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Protonated 1-Methylcytosine Triiodide

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Abstract. $(C_5H_8N_3O)(I_3)$, orthorhombic, *Pnma*, a = 12·980 (3), b = 7·113 (3), c = 13·415 (4) Å, V = 1238·6 Å^3, Z = 4, M_r = 506·84, D_c = 2·718, D_m = 2·729 (4) g cm^{-3}. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic with the inclusion, but no refinement, of the H atoms) based on 1881 counter-collected F_o's led to a final R value of 0·051. The structure consists of protonated 1-methylcytosine cations and unsymmetrical and nonlinear triiodide anions [$d_{\mathrm{I-I}}$ = 2·794 (1) and 3·123 (1) Å, and the intramolecular angle = 177·6 (1)°]. The structure is dominated by layers ($y = \pm\frac{1}{4}$) of linear chains of cations (intermolecularly hydrogen bonded) and anions [with a triiodide I—I intermolecular distance of 3·755 (1) Å] generated by screw axes parallel to **a**. Within these layers, the coupling between the cationic and anionic chains is accomplished *via* hydrogen bonding between one of the terminal I atoms of the triiodide anion and the protonated cation. Interlayer interactions are clearly electrostatic in nature. A rationale for the instability of the crystals owing to the loss of I_2 is presented on the basis of the crystal structure.

Introduction. Over the past several years, there has been considerable interest in crystalline polyhalides, not the least of which are the polyiodides. Crystalline polyiodides range in size from the I_3^- anion to discrete, macromolecular species such as I_{16}^{4-} (Herbstein & Kapon, 1975). Broadly speaking, the polyiodide salts may be classified into the following four categories (with examples given for each): (1) large-cation polyiodides [tetraphenylarsonium triiodide (Runsink, Swen-Walstra & Migchelsen, 1972), cesium triiodide (Runsink *et al.*, 1972), tetraethylammonium heptaiodide (Havinga & Wiebenga, 1958), ferricinium triiodide (Bernstein & Herbstein, 1968)]; (2) neutral organic alkali-metal triiodides [$(\text{xanthotoxin})_2KI_3$ (Kapon & Herbstein, 1974)]; (3) protonated organic heterocycles with polyiodides [$(\text{phenacetin})_2HI_5$ (Herbstein & Kapon, 1972), $(\text{theobromine})_2H_2I_8$ (Herbstein & Kapon, 1975)]; (4) radical-cation (open-shell) polyiodides [hepta(tetrathiofulvalene) pentaiodide (Daly & Sanz, 1975; Johnson & Watson, 1976), bis(tetrathiotetracene) triiodide (Isett & Perez-Albuerne, 1977; Smith & Luss, 1977; Buravov *et al.*, 1976)]. The radical-cation polyiodide salts in this last category fall into the range of quasi-one-dimensional conductors in which the linear (normally disordered) polyiodide chains may contribute to the conductivity properties.

Our continuing interest in the structural properties of protonated nucleic acid derivatives and their interaction with different types of anionic species (Kistenmacher, Rossi & Marzilli, 1978*a*,*b*) prompted us to report here a structural analysis of the salt formed from protonated 1-methylcytosine and the triiodide anion, which falls into category (3) above. The crystal structure is highly ordered (but unstable owing to the loss of I_2 in air) and allows a detailed determination of the structural properties to be made.

Protonated 1-methylcytosine triiodide was prepared by the oxidation of 1-methylcytosine hemihydroiodide hemihydrate (Kistenmacher, Rossi & Marzilli, 1978*a*) in aqueous 1*N* perchloric acid. Multifaceted, red-orange crystals were obtained directly from the reaction mixture. The crystals decompose in air, owing to a loss of I_2 (see below), so all further manipulations were performed on crystals coated with a thin film of lowmolecular-weight grease and sealed in glass capillaries. Preliminary photographic data indicated an orthorhombic lattice with systematic absences ($hk0$, $h = 2n + 1$, and $0kl$, $k + l = 2n + 1$) consistent with the space groups $Pnma$ and $Pn2_1a$. The crystal used in our diffractometer study (mounted approximately along the a axis) had the following faces and mean distances: (010)–$(0\bar{1}0)$ 0·24 mm, (001)–$(00\bar{1})$ 0·14 mm, $(10\bar{1})$–$(\bar{1}01)$ 0·18 mm, and (201)–$(\bar{2}0\bar{1})$ 0·22 mm. Precise cell dimensions and their associated standard deviations were obtained from a least-squares fit to the setting angles of 15 carefully centered reflections.

8714 intensities (the $+h$ hemisphere to $2\theta = 60°$) were measured on a Syntex $P\bar{1}$ automated diffractometer employing Mo $K\alpha$ graphite-monochromated radiation. The intensity data were collected in the θ–2θ scan mode; individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning (2θ) ranged from 2° min^{-1} (less than 100 counts during the rapid scan) to 24° min^{-1} (more than 1000 counts during the rapid scan). All intensities were assigned observational variances based on the equation: $\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$, where S, B_1 and B_2 are the scan and extremum background counts ($T_B = T_S/4$), and p was taken to be 0·03 (the maximum deviation of any of three standards measured after every 100 observations was 3%). The intensities and their standard deviations were corrected for Lorentz, polarization and absorption effects [μ(Mo $K\alpha$) = 7·63 mm^{-1}, maximum and minimum transmission factors, on F^2, of 0·40 and 0·17]. The amplitudes of reflections with $I \leq 0{\cdot}2\sigma(I)$ were set equal to zero. The data were then averaged (mmm point-group symmetry) to yield 1884 symmetry-independent values [68 reflections with $I_{\text{AVE}} \leq \sigma(I)_{\text{AVE}}/n$, where n is the number of independent observations contributing to the average (normally four), were considered statistically unobserved and removed from the data set].

The structure was solved by standard heavy-atom Patterson and Fourier methods, assuming space group $Pnma$ which requires all but two methyl H atoms to lie on the mirror planes at $y = \pm\frac{1}{4}$. Five cycles of isotropic and three cycles of anisotropic refinement [minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$] led to an R value $[\sum ||F_o| - |F_c||/\sum |F_o|]$ of 0·054. A difference-Fourier synthesis permitted the positioning of the H atoms. The refinement was continued with the inclusion, but no refinement, of the H atom parameters. In these last cycles, three reflections [020, 040, and 401] were excluded as they were apparently affected by secondary extinction. Two further cycles produced convergence (no shift/error greater than 0·5) and a final R value of 0·051. The final weighted R value $\{[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ and goodness-of-fit $\{[\sum w(|F_o| - |F_c|)^2/(\text{NO}-\text{NV})]^{1/2}$, where NO = 1881 observations and NV = 73 variables$\}$ were 0·045 and 2·7 respectively. A final difference-Fourier map showed no features exceeding ±0·7 e Å^{-3} [near the I atoms].

The scattering curves for the non-hydrogen atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964), while the scattering curve for H was that of Stewart, Davidson & Simpson (1965). The real parts of the scattering curves for all non-hydrogen atoms were corrected for anomalous-dispersions effects (Cromer & Liberman, 1970). Final atomic parameters are collected in Table 1.*

Table 1. *Final atomic parameters* (×10^4, *except for* I ×10^5 *and* H ×10^3)

	x	y*	z
I(1)	12807 (4)	$\frac{3}{4}$	48660 (4)
I(2)	31089 (4)	$\frac{3}{4}$	63804 (4)
I(3)	46831 (5)	$\frac{3}{4}$	78012 (5)
O(2)	662 (4)	$\frac{3}{4}$	1351 (5)
N(1)	2217 (4)	$\frac{3}{4}$	555 (5)
N(3)	2102 (4)	$\frac{3}{4}$	2295 (5)
N(4)	3521 (5)	$\frac{3}{4}$	3287 (5)
C(1)	1713 (8)	$\frac{3}{4}$	−417 (7)
C(2)	1588 (6)	$\frac{3}{4}$	1386 (5)
C(4)	3144 (5)	$\frac{3}{4}$	2406 (6)
C(5)	3725 (6)	$\frac{3}{4}$	1530 (7)
C(6)	3245 (6)	$\frac{3}{4}$	642 (7)
H(3)	162	$\frac{3}{4}$	290
H(4)	310	$\frac{3}{4}$	395
H(41)	430	$\frac{3}{4}$	345
H(5)	450	$\frac{3}{4}$	156
H(6)	360	$\frac{3}{4}$	0
H(11)	220	$\frac{3}{4}$	−95
H(12)	128	640	−50

* Fixed by symmetry.

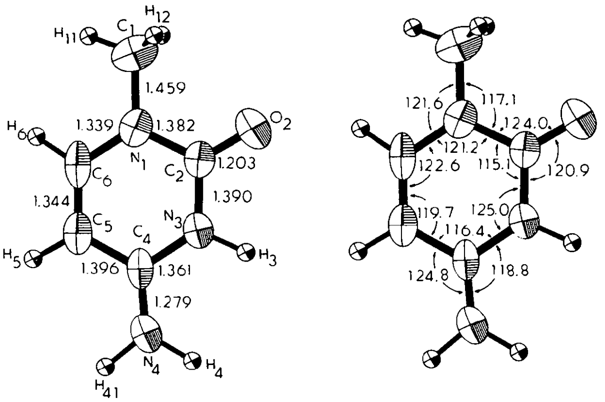

Fig. 1. The protonated 1-methylcytosine cation. The thermal ellipsoids of the nonhydrogen atoms are drawn at the 40% probability level. The isotropic thermal ellipsoids of the H atoms have been artificially set to 1 Å^2.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33379 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The crystallographic computations were performed with the following set of programs: *ORFLS* (Busing, Martin & Levy, 1962); *FORDAP* (Zalkin, 1965); *ORABS* (Wehe, Busing & Levy, 1962); *ORTEP* (Johnson, 1965); plus a variety of locally written programs.

Discussion. An illustration of the protonated 1-methylcytosine cation and its intramolecular bond lengths (e.s.d.'s about 0·006–0·007 Å) and angles (e.s.d.'s about 0·4°) are presented in Fig. 1. The parameters in the cation are similar to those found in other N(3)-protonated 1-methylcytosine salts [see, for example, the structures of protonated 1-methylcytosine chloride (Trus & Marsh, 1972) and perchlorate (Kistenmacher, Rossi & Marzilli, 1978*b*)]. As is typical (Singh, 1965), the major perturbation in the geometric parameters owing to the protonation at N(3) lies in the interior angle at N(3) [∠C(2)–N(3)–C(4) = 120·1 (1)° in 1-methylcytosine itself (Rossi & Kistenmacher, 1977) while this angle is 126·1 (1)° in the chloride salt, 124·7 (3)° in the perchlorate salt, and 125·0 (4)° in the triiodide salt reported here].

The triiodide anion (Fig. 2) is both unsymmetrical and nonlinear [see, for example, Runsink *et al.* (1972), and Bats, de Boer & Bright (1971)]. The intramolecular I–I distances at 2·794 (1) and 3·123 (1) Å can be compared with 2·715 (1) Å in crystalline I_2 (van Bolhuis, Koster & Migchelsen, 1967) and the expected I–I distance of 2·92 Å in the 'free' triiodide anion derived from the relatively noninteracting anion in the tetraphenylarsonium salt (Runsink *et al.*, 1972). Screw-related (*a* axis) anions are coupled *via* an I(3)···I(1)-$[\frac{1}{2}+x, \frac{3}{2}-y, \frac{3}{2}-z]$ contact of 3·755 (1) Å, ultimately leading to an infinite zigzag chain of approximately orthogonal triiodide anions (Figs. 2 and 3). The triiodide chain observed here is similar to that found in $[(\text{phenacetin})_2\text{H}][I_3^-,I_2]$ (Herbstein & Kapon, 1972), where the zigzag chain is composed of alternating and mutually orthogonal I_3^- anions [centrosymmetric, *d*(I–I) = 2·907 (1) Å] and I_2 molecules [*d*(I–I) = 2·748 (2) Å]; the distance between neighboring triiodide anions and I_2 molecules is 3·550 (2) Å. Both of the above interaction distances are significantly longer than those observed in the zigzag chains in crystalline I_2 (3·50 Å) and suggest that the order of attractive interaction is as follows: neutral–neutral > neutral–anion > anion–anion.

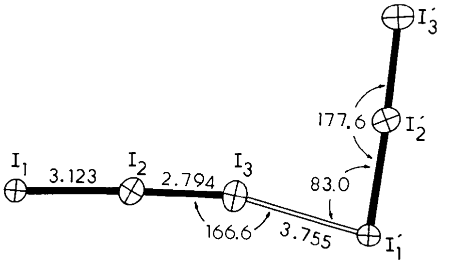

Fig. 2. Stereochemistry and dimensions of two interacting triiodide anions.

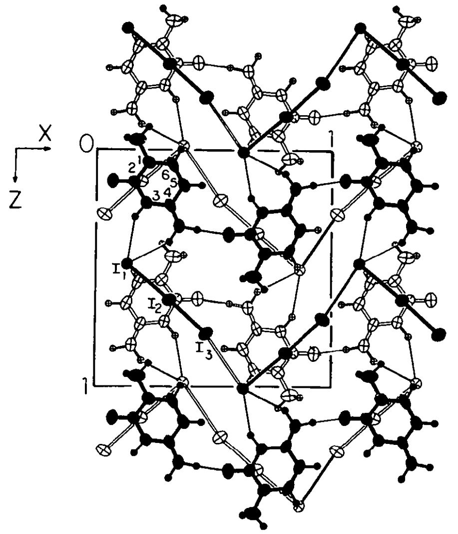

Fig. 3. A projection of the structure of protonated 1-methylcytosine triiodide onto the *ac* plane. The labeled cation and anion have their coordinates as given in Table 1. Thin lines denote hydrogen bonds.

The crystal structure of protonated 1-methylcytosine triiodide is dominated by the presence of layers of molecular ions at $y = \pm\frac{1}{4}$ (Fig. 3). Within these layers, the structure consists of parallel zigzag chains of protonated 1-methylcytosine cations and triiodide anions. As noted above, the interaction in the triiodide chain is accomplished *via* the moderately short I(3)···I(1)$[\frac{1}{2}+x, \frac{3}{2}-y, \frac{3}{2}-z]$ contact of 3·755 (1) Å. Coupling in the protonated 1-methylcytosine chain is provided by an interpyrimidine hydrogen bond with the exocyclic amino group (Fig. 1) acting as a donor and the carbonyl oxygen atom, O(2), of a screw-related (*a* axis) cation as the acceptor {N(4)–H(41)···O(2)-$[\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}-z]$, H(41)···O(2) 1·79, N(4)···O(2) 2·821 (6) Å, ∠N(4)–H(41)···O(2) 176°}. In-plane interactions between the triiodide and the protonated 1-methylcytosine chains are confined to hydrogen bonds involving the terminal iodine atom I(1) and the protonated ring-nitrogen-atom site N(3) and again the exocyclic amino group (Fig. 3). The parameters in these interchain hydrogen bonds are as follows: N(3)–H(3)···I(1)$[x,y,z]$, H(3)···I(1) 2·67 Å, N(3)···I(1) 3·610 (3) Å, ∠N(3)–H(3)···I(1) 152°; N(4)–H(4)···I(1)$[x,y,z]$, H(4)···I(1) 2·66 Å, N(4)···I(1) 3·597 (3) Å, ∠N(4)–H(4)···I(1) 149°. There is also a short C–H···I contact, again involving I(1), that is worthy of mention: C(5)–H(5)···I(1) $[\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}-z]$, H(5)···I(1) 3·00 Å, C(5)···I(1) 3·810 (4) Å,

∠C(5)—H(5)···I(1) 138°. It is important to note that only the terminal iodine atom I(1) acts as an acceptor in all of the interactions just cited. Furthermore, I(1) is involved in the long intramolecular I—I distance of 3·123 (1) Å in the triiodide anion (Fig. 2). In the light of the strong crystal field about I(1) and the absence of any strong in-plane interactions involving I(2) and I(3) [separated by 2·794 (1) Å], it is not surprising that the crystal is unstable owing to the loss of free iodine. Fig. 3 clearly shows channels parallel to the *a* axis which must almost certainly serve as conduits for the flow of I_2 derived from atoms I(2) and I(3).

The interaction between layers at $y = \pm\frac{1}{4}$ seems clearly to be electrostatic in nature (Fig. 3). The two layers are shifted relative to each other by a half translation along the *c* axis such that triiodide chains from one layer lie approximately over protonated 1-methylcytosine chains from the other layer and *vice versa* (Fig. 3). The only noteworthy interlayer contact involves the central atom I(2) and the carbonyl C(2) of the pyrimidine ring, I(2)···C(2)$[\frac{1}{2}-x,\ 1-y,\ \frac{1}{2}+z]$ 3·578 (4) Å. Several other interlayer I···C(N) contacts of about 3·75 Å are also present.

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