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## The Crystal Structure of Bis(tetrathiotetracene) Triiodide, a One-Dimensional Organic Metal

BY DOUGLAS L. SMITH AND HENRY R. LUSS

*Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, USA*

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The crystal structure of the organic metal  $\text{TTT}_2\text{I}_3$  has been determined at room temperature from X-ray diffraction data collected on a diffractometer. The crystals are orthorhombic, *Abam*, with  $a = 18.394(12)$ ,  $b = 4.962(5)$ ,  $c = 18.319(11)$  Å,  $d_m = 2.16$ ,  $d_c = 2.156$  g cm<sup>-3</sup>,  $Z = 2$ . Diffuse streaks on precession photographs indicate a disordered lattice incommensurate along **b** with  $b' = 9.54$  Å =  $1.92b$ . The structure was solved in the subcell by Patterson and Fourier methods and refined by full-matrix least-squares calculations to  $R_1 = 0.042$ . The structure consists of planar TTT radical cations with  $2/m$  crystallographic symmetry stacked uniformly along **b**, the axis of high electrical conductivity, with a 3.32 Å interplanar spacing and a ring-bond overlap. A short S...S contact [3.373(2) Å] links stacks in (100) planes. The I atoms are present as triiodide ions lying in chains along  $2_b$  axes parallel to the TTT stacks. For some crystal domains the triiodide ions lie on the incommensurate lattice but for others they are forced to conform to the subcell dimensions by a close hydrogen approach. The dual nature of the triiodide ions also causes a possible disorder in the TTT moieties. These disorders are possibly the reason no metal–insulator transitions are observed down to 3.3 K.

### Introduction

Isett & Perez-Albuerna (1977) have prepared and studied a novel ion-radical salt of tetrathiotetracene (TTT) and iodine with stoichiometry  $\text{TTT}_2\text{I}_3$ . They report that single crystals of  $\text{TTT}_2\text{I}_3$  have a room-temperature electrical conductivity of  $1000 \Omega^{-1} \text{cm}^{-1}$  along the needle axis which rises to  $3000 \Omega^{-1} \text{cm}^{-1}$  in the range 40 to 80 K and then decreases to  $100 \Omega^{-1} \text{cm}^{-1}$  at 4 K. The temperature dependence of the conductivity is essentially metallic and there is no evidence of a metal–semiconductor transition down to 3.3 K. This behavior places  $\text{TTT}_2\text{I}_3$  among the best organic ‘metals’ known to date, such as TTF–TCNQ (tetrathiofulvalene/tetracyanoquinodimethane) (Ferraris,

Cowan, Walatka & Perlstein, 1973) and HMTSF–TCNQ (hexamethylenetetraselenofulvalene–tetracyanoquinodimethane) (Bloch, Cowan, Bechgaard, Pyle, Banks & Poehler, 1975).

We have determined the crystal structure of  $\text{TTT}_2\text{I}_3$  to provide a sound structural basis for the interpretation of the high conductivity of this material.

### Experimental

Brown, long, square, prismatic (*b*) crystals, grown in vacuum by cosublimation of TTT and iodine, were supplied by Dr L. C. Isett of the Eastman Kodak Research Laboratories. Crystal data, given in Table 1,

were obtained from precession photographs and the lattice constants were refined by least-squares analysis of the setting angles of eleven reflections ( $25^\circ < 2\theta < 33^\circ$ ) centered through narrow slits on a Picker diffractometer.

In addition to the normal Bragg pattern, the precession photographs show a pattern of diffuse streaks for a cell incommensurate along **b** with the primary lattice. The original photographs, taken with Cu  $K\alpha$  radiation, contain a single prominent diffuse streak perpendicular to **b\*** and parallel to **a\*** and **c\***, with a period of 3.18 Å along **b**. A  $0kl$  photograph taken with Mo  $K\alpha$  radiation shows five additional diffuse lines parallel to but very much weaker than the original one. The supercell period along **b** becomes  $b' = 3 \times 3.18 \text{ \AA} = 9.54 \text{ \AA} = 1.92b$ .

On the  $hk0$ ,  $1kl$  and  $3kl$  photographs, the strong streak ( $k' = 3$ ) is resolved into diffuse spots with  $h$  odd and  $l$  even. A photograph (Mo  $K\alpha$ ) of the  $h3'l$  diffuse layer contains no streaks but does contain diffuse spots coincident with the subcell  $a^*c^*$  grid with  $h$  odd and  $l$  even. The lack of streaks indicates a continuous diffuse sheet perpendicular to **b\***, characteristic of one-dimensional ordering. On the other hand, the presence of diffuse spots superimposed on the diffuse sheet indicates three-dimensional ordering, at least over limited domains of the crystal.

The continuous streaks are obviously for a lattice incommensurate with the subcell since for the  $0kl$  layer the streak for  $k' = 4$  is visible and is well resolved from the  $k = 2$  line of primary spots. However, because of the weakness of the lines and the focusing features of the precession camera, we cannot be certain that the diffuse spot pattern is also incommensurate. In fact, a 43 h  $hk0$  photograph (Cu  $K\alpha$ ) seems to show resolution of the diffuse spots from the diffuse line, with the spots consistent with a period  $2b$  of the subcell. More careful experimental work is necessary to resolve this ambiguity.

A crystal measuring  $0.10 \times 0.14 \times 0.28$  mm was used for intensity data collection on a card-controlled Picker four-circle diffractometer at  $25^\circ\text{C}$  with Zr-filtered Mo radiation. 999 unique reflections for  $2\theta < 55^\circ$  were measured by the  $\theta$ - $2\theta$  scan technique at

a  $2\theta$  scan rate of  $1^\circ \text{ min}^{-1}$ . Scans were from  $1.1^\circ$  below the  $K\alpha_1$  peak to  $0.75^\circ$  above the  $K\alpha_2$  peak, except for some low-angle reflections where the range was adjusted to avoid the residual  $K\beta$  peak. At each end of the scan, a fixed 20 s background was recorded. A standard reflection, 562, remeasured every 50 reflections, did not change systematically.

The intensities were reduced to structure amplitudes after correction for background, Lorentz and polarization effects. Absorption corrections were not applied. Standard deviations  $\sigma(I)$  were based on counting statistics and corrected to  $\sigma(F)$ . The 293 intensities less than  $2\sigma(I)$  were considered unobserved. These intensities were set equal to  $2\sigma(I)$ , corrected to  $F_{\text{lim}}$ , and included in the refinement whenever  $|F_c| > F_{\text{lim}}$ .

### Structure determination and refinement

The structure was initially solved in the noncentrosymmetric space group  $Aba2$ , in which the TTT molecules must possess twofold crystallographic symmetry. The orientation of TTT was deduced by comparison of the lattice constants with the expected molecular dimensions. A sharpened ( $E^2 - 1$ ) Patterson map yielded all 12 unique nonhydrogen atoms for TTT. Subsequent electron density maps indicated a channel of density parallel to **b** and several disordered models were tested for the I atoms. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) of twelve atoms of TTT and three disordered I atoms, all with anisotropic temperature factors, proceeded slowly with severe oscillation and high correlation of parameters. A difference electron density map ( $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.051$ ) clearly showed the four H atoms. Further refinement reduced  $R_1$  to 0.037 but did not converge.

Inspection of the atomic parameters and their correlations and oscillations made it apparent that the space group must be the centrosymmetric  $Abam$ , in which the TTT radical cations must possess crystallographic  $2/m$  symmetry and the I atoms lie on the twofold axes parallel to **b**. Refinement was resumed and several models for the disordered I atoms were tested. In particular, it was determined that the I atoms make large contributions to the  $h2l$  structure factors as well as to  $h0l$ , and therefore the iodine lattice cannot be completely incommensurate along **b** with the TTT lattice. The most reasonable model assumed  $I_3^-$  ions with fixed 2.977 Å bond lengths and fixed  $y$  parameters governed by the near approach of H atoms from TTT. These  $I_3^-$  ions occupy two cells along **b** and a disorder arises because adjacent iodine columns may be shifted arbitrarily relative to one another by increments of  $b/2$ .

Refinement was concluded with  $R_1 = 0.042$  and  $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2} = 0.047$  for the 706 observed reflections plus 22 unobserved reflections with

Table 1. *Crystal data*

$(C_{18}H_8S_4)_2I_3$ , FW 1085.8
Orthorhombic (Mo $K\alpha$ , $\lambda = 0.70926 \text{ \AA}$ ), $25^\circ\text{C}$
$a = 18.394 (12)$ , $b = 4.962 (5)$ , $c = 18.319 (11) \text{ \AA}$
$V = 1672 (2) \text{ \AA}^3$ , $d_m = 2.16$ , $d_c = 2.156 \text{ g cm}^{-3}$
$Z = 2$ , $F(000) = 1038$ , $\mu(\text{Mo } K\alpha) = 3.4 \text{ mm}^{-1}$
Systematic absences: $hkl: k + l \text{ odd}$ , $0kl: k \text{ and } l \text{ odd}$ ,
$h0l: h \text{ and } l \text{ odd}$
Space group $Abam (D_{2h}^{14})$
General positions: $(0,0,0; 0, \frac{1}{2}, \frac{1}{2}) \pm (x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2} - x, \frac{1}{2} + y, z;$
$\frac{1}{2} + x, \frac{1}{2} - y, z)$

Table 2. Final atomic parameters with estimated standard deviations in parentheses

The anisotropic thermal parameters ( $\text{\AA}^2$ ) are in the form  $\exp[-0.25(h^2a^{*2}B_{11} + \dots + 2klb^*c^*B_{23})]$ . The I atoms each have an occupancy of  $\frac{1}{8}$  relative to the equivalent positions of Table 1.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
I(1)	$\frac{1}{4}$	0.19	$\frac{1}{4}$	5.36 (23)	21.6 (8)	4.64 (21)	0	2.26 (22)	0
I(2)	$\frac{1}{4}$	0.79	$\frac{1}{4}$	3.03 (18)	22.8 (5)	2.46 (18)	0	-0.01 (22)	0
I(3)	$\frac{1}{4}$	1.39	$\frac{1}{4}$	6.98 (30)	26.2 (10)	4.82 (24)	0	-2.06 (25)	0
S	0.03876 (5)	0.1524 (2)	0.17086 (5)	4.21 (5)	3.23 (4)	1.87 (3)	-0.68 (4)	-0.24 (3)	-0.31 (3)
C(1)	0	0	0.03899 (22)	1.96 (16)	1.71 (16)	1.99 (17)	0.04 (14)	0	0
C(2)	0.04446 (18)	0.1794 (6)	0.07644 (16)	2.25 (12)	2.25 (14)	1.93 (11)	0.10 (11)	-0.05 (10)	-0.11 (11)
C(3)	0.08943 (16)	0.3659 (6)	0.03942 (16)	2.02 (11)	1.94 (12)	2.62 (13)	0.26 (11)	-0.33 (11)	0.01 (12)
C(4)	0.13423 (19)	0.5532 (7)	0.07588 (22)	2.27 (13)	2.65 (16)	3.34 (17)	0.01 (12)	-0.61 (12)	-0.45 (14)
C(5)	0.17608 (19)	0.7311 (8)	0.03833 (22)	1.93 (13)	2.47 (14)	5.49 (19)	-0.23 (12)	-0.55 (14)	-0.44 (15)
H(1)	0.1369 (19)	0.552 (7)	0.1227 (21)	3.2 (9)					
H(2)	0.2089 (24)	0.853 (7)	0.0618 (21)	3.8 (9)					

$|F_c| > |F_{lim}|$ . In the final cycle, all shifts were less than  $0.1\sigma$  except for the  $\beta_{13}$  parameters of the three iodide atoms which were oscillating by  $0.4\sigma$ . A final difference electron density map contained residual electron densities between  $-0.66$  and  $+0.41 \text{ e \AA}^{-3}$ , with the range  $-0.66$  to  $-0.37 \text{ e \AA}^{-3}$  for the  $\frac{1}{4}, y, \frac{1}{4}$  line occupied by iodine. A final electron density map showed strong symmetrical peaks for TTT and a column of density along  $\frac{1}{4}, y, \frac{1}{4}$  which varied smoothly between 16 and  $37 \text{ e \AA}^{-3}$ . The final atomic parameters and their estimated standard deviations are given in Table 2.

In the refinement, weights were defined as  $w = [\sigma^2(F_o) + (0.02F_o)^2]^{-1}$  and the atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

### Discussion of the structure

The TTT radical cation has crystallographic  $2/m$  symmetry; the twofold axis along *c* passes through the S—S bonds and the mirror plane bisects the cation along its length. For this highly symmetrical moiety, the bond lengths and angles and the thermal ellipsoids are shown in Fig. 1. These distances are compared in Table 3 with averaged distances found for neutral TTT (Dideberg & Toussaint, 1974) and for the radical-cation radical-anion (TTT)(TCNQ)<sub>2</sub> salt (Shibaeva & Rozenberg, 1976). The values for the present structure agree with those of (TTT)(TCNQ)<sub>2</sub> to within  $3\sigma$  except for C(1)—C(1') where the difference is  $3.2\sigma$ , so that the two radical cations are very similar despite the difference of one-half unit in formal charge. On the other hand, comparison with neutral TTT shows significant

differences for S—S' ( $7\sigma$ ), S—C(2) ( $6\sigma$ ), C(2)—C(3) ( $5\sigma$ ) and C(3)—C(4) ( $4\sigma$ ). The significant shortening of S—S', S—C(2) and C(3)—C(4) and the lengthening of C(2)—C(3) indicate an appreciable increase of the involvement of the S atoms in the conjugation of the TTT

Table 3. A comparison of the mean molecular dimensions ( $\text{\AA}$ ) in TTT, TTT<sub>2</sub>I<sub>3</sub> and (TTT)(TCNQ)<sub>2</sub>

	TTT*	TTT <sub>2</sub> I <sub>3</sub> †	(TTT)(TCNQ) <sub>2</sub> ‡
S—S'	2.100 (2) $\text{\AA}$	2.078 (2) $\text{\AA}$	2.082 (2) $\text{\AA}$
S—C(2)	1.781 (6)	1.738 (3)	1.732 (7)
C(1)—C(1')	1.422 (13)	1.429 (8)	1.375 (15)
C(3)—C(3')	1.455 (9)	1.444 (6)	1.413 (12)
C(5)—C(5')	1.421 (11)	1.404 (8)	1.401 (12)
C(1)—C(2)	1.406 (7)	1.390 (4)	1.401 (8)
C(2)—C(3)	1.374 (7)	1.414 (4)	1.431 (8)
C(3)—C(4)	1.450 (7)	1.410 (5)	1.426 (8)
C(4)—C(5)	1.367 (7)	1.358 (5)	1.360 (8)
Plane spacing	3.47 (3)	3.32 (2)	3.52
	3.48 (3)		

\* Dideberg & Toussaint (1974).

† This study.

‡ Shibaeva & Rozenberg (1976).

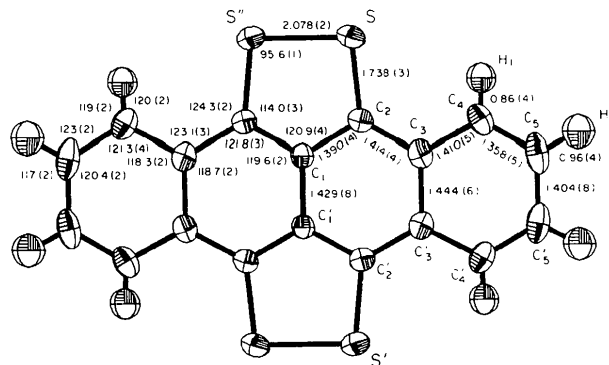


Fig. 1. Interatomic distances and angles in the TTT radical cation. Thermal ellipsoids are drawn at the 50% probability level.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32320 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

radical cations compared to TTT molecules. From bond length–bond order correlation curves (Hordvik, 1966; Hordvik & Sletten, 1966) the  $\pi$  bond orders in the present compound are about 0.1 for S–S' and 0.48 for S–C(2), compared with 0 and 0.24, respectively, for TTT.

The bond angles agree reasonably well for the three structures, particularly for C(2)–S–S' where the values are 95.6(1), 95.4 and 95.9(2)° for TTT<sub>2</sub>I<sub>3</sub>, (TTT)(TCNQ)<sub>2</sub> and TTT respectively.

The nonhydrogen atoms of the radical cation fit the least-squares plane (unit weights,  $X$  and  $Y$  in Å) with the equation  $-0.74385X + 0.66835Y = 0$  reasonably well with 0.025 Å maximum (S) and 0.014 Å r.m.s. deviations. However, the departures from planarity are systematic. A good plane with 0.006 Å maximum and 0.004 Å r.m.s. deviations can be fitted to atoms S, C(2) to C(5), and their mirror-related primed counterparts. This plane,  $-0.74964X + 0.66185Y = -0.03012$ , passes 0.03 Å from the origin and is thus separated by 0.06 Å from the parallel plane formed by the centrosymmetrically related atoms on the other side of the cation. Between these two end planes lies a plane formed by the two dithiolane rings,  $-0.73273X + 0.68052Y = 0$ , with 0.008 Å maximum and 0.007 Å r.m.s. deviations. The end and central planes form a dihedral angle of 1.4°.

Projections of the crystal structure are shown in Figs. 2 and 3. As in other good one-dimensional organic conductors, the structure is dominated by columns of radical cations stacked face to face along the direction of high electrical conductivity, **b**. The long axis of the TTT moiety is inclined 41.9° to the stacking direction and the interplanar spacing is a short 3.32(2) Å. The corresponding figures are 69.7° and 3.52 Å for (TTT)(TCNQ)<sub>2</sub> and 61.0° and 3.47 Å or 61.3° and 3.48 Å for the two unique stacks of TTT.

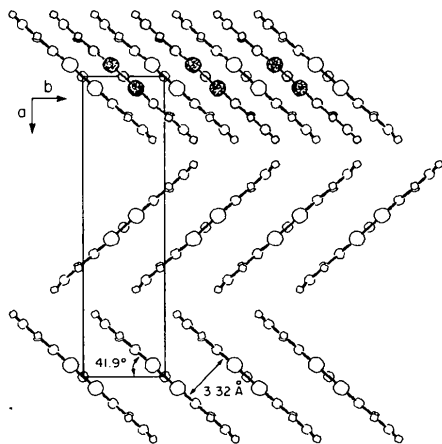


Fig. 2. (001) projection of the structure. The radical cations with unshaded S atoms are centered at  $z = 0$ ; those with shaded S atoms are centered at  $z = 0.5$ . The I atoms are not shown.

The overlap of neighboring TTT cations (Fig. 4) is of the ring-bond type commonly found in TCNQ salts (Herbstein, 1971). This type of overlap allows a closer approach of neighboring planes without causing interatomic approaches less than van der Waals distances. All intermolecular distances conform to van der Waals contacts except that between columns related by the  $A$  centering there is a short  $S \cdots S$  ( $-x, \frac{1}{2} - y, \frac{1}{2} - z$ ) contact of 3.373(2) Å, 0.3 Å shorter than twice the van der Waals radius of S given by Pauling (1960) and slightly shorter than contacts of about 3.43 Å reported more recently (Walker, Folting & Merritt, 1969).

The I atoms lie in chains on the twofold axes parallel to **b** and to the TTT stacks. A two-dimensional disorder is produced by a statistically random mutual shift of the iodine columns along their longitudinal axes and manifests itself by diffuse sheets of intensity in the diffraction photographs. It follows from the intensities of the diffuse streaks that distances of the I atoms are

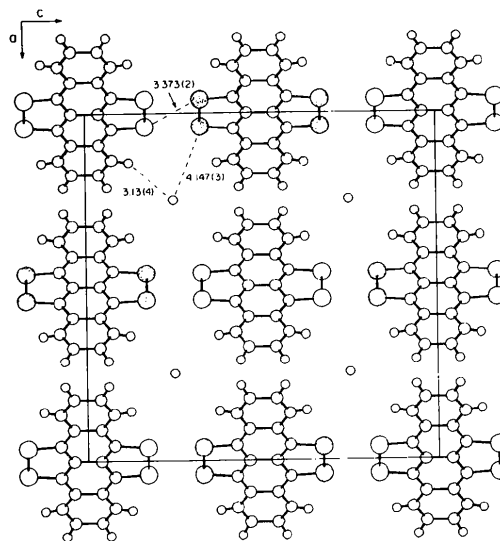


Fig. 3. (010) projection of the structure. The radical cations with unshaded S atoms are centered at  $y = 0$ . Those with shaded S atoms are centered at  $y = 0.5$ . The distances shown to the iodine channels are actually distances to  $2b$  rather than to I.

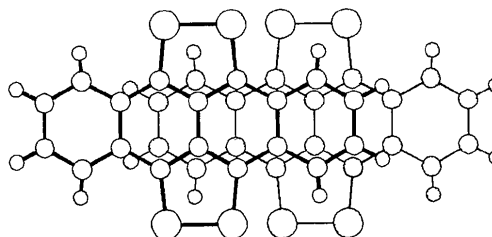


Fig. 4. Overlap of neighboring TTT radical cations in the donor stack.

modulated in the columns and that the molecular species present is the triiodide ion,  $I_3^-$ .<sup>\*</sup> The spacing of the diffuse layers indicates a superlattice incommensurate along **b** with the TTT lattice. The supercell spacing is  $b' = 9.54 \text{ \AA} = 1.92b$  and is consistent with I—I distances of approximately 2.98, 2.98 and 3.58  $\text{\AA}$  along the chain. The diffuse scattering is very similar to that observed for the iodide of the *N,N'*-diphenyl-*p*-phenylenediamine radical (Huml, 1967), where the triiodide repeat is 9.43  $\text{\AA}$ , and for an iodide oxidation product of bis(1,2-benzoquinone dioximato)nickel (Endres, Keller, Megnamisi-Bélombé, Moroni, Pritzkow & Weiss, 1975), where the spacing is 9.46  $\text{\AA}$ . Such a spacing indicates considerable interaction between triiodide ions since normal triiodide bonds are about 2.92  $\text{\AA}$  (Runsink, Swen-Walstra & Migchelsen, 1972) and the van der Waals radius of iodine is 2.15  $\text{\AA}$  (Pauling, 1960), giving an expected repeat distance of at least 10.1  $\text{\AA}$  for noninteracting  $I_3^-$  ions.

However, there is strong evidence that an appreciable fraction of the I atoms do not lie on the incommensurate lattice. In particular, on all electron density maps a variation by at least a factor of two was observed for the electron density along  $\frac{1}{4}, \frac{3}{4}$ . In addition, incommensurate I atoms would contribute only to the  $h0l$  structure factors of the subcell, but in fact a large contribution of iodine to  $h2l$  reflections was found. A refinement of the structure (S, C anisotropic; I, H isotropic) with  $h0l$  and  $hkl$ ,  $k$  odd, reflections converged to  $R_1 = 0.066$  for the subset (isotropic I atoms do not contribute to reflections with  $k$  odd). Calculated for TTT only, the  $R$  value for the omitted  $h2l$ ,  $h4l$  and  $h6l$  reflections was 0.32 and for the subset of 98  $h2l$  ( $h$  even) reflections, 0.66. Clearly, the I atoms contribute to the subcell reflections, and the final refinement included contributions by triiodide ions statistically distributed over selected positions in the subcell lattice.

The final anisotropic thermal parameters of the I atoms indicate that the r.m.s. amplitudes of vibration perpendicular to the chain are normal at about 0.24  $\text{\AA}$ , but average a large 0.55  $\text{\AA}$  along the chain. The large vibration amplitude and the electron density distribution along the chain show that the disordered model used in the refinement cannot by itself completely account for the observed intensities either, but these observations are consistent with a mixture of incommensurate and commensurate domains in the crystal.

Evidence for a partial ordering of the triiodide chains occurs in the resolution of the diffuse diffraction streaks into diffuse spots. However, because of the weakness of the effect, we were not able to determine whether the diffuse spots fall on the incommensurate

reciprocal lattice or are for a supercell with period  $2b = 9.92 \text{ \AA}$ . Such a period would agree with the van der Waals length of a triiodide ion.

A plausible explanation for the coexistence of two iodine lattices arises from the intermolecular contacts. An initial examination showed that the S atoms lie more than 4  $\text{\AA}$  [4.147(3)  $\text{\AA}$ ] from the nearest  $2_b$  axis, so there can be no appreciable donor—acceptor interaction between S and I such as occurs in hepta(tetra-thiafulvalene) pentaiodide (Johnson & Watson, 1976). However, the distance of H(1) from  $2_b$  is only 3.13  $\text{\AA}$  which becomes 2.97  $\text{\AA}$  when the C—H bond is lengthened to a realistic 1.08  $\text{\AA}$ . Compared to an expected van der Waals separation of at least 3.15  $\text{\AA}$ , it is evident that the iodine channels are somewhat constricted at intervals of  $b/2$  by H(1) atoms. This constriction is apparently enough to partially inhibit the formation of the incommensurate lattice and to encourage the ordering of the triiodide ions. Crystal formation at temperatures lower than the 215°C used to grow the present crystals (Isett, 1976) could conceivably result in greater ordering. A consequence of the two different possible repeat distances for triiodide ions along **b** is that the composition of the crystal can vary within narrow limits as  $(TTT)_2(I_3)_{1+x}$ , with  $0 \leq x \leq 0.04$ .

The thermal ellipsoids (Fig. 1) of TTT show a rocking motion about an axis perpendicular to the molecular plane. This could actually be a slight disorder effect caused by the interactions of incommensurate I atoms with H(1) since the TTT would have to shift its position slightly to accommodate such atoms.

### Conclusion

For  $TTT_2I_3$  the metal-like conductivity arises from the stacking of partially oxidized radical cations (net charge  $+\frac{1}{2}$ ) with the close interplanar spacing of 3.32  $\text{\AA}$ . The stability down to 3.3 K against a metal—insulator transition is possibly caused by the various disorders of the structure. The non-stoichiometry suggested by the incommensurability of the triiodide lattice may also be very important in preserving the disorder and preventing a low-temperature transition to an insulating state.

We are indebted to our colleagues L. C. Isett and E. A. Perez-Albuerne for suggesting the problem and furnishing the crystals and J. H. Perlstein for informative discussion. Figures were drawn with the aid of the computer program *ORTEP* (Johnson, 1971).

*Note added in proof:*—Independent of our work, a brief communication describing the crystal structure of  $TTT_2I_3$  has been published recently: Buravov, L. I., Zvereva, G. I., Kaminskii, V. F., Rosenburg, L. P., Khidekel, M. L., Shibaeva, R. P., Shchegolev, I. F. & Yagubskii, E. B. (1976). *Chem. Commun.* pp. 720–721.

\* Trotter (1976) of the Eastman Kodak Research Laboratories has recently verified the presence of  $I_3^-$  ions from resonance Raman spectra excited at 488.0 nm for crystalline powders of  $TTT_2I_3$ . The spectra show the symmetric  $I_3^-$  stretching band near 109  $\text{cm}^{-1}$  along with five overtones of this  $\nu_1$  vibration.

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## A New Pattern of Hydrogen Bonding between Perpendicular Bases in the Crystal Structure of 5-Nitro-6-methyluracil\*

BY R. PARTHASARATHY† AND T. SRIKRISHNAN

*Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York 14263, USA*

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Crystals of 5-nitro-6-methyluracil are monoclinic,  $a = 5.612(1)$ ,  $b = 9.521(3)$ ,  $c = 13.116(2)$  Å,  $\beta = 102.37(3)^\circ$ , space group  $P2_1/c$  with  $Z = 4$ . The structure was determined from three-dimensional diffractometer data by the multiresolution technique and refined by the least-squares method to an  $R$  of 0.062. The pattern of hydrogen bonding [N(3)–H(N3)  $\cdots$  O(2) (2.853 Å) and N(1)–H(N1)  $\cdots$  O(4) (2.856 Å)] is different from that for uracil; this difference is presumably caused by the substitutions at the 5 and 6 positions of uracil. A pair of molecules related by a center of inversion are 'self-paired' by two N(3)–H(N3)  $\cdots$  O(2) bonds. On the other hand, the molecules related by the N(1)–H(N1)  $\cdots$  O(4) hydrogen bonds are nearly perpendicular ( $81^\circ$ ) to each other and form a linear chain. The nitro group is disordered with the major fraction (0.84) twisted by  $\pm 41.4^\circ$  with respect to the plane of uracil and the minor fraction (0.16) twisted by  $\mp 37.0^\circ$ . Our analysis provides a structural basis for the interpretation of ESR and ENDOR spectra by Box, Potienko & Budzinski [*J. Chem. Phys.* (1976), in the press].

### Introduction

Crystal structure studies on a series of derivatives of uracil have been undertaken in our laboratory with a view to investigate the influence of different substituents on uracil on its hydrogen-bonding pattern.

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† Author to whom correspondence should be addressed.

The structure of 5-nitro-6-methyluracil (hereinafter referred to as 5N6MU) was determined as part of the above scheme, as well as to correlate the results of crystal-structure analysis with electron and nuclear spin resonance studies at this Institute (Box, Potienko & Budzinski, 1976). The crystal structure of another derivative of uracil, 6-methyl-5,6-dihydrouracil, has also been elucidated in our laboratory and published separately (Kou & Parthasarathy, 1977).