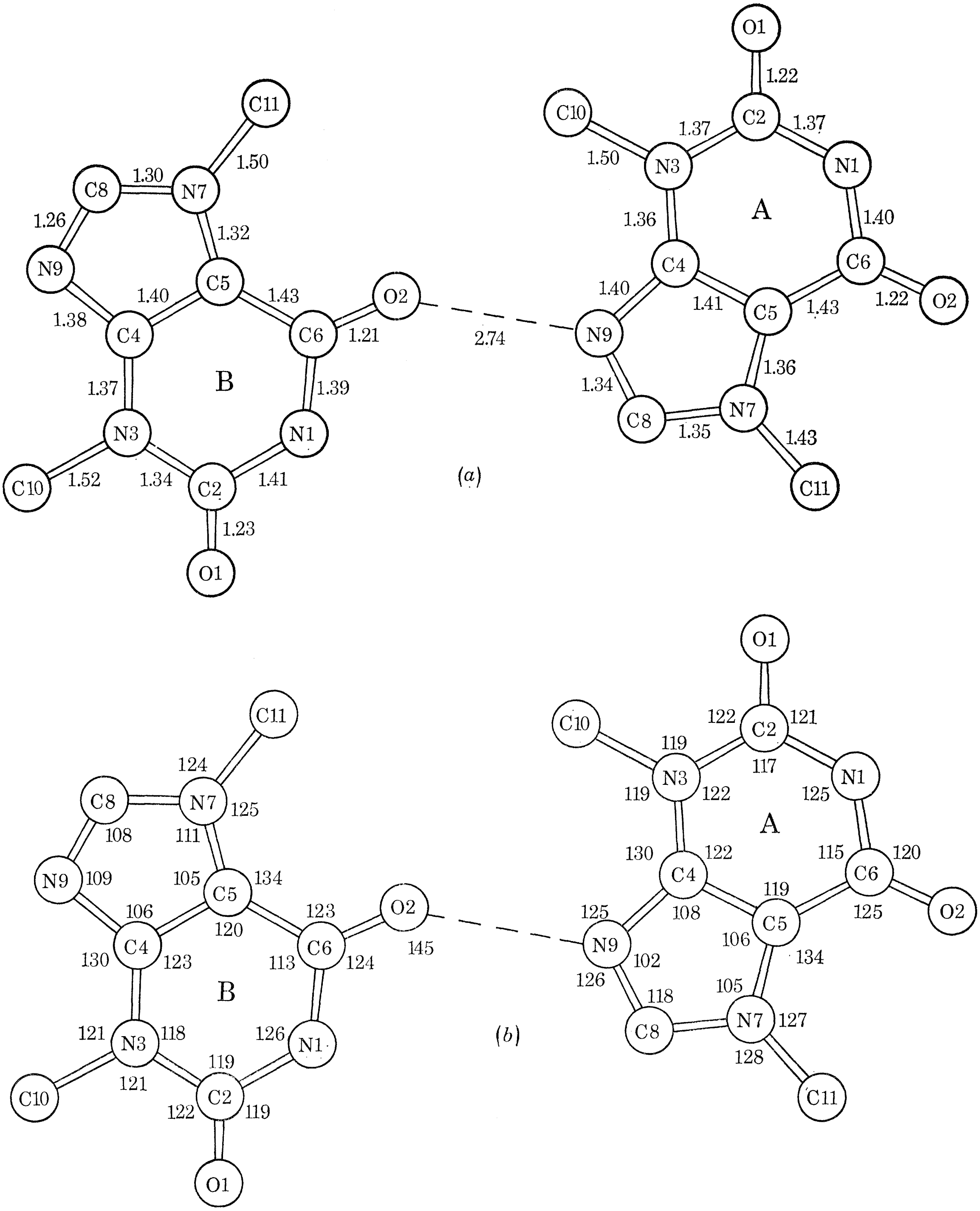


FIGURE 11. (Theobromine)$_2$·H$_2$I$_8$: dimensions of the two crystallographically independent theobromine moieties (*a*), bond lengths (e.s.d.s ~ 0.02 Å); (*b*), bond angles (e.s.d.s ~ 1°).

radii (1963, table 7-20, p. 260), it appears that only van der Waals interactions are involved in the above approaches. The approximately parallel orientation of polyiodide layer and organic molecules does not permit hydrogen bonding between these layers, in contrast to the situation in (phenacetin)$_2\cdot HI_5$ where the planes of the organic molecules are steeply inclined to the polyiodide layer, thus creating appropriate geometrical conditions for hydrogen bonding.

(*c*) *Conclusions*

The results of the crystal structure analysis show that (theobromine)$_2\cdot H_2I_8$ is in fact a polyiodide salt composed of an I_{16}^{4-} anion and four theobrominium cations as counterions. The crystal structure consists of positive and negative layers alternating in the [001] direction. The I_{16}^{4-} anions are bonded to one another by a tertiary interaction of length 3.84 Å, in addition to the usual dispersion forces. If the I_{16}^{4-} anions are considered as structural units, then they are the largest polyiodide anions encountered until now. The theobrominium cations are hydrogen bonded in two approximately perpendicular directions in the (001) plane. A concise and reasonably accurate formulation of crystalline (theobromine)$_2\cdot H_2I_8$ is thus

$$(C_7H_9N_4O_2^+)_4(I_3^-\cdot I_2\cdot I_3^-\cdot I_3^-\cdot I_2\cdot I_3^-).$$

and the appropriate name could be tetrakis(theobrominium)bis(tri-iodidespiodine tri-iodide).

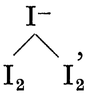
4. DISCUSSION

(*a*) *The crystal structures*

Crystal structures in which two components are segregated on to alternating parallel layers are not uncommon (we exclude here 'Layer intercalation complexes' such as the graphite-alkali metal complexes, where the second component is added to an existing structure without perturbing it drastically). Examples are tetrakis(thiourea)lead(II)picrate (Herbstein & Kaftory 1972), 1,2-4,5-tetrabromobenzene:hexabromobenzene molecular complex (Gafner & Herbstein 1964) and tetramethylammonium penta-iodide (Hach & Rundle 1951). There are charged layers in the first and last of these examples, and hydrogen bonding between layers in the first.

(*b*) *The polyiodide layers*

Penta-iodides of four types are known: (i) isolated V-shaped ions which can be approximately described as



$$\overset{I^-}{I_2\quad I_2}$$

, for example in bis(potassium valinomycin)penta-iodide tri-iodide (Neupert-Laves & Dobler 1975); (ii) interacting V-shaped ions as in $(CH_3)_4NI_5$ (Hach & Rundle 1951); (iii) linear, interacting ions which can be approximately described as $\ldots I_2\cdot I^-\cdot I_2\ldots$ as in trimesic acid penta-iodide (Herbstein & Kapon 1977, unpublished results) and (α-cyclodextrin)$_2\cdot Cd_{\frac{1}{2}}\cdot I\cdot 2I_2\cdot 26H_2O$ (Noltemeyer & Saenger 1976); (iv) the zigzag chains of I_3^- ions and I_2 molecules as in (phenacetin)$_2\cdot HI_5$ and (α-cyclodextrin)$_2\cdot LiI_3\cdot I_2\cdot 8H_2O$ (Noltemeyer & Saenger 1976).

The I_{16}^{4-} ion found in (theobromine)$_2.H_2I_8$ does not have a direct counterpart but the octa-iodide ion in Cs_2I_8 (Havinga *et al.* 1954) which can be denoted as $I_3^-\cdot I_2\cdot I_3^-$ is clearly closely related (tetra-iodides with approximate structure $I^-\cdot I_2\cdot I^-$ have been found in $Cu(NH_3)_4I_4$ (Dubler & Linowsky 1975) and in some other compounds but are not related to I_{16}^{4-} and I_8^{2-}). The I_8^{2-} ion can be transformed into half of the I_{16}^{4-} ion by reflecting one of the I_3^- groups in the line through the iodine atoms of the I_2 molecule. The geometries are then very similar except that the transformed octa-iodide ion is appreciably more planar than the half hexadeca-iodide ion ($[\Sigma_{i=1}^{8}\delta_i^2]^{\frac{1}{2}} = 0.13$ Å, 0.44 Å respectively where δ_i are the displacements of the individual iodine atoms from the best plane).

The arrangements of I_3^- and I_2 moieties in the penta-iodide chains and the hexadeca-iodide ions have many similarities: the angles within the I_3^- moieties are all close to 177° while the angles between I_2 and I_3^- moieties lie within the range $84.8 \pm 0.5°$. The I_3^- ion in (phenacetin)$_2$·HI$_5$ is symmetric, and one of those in (theobromine)$_2$·H$_2$I$_8$ is nearly so (but the other is appreciably asymmetric). The iodine molecules in both structures, with d(I–I) = 2.75–2.76 Å, are significantly longer than in those in crystalline I_2 (2.715 (6) Å(110°K), van Bolhuis *et al.* 1967) which is itself extended in comparison with gaseous I_2(2.662 Å; Karle 1955). On the other hand, the results for the I_3^- ion are not as clear cut. The mean bond length in an isolated I_3^- ion is 2.93–2.94 Å (e.g. $N(C_2H_5)_4I_3$(I), 2.928 (2), 2.943 (2) Å (Migchelsen & Vos 1967)), close to the values found here in (theobromine)$_2$·H$_2$I$_8$ but significantly longer than that in (phenacetin)$_2$·HI$_5$. Thus the evidence for transfer of charge from I_2 to I_3^- is equivocal. Perhaps an explanation for these differences can be found in the lengths of the secondary bonds between I_2 and I_3^-, which are 3.35 and 3.42 Å in (theobromine)$_2$·H$_2$I$_8$ and 3.55 Å in (phenacetin)$_2$·HI$_5$.

Two I_3^- ions related by a centre of symmetry have not been encountered elsewhere, so no comparisons can be made with the value of 3.35 Å found here. However, the tertiary interaction of 3.84 Å between two approximately colinear I_3^- ions appears to be similar to the geometrically analogous distance of 3.88 Å in the approximately linear chains of interacting I_3^- ions in (benzamide)$_2$·HI$_3$ (Reddy *et al.* 1964). Quinuclidinium penta-iodide (Jander *et al.* 1975) has a structure which combines features found individually in the structures discussed in this section – there are approximately linear chains of I_3^- ions (distance $I_3^- \ldots I_3^-$ = 3.88 Å), *bridged* by iodine molecules, the angle between I_3^- and I_2 being 80° and the distance 3.45 Å. Thus many different overall arrangements of I_3^- ions and I_2 molecules are possible, but all are based on similar values for intermoiety distances and angles.

(*c*) *The organic layers*

(i) *The bis(phenacetin)hydrogen cation.* Monobasic acids HX can form acid salts of composition MHX$_2$; when the crystalline salt contains symmetrical $[XHX]^-$ ions with the two X-moieties linked by an O---H---O bond across a symmetry element of the crystal, then this is a type A *acid* salt, according to the classification of Speakman (1972, p. 147). Speakman notes (p. 161) that basic salts of monoacidic bases also exist, with cations $[BHB]^+$; these have been less widely studied. The presence of the centrosymmetric protonated bis(phenacetin) in (phenacetin)$_2$·HI$_5$ shows that this is a good example of a type A *basic* salt. The O---O distance of 2.46(2) Å is close to the average value of 2.445(2)Å for type A acid salts (Speakman 1972, table 7) but slightly longer than the values reported for acetamide hemihydrochloride (2.418(11)Å, neutron diffraction at – 150 °C (Peterson & Worsham 1959)), α-picoline-N-oxide hemihydrobromide (2.40 Å, X-ray diffraction (Mills & Speakman 1963)) and bis-(1-methyl-2-quinolone) hydrogen hexafluoroarsenate (V) (2.439(12)Å, X-ray diffraction, pseudo-type A (Calleri & Speakman 1969)), so the proton may be slightly displaced, in disordered fashion, from the centre of symmetry. If the space group of phenacetin hemihydro-iodide is C2/*c* (Appendix) then this too will contain a type A basic salt cation; no symmetry is required for the cation in (phenacetin)$_4$·HI·HI$_3$·2H$_2$O (Appendix) and these will presumably be pseudo-type A basic salt cations.

Similar symmetric and asymmetric complex cations of formula $(B_1HB_2)^+$, where B_1 and B_2 are various substituted pyridines and quinoline, have been detected spectroscopically (Clements & Wood 1973*a*, *b*; Clements *et al.* 1973); in these cations the proton bridge is between the σ orbitals on the nitrogen atoms. Theoretical calculations made on the proton potential in such complex hydrogen-bonded cations suggest an asymmetric potential with a low barrier (Wood 1973).

(ii) *The protonated theobromine layer.* Crystal structures of theobrominium salts do not appear to have been reported, nor is the crystal structure of the theobromine: (5-chlorosalicylic acid)$_2$ molecular complex (Shefter *et al.* 1971) suitable for comparison with the hydrogen-bonding scheme found here. The additional pseudo-symmetry of the organic layer is unusual but not unprecedented – one example is 9-ethylguanine hemihydrochloride (which is a pseudo-type A basic salt), where the cations are arranged with additional non-crystallographic centres of symmetry (Mandel & Marsh 1975); another is 5-fluorouracil (Fallon 1973) where the molecular layers have fourfold axes in projection as well as non-crystallographic centres of symmetry, but this symmetry is destroyed in three dimensions when the layers stack upon each other.

The molecular dimensions of a number of xanthine derivatives have been reported (Ringertz (1971) summarizes earlier results, to which the two theobromine structures (theobromine: (5-chlorosalicylic acid)$_2$ and (theobromine)$_2 \cdot H_2I_8$ should be added) but the overall level of accuracy does not warrant a detailed comparison, nor study of the effect of substitution or ionization on the xanthine ring system. The best that can be said is that, within their limitations, all available results are mutually consistent.

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APPENDIX

CRYSTAL DATA FOR (PHENACETIN)$_4 \cdot HI \cdot HI_3 \cdot 2H_2O$ AND (PHENACETIN)$_2 \cdot HI$

Phenacetin dissolved in chloroform was mixed with an aqueous solution of HI and evaporated to dryness. Yellow prisms of (phenacetin)$_2 \cdot$HI mixed with red needles of

$$(\text{phenacetin})_4 \cdot HI \cdot HI_3 \cdot 2H_2O$$

were obtained. An excess of phenacetin gave pure iodide; equimolar quantities gave the iodide–tri-iodide. Both materials gave satisfactory chemical analyses.

(Phenacetin)$_4 \cdot HI \cdot HI_3 \cdot 2H_2O$

$(C_{10}H_{13}O_2N)_4 \cdot HI \cdot HI_3 \cdot 2H_2O$ f.w. 1246.53
triclinic
space group P1 or P$\bar{1}$

$a = 13.685$ Å	$\alpha = 80.24°$
$b = 12.838$ Å	$\beta = 93.32°$
$c = 7.209$ Å	$\gamma = 104.00°$

cell volume 1210.9 Å^3
$\rho_{\mathrm{meas}} = 1.72$ g cm^{-3} (flotation, toluene–tetrabromoethane solution).
$\rho_{\mathrm{calc}} = 1.69$ g cm^{-3} for $Z = 1$
$F(000) = 618$

(phenacetin)$_2$·HI ('phenacetin hemi-hydro-iodide')
$(\mathrm{C}_{10}\mathrm{H}_{13}\mathrm{O}_2\mathrm{N})_2\cdot\mathrm{HI}$ f.w. 486.31
monoclinic
space group Cc or $C2/c$
$a = 14.18$ Å $\beta = 97.8°$
$b = 9.14$
$c = 17.16$
cell volume 2203 Å^3
$\rho_{\mathrm{meas}} = 1.48$ g cm^{-3} (flotation, toluene-ethyl iodide solution)
$\rho_{\mathrm{calc}} = 1.47$ g cm^{-3} for $Z = 4$
$F(000) = 984$

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