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## Hepta(tetrathiafulvalene) Pentaiodide: the Projected Structure

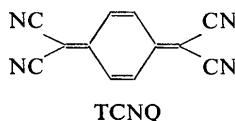
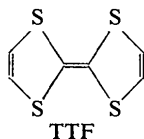
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**Abstract.**  $(C_6H_4S_4)_7I_5$ , monoclinic,  $P2_1/a$ ,  $a=48.165$  (39),  $b=16.052$  (13),  $c=24.943$  (20) Å,  $\beta=91.13$  (20),  $Z=12$ ,  $D_o=2.132$ ,  $D_x=2.134$  Mg m<sup>-3</sup>. The structure of the  $(hk0)$  projection has been solved with a final  $R$ , for 133 measured reflexions, of 0.051. The TTF units are nearly perpendicular to  $c$  and repeat by a pseudo-translation of 3.56 Å along  $c$ . The iodide ions are distributed along lines parallel to  $c$  with a second pseudo-translation of 4.99 Å. The projected structure shows tetragonal symmetry in the coordinates.

## Introduction.



Crystals of  $(TTF)_7I_5$  show high room-temperature conductivity (Dahm, Miles & Wilson, 1973) and a knowledge of the structure is vital to the understanding of the conduction process.

The dark-red crystal used was needle-shaped with a square cross-section of  $0.1 \times 0.1$  mm<sup>2</sup>, and was 1 mm long. Previous crystals examined showed multiple twinning of the type described for  $K(TCNQ)$  (Hoekstra, Spoelder & Vos, 1972). The following photographs were obtained with  $c$  as the needle axis:  $15^\circ$  oscillation,  $(hk0)$ ,  $(hk5)$ , and  $(hk7)$  from a Weissenberg camera and  $(h0l)$ ,  $(h1l)$ ,  $(h2l)$ ,  $(h3l)$ , and a cone axis photograph about  $b$  on the precession camera. The intensities of the  $hk0$  reflexions were measured on a linear diffractometer equipped with a graphite monochromator. The cell dimensions were calculated from reciprocal cell dimensions measured on the  $(h0l)$  precession photograph with the assumption [from the  $(hk0)$  Weissenberg] that  $3a^* = b^*$ . The photographs showed the following features.

1. The spectra with  $l$  values which were multiples of 5 or of 7 were, in general, strong. Spectra with  $l$  values of 2, 3, 8, 9, 12, and 19 were very weak, but could be seen. No spectra with  $l=1, 4, 6, 11, 13, 16, 17, 18, 22, 23, 24, 25, 26,$  or  $27$  were observed.

2. Along any line in reciprocal space parallel to  $a^*$  the visible adjacent spectra were separated by  $6a^*$ . A possible exception to this was the observation of a weak reflexion where  $\bar{1}, 0, 14$  should be.

3. The photographs exhibit approximate tetragonal symmetry about  $c$  and in the  $(hk0)$  projection this symmetry is almost perfect.

These photographs suggested that the structure could be described in terms of two sub-cells: one with

the space group  $A2$ ,  $Am$ , or  $A2/m$  with  $a_1=8.230$ ,  $b_1=16.052$ ,  $c_1=4.989$  Å, and  $\beta_1=102.784^\circ$  and a second with space group  $C2$ ,  $Cm$ , or  $C2/m$  with  $a_2=16.055$ ,  $b_2=16.052$ ,  $c_2=3.563$  Å,  $\beta_2=91.13^\circ$ . These cells are related to the main cell by the equations:  $a_1 = a/6 - c/15$ ,  $b_1 = b$ ,  $c_1 = c/5$ ; and  $a_2 = a/3$ ,  $b_2 = b$ ,  $c_2 = c/7$ . A few weak spectra which should be forbidden in the  $A$ -centred lattice were in fact observed in the first sub-cell, e.g.  $h_121$ . The three cells are illustrated in Fig. 1.

The complete structure in  $P2_1/a$  is very large: there are 225 ( $3 \times TTF \cdot I_5$ ) non-hydrogen atoms in the asymmetric unit and we estimate that there are about 35000 independent intensities with  $\theta \leq 25^\circ$  ( $\lambda = 0.71069$  Å) available for measurement. Accordingly we turned our attention to the  $(hk0)$  projection with the plane group symmetry  $p4g$  (or perhaps  $cm\bar{m}$ ). The reciprocal tetragonal axes are given by  $a_i^* = a_2^* + b_2^*$  and  $b_i^* = -a_2^* + b_2^*$  with the asymmetric unit of  $TTF_7I_5$ . The short pseudo-translations  $c_1$  and  $c_2$  suggest that all seven TTF groups superimpose on special positions of symmetry  $mm$  (in  $p4g$ ) and that five iodides superimpose on the special position of symmetry 4 (in  $p4g$ ).

The  $P(uv)$  Patterson function confirmed the postulated arrangement and gave a trial structure which was refined in the plane group  $cm\bar{m}$  with anisotropic temperature factors for I, S, and C until  $R$  was 0.056 for the 133 observed planes. Inclusion of the hydrogen coordinates gave a slight improvement in  $R$  (0.051).<sup>\*</sup> The final coordinates show small, probably non-significant, deviations from  $p4g$  symmetry while the temperature factors, especially of the iodide, do show significant deviations from this symmetry.

<sup>\*</sup> A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30741 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

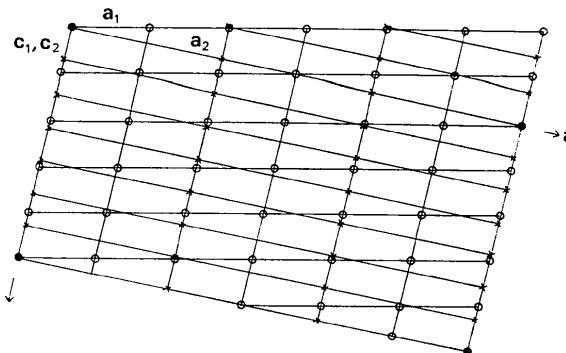


Fig. 1. Lattice points in the  $ac$  plane: ● main cell  $P2_1/a$ ; ○ first sub-cell; × second sub-cell.

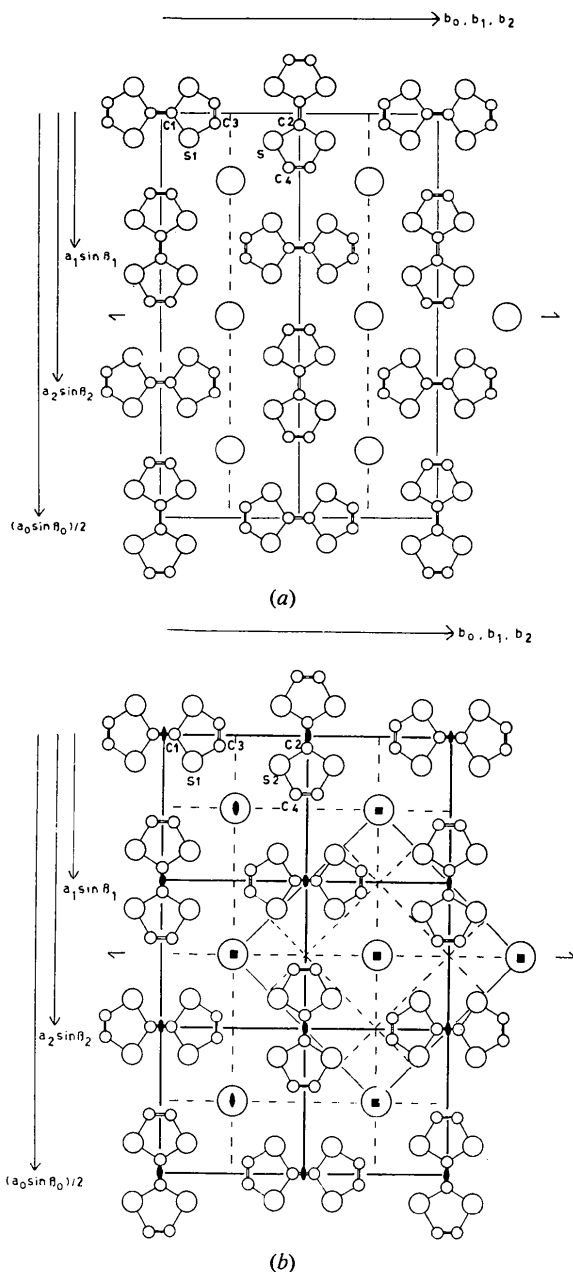


Fig. 2. (a) The  $P2_1/a$  structure. (b) The  $p4g$  and  $cmm$  projected structures.

**Discussion.** The structure in the main cell is shown in Fig. 2(a), and Fig. 2(b) shows the  $cmm$  and  $p4g$  sub-cell structures in relation to the main cell.

Though the analysis does not carry the authority of the usual three-dimensional work, certain conclusions may be drawn with reasonable confidence. The structure contains infinite columns of TTF groups whose planes are nearly perpendicular to  $c$  and which repeat with a pseudo-translation of  $c_2$  (3.56 Å) along  $c$ . There are infinite rows of iodides, running parallel to  $c$ , with a pseudo-translation of  $c_1$  (4.99 Å) along  $c$ .

The centroid of the TTF group containing S(1) is assumed to lie on 000. The projected distance from S(2) to the hydrogen atom of C(3) is close to 2.5 Å, too short for a normal van der Waals contact (Bondi, 1964). The TTF columns containing S(2) are therefore probably displaced by  $c_2/2$  with respect to those containing S(1) [see Fig. 2(a)] making a more reasonable S...H contact of 3.1 Å. An examination of the intensities indicates that the  $z$  coordinate of the iodide at  $(\frac{1}{4}, \frac{1}{4}, z)$  is 0 or  $c/10$  and the observation of some weak, forbidden,  $A$ -lattice spectra suggests that the iodide arrangement is not quite regular. The coordinates and temperature factors are listed in Table 1. The overall structure is similar to that (Hoekstra, Spoelder & Vos, 1972) of Rb(TCNQ) which is also pseudo-tetragonal (about its  $a$  axis), the TCNQ's corresponding to our TTF's and the Rb's to our iodides. However there is only one kind of overlap of the TTF groups, while in Rb(TCNQ) the TCNQ groups show two different kinds of overlap.

Table 1. Final parameters for (TTF)<sub>7</sub>I<sub>5</sub> with standard deviations

(a)  $X$  and  $Y$  coordinates in Å, plane group  $cmm$ . The remaining coordinates in  $P2_1/a$  are produced by translation of  $a/3$  along  $a$ .

	$X$	$Y$	$Z_o$ (see Discussion)
I	4.013 (0)	4.013 (3)	(0 or $c_o/10$ ) + $nc_o/5$ , $n=1 \rightarrow 4$
S(1)	1.460 (5)	1.601 (6)	0
S(2)	1.625 (5)	6.577 (6)	$c_o/14$
C(1)	0.000 (0)	0.621 (26)	0
C(2)	0.673 (23)	8.026 (0)	$c_o/14$
C(3)	0.635 (25)	3.097 (21)	0
C(4)	3.140 (18)	7.396 (24)	$c_o/14$
H(3)	1.05 (25)	3.27 (27)	0
H(4)	3.43 (28)	7.06 (22)	$c_o/14$

+  $mc_o/7$ ,  $m=1 \rightarrow 6$

(b) Thermal parameters from the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + 2hka^*b^*U_{12})]$

	$U_{11}$	$U_{22}$	$2U_{11}$	$U_{180}$
I	0.0378 (11)	0.0400 (10)	-0.0100 (16)	
S(1)	0.0456 (20)	0.0755 (30)	-0.0378 (52)	
S(2)	0.0491 (23)	0.0697 (27)	0.0243 (47)	
C(1)	0.0249 (86)	0.0688 (146)	0.0 (0)	
C(2)	0.0449 (112)	0.0193 (81)	0.0 (0)	
C(3)	0.0980 (160)	0.0655 (10)	-0.0152 (224)	
C(4)	0.0372 (77)	0.1138 (163)	0.0032 (182)	
H(3)				0.100
H(4)				0.085

This discussion ignores weak spectra for which  $l$  is not a multiple of 5 or 7, but taking these into account is not expected to have a drastic effect on the proposed structure.

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