

$\alpha_4$  is the corresponding value calculated for the finite aperture ( $\theta-2\theta$  scan) and it can be seen that the approximation of an infinite slit in this case gives an error of the order of 30% in the TDS contribution to the peak scan. The values obtained for a spherical volume ( $\alpha_5$ ) are in this case also quite good approximations for  $\theta > 40^\circ$ ; the effective scan range being  $\pm 1.47^\circ$ . A sphere of equal volume would give an effective scan range of  $\pm 1.43^\circ$  resulting in values of  $\alpha$  3% lower than  $\alpha_5$ . These effective scan ranges may be compared with the true scan range of  $\pm 1.2^\circ$ ; a spherical volume using the true scan range would thus give values of  $\alpha$  of the order of 20% too small in this case. The error in the intensities resulting from ignoring the TDS correction would again be less than about 1% with a corresponding error in the mean temperature factor. The relative agreement between the various  $\alpha$  values is also illustrated in Fig. 2.

We have also estimated the 'mosaic spread' effect for the barium fluoride measurements. The full width at half height of the measured peaks varied from  $0.2^\circ$  up to  $0.8^\circ$  resulting in a reduction of the TDS correction between 1% and 10%. This can therefore be an

important factor particularly if the width of the measured peaks changes rapidly with the scattering angle and passes through a focusing position.

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## A Neutron Diffraction Determination of the Crystal Structures of Thiourea and Deuterated Thiourea above and below the Ferroelectric Transition

BY MARGARET M. ELCOMBE AND J. C. TAYLOR

*Solid State Physics Section, Australian Atomic Energy Commission, Lucas Heights, Sutherland, N.S.W. Australia*

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The structures of thiourea,  $\text{SC}(\text{NH}_2)_2$ , and deuterated thiourea,  $\text{SC}(\text{ND}_2)_2$ , have been determined at room and liquid nitrogen temperatures from three-dimensional neutron diffraction data. No significant structural change on deuteration has been found. N-H...S hydrogen bonds occur in both materials at both temperatures with N-S distances of 3.35–3.43 Å and N-H-S angles of  $169$ – $171^\circ$  and, apart from these hydrogen atoms, the molecules are planar to within 0.010 Å. An analysis of the thermal parameters of the atoms in each molecule in terms of rigid vibration parameters shows that at liquid nitrogen temperature the molecules are fairly rigid whereas at room temperature there are serious deviations from rigidity. Excellent agreement has been found between the thermal vibrations of the molecules at room temperature and the observed structure change to the lower ferroelectric state. A qualitative theory of the ferroelectric nature of thiourea is proposed which explains the observed temperature variation of the spontaneous polarization and coercive field in the lower ferroelectric region, in terms of a variable molecular orientation and a single hydrogen bond which is switched from one sublattice to the other during ferroelectric reversal.

### 1. Introduction

On cooling from room temperature, thiourea,  $\text{SC}(\text{NH}_2)_2$ , passes through at least five different phases, two of which are ferroelectric (Goldsmith & White, 1959). The ferroelectric phases occur in the temperature ranges  $179$ – $173^\circ\text{K}$  and  $< 169^\circ\text{K}$ . Substitution of deuterium for hydrogen raises the temperature of the three

major dielectric anomalies by  $16^\circ$ ,  $16^\circ$ , and  $11^\circ$ . The coercive field is small, 200 volts.cm<sup>-1</sup> at  $120^\circ\text{K}$ .

An X-ray diffraction study of the room temperature structure of thiourea has been made by Kunchur & Truter (1958) using photographic data, and again by Truter (1967) using counter data. The structure at  $293^\circ\text{K}$  is orthorhombic with space group *Pnma* and lattice parameters  $a = 7.655$ ,  $b = 8.537$ ,  $c = 5.520$  Å, all

$\pm 0.007$  Å. There are 4 molecules per cell and the S and C atoms are in special positions on the mirror plane. Even with complete counter data using Mo  $K\alpha$  radiation, only one of the two non-equivalent hydrogen atom positions was definitely located. Dvoryankin & Vainshtein (1960), by means of electron diffraction, found hydrogen coordinates which were nearly coplanar with the rest of the molecule.

Goldsmith & White (1959) in a two-dimensional X-ray study at 120°K, in the lower ferroelectric region, found that the cell was still orthorhombic, with  $a = 7.516 \pm 0.007$ ,  $b = 8.519 \pm 0.010$ , and  $c = 5.494 \pm 0.005$  Å, but the  $n$ -glide was no longer present and the space group had become  $P2_1ma$ . The four molecules in the cell were two non-equivalent pairs, with different inclinations to the ferroelectric  $a$  axis. Goldsmith & White concluded that the ferroelectric reversal was caused by the action of the field on the resultant of the dipole moments of the molecules (in the [100] direction), causing the molecules to rotate and interchange their tilts with respect to the [100] direction.

The aim of the present neutron diffraction study of thiourea and deuterated thiourea, SC(ND<sub>2</sub>)<sub>2</sub>, at 293 and 110°K was to locate the hydrogen positions unequivocally, to determine the part played by hydrogen bonding in the ferroelectric reversal, and to determine the effect of isotopic substitution. We also hoped to be able to determine sufficiently accurate thermal parameters to enable us both to determine whether the molecules vibrate rigidly or non-rigidly, and to correlate the atomic vibrations at the two temperatures with the relative displacements between the two structures.

## 2. Experiment and analysis

Large crystals of thiourea with well defined faces, (010), (100), (101) and (10 $\bar{1}$ ), were grown from water, and, in the case of the deuterated crystals, from 99.8% D<sub>2</sub>O with several recrystallizations. Chemical analyses of the deuterated crystals by the spectroscopic method of Whateley & Whitem (1966) gave the deuteration as (95.3  $\pm$  1.0%).

All the data were collected on the 6H1 spectrometer on HIFAR, the A.A.E.C.'s research reactor at Lucas Heights. The wavelength was (1.075  $\pm$  0.010) Å and the flux at the specimen was about  $5 \times 10^6$  n.cm<sup>-2</sup>.sec<sup>-1</sup>.  $\theta$ - $2\theta$  scans were used throughout, with a step size of 4' and widths of 6-8° in  $2\theta$ . The crystal orientation angles,  $\varphi$  and  $\chi$ , were set up manually for each reflexion.

The room temperature data for thiourea (HT293) and deuterated thiourea (DT293) consisted of complete data to  $\sin \theta/\lambda = 0.60$  cm<sup>-1</sup>. The number of non-equivalent reflexions was 320, with 64 and 16 unobserved for HT293 and DT293 respectively. The data at 110°K consisted of the 412 non-equivalent reflexions to  $\sin \theta/\lambda = 0.62$  cm<sup>-1</sup>, with 34 and 26 unobserved in HT110 and DT110 respectively. For the low temperature measurements the crystals were mounted, with a [1 $\bar{1}$ 0] axis vertical, inside a small liquid nitrogen cryo-

stat which fits on a goniometer head (Bastow & Street, 1966). It was necessary to keep the crystals continuously cooled, because they break up if taken repeatedly through the transitions, with a marked falling-off of the intensities. The crystal orientation used enabled all the reflexions to be measured in either the ( $hkl$ ) or ( $\bar{h}\bar{k}\bar{l}$ ) octants without tipping the cryostat more than 50° from the vertical, and since the cryostat was filled from the top, this kept the liquid nitrogen capacity as large as possible. Preliminary measurements showed that the space group  $P2_1ma$  (Goldsmith & White, 1959) was correct. Tests with a reversible electric field of 1000 V.cm<sup>-1</sup> along the ferroelectric axis produced no detectable change in the intensities, confirming that the two ferroelectric phases are related to each other by a centre of symmetry. Because of this the low temperature data were collected without an electric field across the crystal. The temperature, continuously recorded by a thermocouple glued to the pin on which the crystal was mounted, varied by  $\pm 4$ °K. The actual temperatures recorded were 115°K for HT and 96°K for DT but, because of the different glue thicknesses between the crystals, pin and thermocouple, the crystal temperatures are not easily obtainable. Since, for the present study, the actual temperature is not critical, a nominal temperature of 110°K is used, chiefly as a distinguishing label, and the low temperature structures are referred to as HT110 and DT110 for hydrogen thiourea and deuterated thiourea respectively.

The linear absorption coefficients of HT and DT were experimentally determined, by direct transmission at room temperature, as (1.82  $\pm$  0.02) cm<sup>-1</sup> and (0.43  $\pm$  0.02) cm<sup>-1</sup> respectively. The crystals used were roughly equidimensional and had volumes between 0.022 and 0.040 cm<sup>3</sup>. The measured crystal dimensions and absorption coefficients were used to correct the observed intensities  $Q(hkl)$ , with background  $B(hkl)$  subtracted, for absorption using the program CDRABS (Cox & Craven, A.A.E.C. program library). The program also converted them to the structure amplitudes  $F(hkl)$ . The  $Q(hkl)$  were assigned standard deviations according to the expression  $\sigma^2(Q) = \sigma_1^2(Q) + \sigma_2^2(Q)$ , where  $\sigma_1(Q) = (Q + 2B)^{1/2}$  is the statistical error, and  $\sigma_2(Q) = (\alpha + \beta Q)$ .  $\alpha$  and  $\beta$  are constants chosen to allow for systematic errors in the data;  $\alpha$  was taken as  $Q_{\min}$ , the minimum observed intensity, so that the standard deviation of a just observed peak was the same as that of an unobserved peak, and  $\beta$  was taken as the fractional standard deviation in the intensity of the standard reflexions, one of which was measured every 15-20 reflexions. The unobserved reflexions were assigned intensities of  $Q_{\min}/2$  and standard deviations of  $Q_{\min}$ , giving a structure amplitude of  $(F_{\min}/2 \pm F_{\min}/2)$ . The least-squares weighting factors were  $w(hkl) = [\sigma^2\{F(hkl)\}]^{-1}$ . The atomic scattering lengths used were: carbon 0.661, nitrogen 0.940, hydrogen -0.378 and deuterium 0.65, all in units of 10<sup>-12</sup> cm, as given by Bacon (1962). The value obtained for sulphur in a check refinement on all the scattering lengths was (0.280

$\pm 0.005$ ) $10^{-12}$  cm, which differs sufficiently from Bacon's value of 0.31 to warrant this value being used instead. All the other scattering lengths obtained in this refinement agreed with Bacon's values within 2 standard deviations.

At room temperature the hydrogen positions were located in a difference map from which the C, S and N atoms, as determined from the X-ray measurements of Kunchur & Truter (1958), had been subtracted. Refinement was then completed, first with isotropic and finally with anisotropic temperature factors, with *ORFLS*, the least-squares program of Busing, Martin & Levy (1962a). The deuterated thiourea structure was refined from the isotropic hydrogen thiourea structure. The deuterium atoms were given a 95% occupancy factor to correct for the small amount of hydrogen in the specimen.

At the low temperature, direct refinement of the Goldsmith & White (1959) Fourier parameters, in-

cluding their estimated hydrogen positions, proved successful. The deuterated structure was then refined directly from the final, anisotropic hydrogen parameters. The *x* coordinate of one of the nitrogen atoms was fixed to define the origin of the space group *P2<sub>1</sub>ma*. The fractional coordinates and thermal parameters of all four structures are given in Table 1 (parameters which were fixed have no standard deviations). The atoms in the asymmetric unit are, at room temperature, S, C, N, H(1) and H(2) (Fig. 1), and at low temperature, S(1), C(1), N(1), H(1), H(2) (unit 1) and S(2), C(2), N(2), H(3) and H(4) (unit 2). The room temperature and low temperature structures of HT are shown, projected on the *x-z* plane, in Figs. 2 and 3 respectively.

The discrepancy indices  $R_w = [\sum w(F_o - F_c)^2]^{1/2} / (\sum wF_o^2)^{1/2}$  and  $R = \sum |F_o - F_c| / \sum |F_o|$ , (the unobserved reflexions are included), are given for the four structures in Table 2. Marked extinction occurred in the strong reflexions at room temperature, particularly in

Table 1. Atomic parameters of thiourea and deuterated thiourea at 293°K and 110°K, as given by the least-squares refinement

Temperature factor =  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .  
(All parameters  $\times 10^4$ , standard deviation in brackets.)

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Hydrogen thiourea, room temperature									
S	-0073 (12)	2500	1148 (13)	227 (17)	100 (11)	185 (24)	0	-1 (18)	0
C	0906 (4)	2500	-1635 (6)	148 (6)	81 (5)	298 (13)	0	49 (7)	0
N	1307 (3)	3829 (2)	-2773 (5)	328 (5)	95 (4)	488 (11)	-0 (3)	192 (6)	11 (5)
H(1)	1842 (13)	3761 (9)	-4405 (18)	614 (26)	154 (10)	706 (39)	10 (12)	351 (27)	48 (16)
H(2)	0955 (8)	4870 (6)	-2054 (10)	353 (73)	95 (9)	498 (22)	-0 (8)	71 (17)	-1 (11)
Deuterated thiourea, room temperature									
S	-0061 (10)	2500	1144 (11)	244 (14)	122 (9)	239 (19)	0	6 (14)	0
C	0911 (4)	2500	-1628 (5)	165 (5)	122 (4)	340 (10)	0	43 (6)	0
N	1305 (2)	3830 (2)	-2755 (4)	328 (4)	137 (3)	497 (8)	-8 (3)	178 (5)	24 (4)
D(1)	1870 (6)	3797 (4)	-4386 (7)	611 (12)	168 (5)	668 (14)	-16 (7)	412 (12)	34 (7)
D(2)	0930 (4)	4866 (3)	-2046 (5)	325 (7)	116 (4)	503 (13)	-4 (4)	116 (7)	-7 (5)
Hydrogen thiourea, 110°K, unit 1									
S(1)	0062 (16)	0000	3454 (19)	99 (21)	26 (12)	52 (30)	0	-20 (19)	0
C(1)	0733 (10)	0000	0455 (7)	73 (10)	19 (5)	54 (13)	0	6 (8)	0
N(1)	1000	1337 (3)	-0756 (4)	113 (4)	36 (4)	94 (8)	1 (5)	33 (7)	5 (4)
H(1)	1365 (12)	1305 (10)	-2506 (13)	242 (25)	70 (10)	151 (26)	-3 (11)	94 (17)	14 (11)
H(2)	0772 (18)	2378 (8)	0052 (14)	183 (17)	50 (9)	198 (20)	14 (13)	34 (18)	-7 (12)
Hydrogen thiourea, 110°K, unit 2									
S(2)	0272 (16)	5000	1215 (17)	86 (17)	35 (12)	34 (27)	0	-14 (18)	0
C(2)	-0985 (9)	5000	3860 (8)	51 (7)	49 (7)	61 (13)	0	9 (9)	0
N(2)	-1475 (5)	3656 (3)	4912 (6)	84 (4)	40 (4)	117 (8)	-9 (5)	37 (5)	3 (5)
H(3)	-2169 (13)	3698 (9)	6506 (14)	174 (14)	85 (10)	189 (25)	-9 (11)	118 (20)	15 (13)
H(4)	-1028 (16)	2614 (10)	4271 (13)	133 (13)	66 (12)	217 (23)	-5 (11)	40 (14)	21 (12)
Deuterated thiourea, 110°K, unit 1									
S(1)	0113 (17)	0000	3412 (21)	70 (21)	75 (15)	133 (34)	0	6 (22)	0
C(1)	0744 (9)	0000	0427 (8)	70 (10)	66 (6)	111 (15)	0	14 (11)	0
N(1)	1000	1333 (3)	-0785 (5)	128 (5)	50 (4)	160 (9)	-2 (5)	47 (7)	-1 (4)
D(1)	1358 (9)	1323 (5)	-2569 (8)	241 (13)	105 (7)	173 (14)	-5 (8)	92 (11)	15 (8)
D(2)	0777 (10)	2381 (5)	0013 (8)	146 (10)	81 (6)	215 (11)	-6 (7)	28 (12)	10 (8)
Deuterated thiourea, 110°K, unit 2									
S(2)	0328 (16)	5000	1217 (20)	69 (19)	64 (14)	123 (32)	0	13 (21)	0
C(2)	-0956 (9)	5000	3852 (10)	62 (8)	54 (7)	168 (15)	0	19 (11)	0
N(2)	-1463 (6)	3659 (3)	4863 (6)	94 (4)	67 (4)	184 (9)	1 (5)	36 (5)	3 (6)
D(3)	-2191 (8)	3690 (6)	6441 (8)	159 (8)	98 (6)	191 (13)	-4 (7)	89 (9)	-6 (8)
D(4)	-0999 (8)	2622 (6)	4232 (8)	130 (9)	79 (7)	241 (14)	6 (7)	43 (10)	1 (7)

the hydrogenous specimen. In the final least-squares cycles such reflexions were therefore given a lower weight than is given by the above formula. The numbers of these reflexions are also included in Table 2.

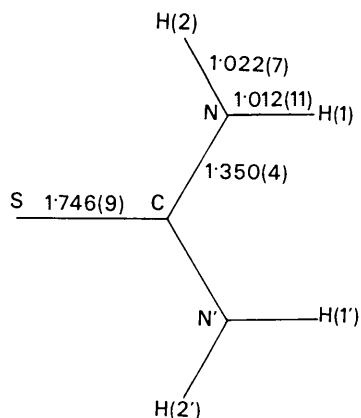


Fig. 1. The thiourea molecule. The bond lengths ( $\text{\AA}$ ) have been corrected for rigid rotation, and apply to hydrogen thiourea at room temperature.

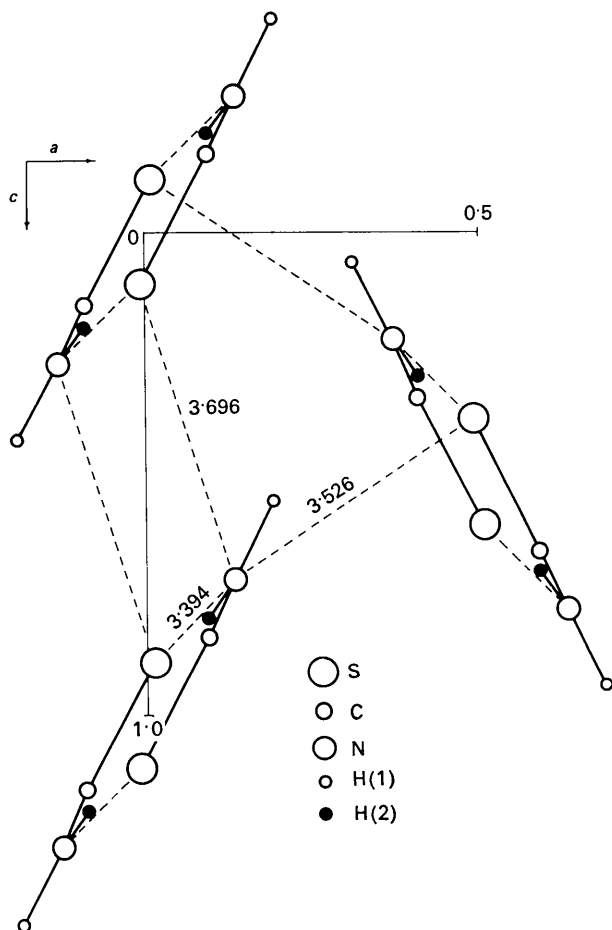


Fig. 2. The room temperature structure of hydrogen thiourea, projected on the  $x-z$  plane. (In this projection atoms  $N'$ ,  $H(1')$  and  $H(2')$  are obscured by atoms  $N$ ,  $H(1)$  and  $H(2)$  respectively.)  $N-S$  distances are given in  $\text{\AA}$ .

This accounts for the higher unweighted  $R$  values at room temperature. At low temperature the effect of extinction was negligible. For deuterated thiourea, low weights were assigned to a few reflexions for which incorrect angular settings ( $\varphi$  or  $\chi$ ) were used during the main run and which, because of further breakup of the specimen on recooling, could not be satisfactorily remeasured. The observed and calculated structure factors, and the phase angles for the low temperature structures, are given in the Australian Atomic Energy Commission's report number AAEC/TM419, and may be obtained on request from the Australian Atomic Energy Commission Research Establishment, Lucas Heights, Sutherland, New South Wales, Australia.

Table 2. Summary of the least-squares data, and final  $R$  values of all four structures

	HT293	DT293	HT110	DT110
Number of reflexions	320	318	412	412
Number unobserved	64	16	34	26
Number with low weight	15	9	0	8
$R_w$	0.070	0.058	0.053	0.051
$R$	0.107	0.090	0.047	0.056

### 3. Calculations and discussion

#### (a) Positional parameters

The atomic coordinates of all four structures, as obtained from the least-squares refinement, are included in Table 1. At room temperature there is no significant difference between the hydrogenous and deuterated structures. Nine of the coordinates agree within  $1\sigma$  ( $\sigma = \sigma_H + \sigma_D$ ) and the remaining four agree within  $3\sigma$ . (Where no ambiguity is likely, both hydrogen and deuterium are referred to as hydrogen throughout this paper). For the S, C and N atoms the X-ray diffraction coordinates given by Truter (1967) are in excellent agreement with our results (within  $2\sigma$ ), while the less accurate electron diffraction coordinates of Dvoryankin & Vainshtein (1960) agree satisfactorily. Both results give hydrogen coordinates which are essentially correct, but which differ from the neutron determined positions by up to  $0.42 \text{\AA}$ .

At the low temperature the agreement between the deuterated and normal structures is not as marked as at room temperature. Although all the  $x$  and  $y$  coordinates agree within  $2\sigma$ , four of the  $z$  coordinates [ $N(1)$ ,  $N(2)$ ,  $H(1)$  and  $H(3)$ ] only agree to  $(3 \text{ to } 5)\sigma$ . These latter parameters are the most sensitive to the molecular orientation and, as will be discussed later, this discrepancy is caused by the slightly different orientations of the molecules with respect to the crystallographic axes, and not by any change in the size or shape of the molecule. The agreement between our results and the X-ray projection coordinates of Goldsmith & White (1959) is of a similar nature. The  $y$  coordinates, including the hydrogen positions, agree within  $1\sigma$ , while the  $x$  and  $z$  coordinates show variable agreement,  $(1 \text{ to } 30)\sigma$ .

*(b) Planarity of molecules*

The planarity of the symmetry-independent thiourea and deuterated thiourea molecules has been investigated by determining the equations of the planes of each molecule by least-squares (Schomaker, Waser, Marsh & Bergman, 1959). Each atom was weighted with respect to both the symmetry of its position and, once the approximate equation of the plane was known, the accuracy of determination of the atomic coordinates. The latter weight is given by  $(a^2\delta x^2 + b^2\delta y^2 + c^2\delta z^2)^{-1}$ . The SCNN', SCNN'H(1)H(1') groups and the complete molecule were fitted independently for all the molecules.

The SCNN' unit is planar within the accuracy of our measurements. The root mean square distance of an atom from its plane, averaged over all the molecules, is  $0.0019 \pm 0.0072$  Å and the largest deviation is  $0.0046$  Å.

The SCNN'H(1)H(1') unit is also planar. Table 3 gives the distances of the symmetry independent atoms in all the molecules from the appropriate least-squares plane. Averaged over all 6 molecules the root mean square distance of an atom [not H(2) or H(4)] from its plane is  $0.0097 \pm 0.0073$  Å, the worst deviation being  $0.0230$  Å  $- 3.2\sigma$ . Table 3 also includes the distances of the H(2) type atoms from these planes. In the room temperature molecules, and in the low temperature molecules (2), the H(2)'s are definitely not coplanar with the rest of the molecule, the distances from the planes being between 8 and 29 standard deviations. In the low temperature molecules (1), however, the H(2) and D(2) atoms are 2.8 and 5.5 standard deviations respectively from the plane, so that these molecules are close to planar. Little improvement in these figures is obtained when these atoms are included in the least-squares fit.

*(c) Bonds including hydrogen*

There are three groups of S-N bonds which involve hydrogen atoms, and the S-N and S-H distances and the S-H-N angles are given for all of them in Table 4. These values were calculated with ORFFE (Busing, Martin & Levy, 1962b). Group I involves only the hydrogen atoms H(2), H(4), D(2), D(4), each of which is non-coplanar with its molecule [§3(b)], and groups

II and III involve only the planar hydrogen atoms [H(1), H(3), D(1), and D(3)].

The group I bonds couple the molecules together in continuous chains parallel to the *y* axis. The S-N and

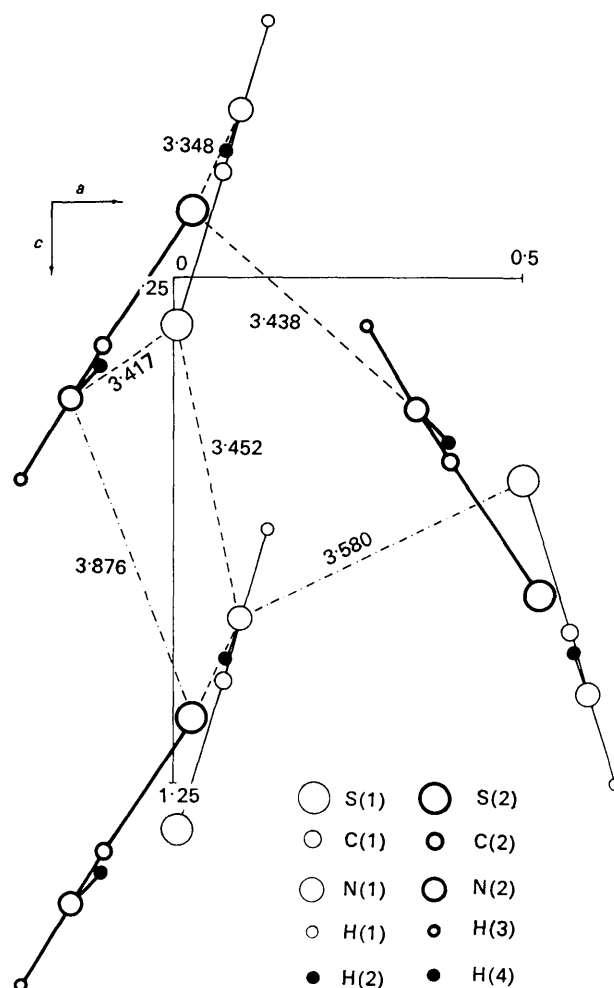


Fig. 3. The low temperature structure of hydrogen thiourea, projected on the *x-z* plane. [In this projection atoms N(1'), H(1'), H(2'), N(2'), H(3') and H(4') are obscured by atoms N(1), H(1), H(2), N(2), H(3) and H(4) respectively.] N-S distances are given in Å. The 'thin' molecules belong to sublattice one and the 'thick' molecules to sublattice two.

Table 3. Distances of the symmetry independent atoms from the least-squares planes fitted to the SCNN'H(1)H(1')\* units

(All distances in Å  $\times 10^4$ .)

Molecule	S	C	N	H(1)*	H(2)*
HT293	$-59 \pm 87$	$-5 \pm 33$	$23 \pm 26$	$-210 \pm 97$	$-675 \pm 61$
DT293	$-28 \pm 73$	$2 \pm 27$	$5 \pm 19$	$-20 \pm 43$	$-868 \pm 29$
HT110,1†	$-93 \pm 119$	$-4 \pm 71$	$1 \pm 7$	$-139 \pm 92$	$-366 \pm 129$
DT110,1	$-111 \pm 128$	$-35 \pm 69$	$2 \pm 7$	$-88 \pm 65$	$-412 \pm 75$
HT110,2	$-176 \pm 114$	$24 \pm 63$	$48 \pm 37$	$-230 \pm 91$	$-906 \pm 105$
DT110,2	$-141 \pm 117$	$-45 \pm 61$	$86 \pm 40$	$-112 \pm 59$	$-925 \pm 56$

\* H(1) refers to H(1), D(1), H(3) or D(3)

H(2) refers to H(2), D(2), H(4) or D(4).

† HT110,1 refers to molecule 1 of hydrogen thiourea at 110°K. The same notation applies in Tables 5, 6 and 7.

S-H bond lengths show very little change between the room temperature and low temperature structures, the two equivalent N-S distances of 3.394 Å at room temperature becoming two non-equivalent distances of 3.348 and 3.417 Å at low temperature. The figures are given for the hydrogen isotope, but there is no significant difference between this and the deuterated material at either temperature. This contrasts with the disagreement found between the atomic coordinates of the two materials at low temperature. These small changes in the N-S distances, together with the roughly constant N-H-S angle of 170°, suggest that these are true hydrogen bonds. This supposition correlates well with the degree of non-planarity of the hydrogen atoms involved, as is clearly shown in Fig. 3. S(2) is much closer to molecule (1), the most planar molecule, than S(1) is to molecule (2) which shows the greatest deviation from planarity. As is discussed later [§3(d)] these hydrogen bonds are probably responsible for the clamping of the rotation of each molecule about the axis perpendicular to its own plane.

Groups II and III contain the N-H...S distances and angles corresponding to bonds which couple the molecules in the *x* and *z* directions respectively. They involve only the hydrogen atoms which are planar with the SCNN' unit and, at low temperature, only link molecules which are on the same sublattice. In group II, two equivalent N-H...S bonds with an N-H-S angle of 134° at room temperature become two non-equivalent N-H...S bonds with angles of 114° and 146° at low temperature. The latter angle, coupled with an S-N distance of 3.436 Å, suggest that this is a hydrogen bond, but it is of insufficient strength to pull the hydrogen involved off the plane of the molecule.

Since this hydrogen is the one which occurs in the group III N-H...S bond with an angle of 112° the latter cannot be a hydrogen bond. By comparison, the bonds with a similar angle (114°) in group II, and probably those in group III with angles of 122° are unlikely to be hydrogen bonds. Whether the remaining bonds, with angles of 135°, are weak hydrogen bonds cannot be decided from our results.

Irrespective of the classification of these bonds, the network of N-S bonds in the *x-z* plane is intimately related to the ferroelectric reversal mechanism. On reversing the direction of polarization parallel to the *x* axis the bond angles of 114° and 146° in group II interchange, as do those of 135° and 112° in group III. This will be discussed more fully later (§ 4).

#### (d) Analysis of thermal motion

From the previous section it is clear that the intramolecular forces of the thiourea molecule are strong enough to be able to maintain a predominantly planar molecule against the intermolecular hydrogen bonding. We have therefore fitted the observed thermal parameters to translation (*T*) and rotation (*ω*) tensors by the least-squares process described by Cruickshank (1956). Since the accuracy of the thermal parameters is high (the average error in the diagonal elements is 5% at room temperature and 20% at low temperature) Cruickshank's method was modified to include the individual weight of each observation [= (standard deviation)<sup>-2</sup>] as well as the symmetry weight for each atom. The *T* and *ω* matrices for each molecule are given in Table 5. For ease of comparison the tensors are given in terms of the inertia axes of the molecules, in which axis **1** is perpendicular to the molecular plane,

Table 4. Intermolecular N-H...S distances and angles

(Standard deviation, in last decimal place, in brackets)

	Atoms	Distance		Angle	Structure
		N-S	H...S		
(I)	N H(2) S*	3.394 (4) Å	2.397 (6) Å	168.9 (0.5)°	HT293
	N D(2) S*	3.393 (3)	2.398 (3)	169.1 (0.3)	DT293
	N(1) H(2) S(2)	3.348 (4)	2.354 (8)	169.5 (0.6)	HT110
	N(1) D(2) S(2)	3.350 (5)	2.352 (5)	170.4 (0.5)	DT110
	N(2) H(4) S(1)	3.417 (6)	2.415 (10)	170.4 (0.7)	HT110
	N(2) D(4) S(1)	3.429 (6)	2.427 (7)	170.6 (0.5)	DT110
(II)	N* H(1)*S*	3.526 (8)	2.767 (12)	133.7 (0.7)	HT293
	N* D(1)*S*	3.539 (7)	2.772 (8)	133.9 (0.4)	DT293
	N(1)*H(1)*S(1)*	3.580 (11)	3.038 (13)	115.2 (0.6)	HT110
	N(1)*D(1)*S(1)*	3.596 (12)	3.074 (13)	113.0 (0.4)	DT110
	N(2)*H(3)*S(2)	3.438 (10)	2.549 (13)	145.4 (0.7)	HT110
	N(2)*D(3)*S(2)	3.429 (12)	2.526 (11)	146.7 (0.5)	DT110
(III)	N* H(1)*S	3.696 (7)	3.055 (12)	123.5 (0.7)	HT293
	N* D(1)*S	3.705 (6)	3.082 (8)	121.6 (0.3)	DT293
	N(1)*H(1)*S(1)	3.452 (10)	2.669 (12)	135.3 (0.7)	HT110
	N(1)*D(1)*S(1)	3.449 (11)	2.649 (12)	135.5 (0.5)	DT110
	N(2) H(3) S(2)*	3.876 (10)	3.360 (13)	113.2 (0.6)	HT110
	N(2) D(3) S(2)*	3.912 (11)	3.423 (12)	111.2 (0.4)	DT110

\* These atoms are related by the symmetry elements to those given. They can be identified in Figs. 2 and 3, where all the N-S distances of HT293 and HT110 respectively are given.

axis 3 is along the C-S bond and axis 2=3×1. Also included in Table 5 is the value of  $\chi$  for each molecule.  $\chi$ , which is defined in Table 5, is the root mean square value of the ratio of the difference between an observed and calculated value to its experimental accuracy. A  $\chi$  value of 1 corresponds to agreement between theory and experiment. At room temperature the hypothesis of rigidity is clearly not valid, with  $\chi$  values of 4.2 and 5.2 for HT293 and DT293 respectively. At low temperature the agreement is much better;  $\chi$  for all the molecules is  $\sim 1.5$ .

To gain further insight into the failure of the hypothesis we have calculated the quantities defined by Burns, Ferrier & McMullan (1967) and these are given in Table 6. (Their notation and definitions have been used exactly.)  $U^o(U^c)$  is the trace of the observed (calculated)  $U$  matrix [ $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ ],  $\sigma(U^o)$  is the standard deviation in  $U^o$ ,  $S$  represents the degree of mismatch between the shapes, and  $\theta$  represents the mismatch in orientation between the observed and calculated thermal ellipsoids of each atom. Classifying the atoms using the agreement levels suggested by Burns *et al.* ( $U^o - U^c < 2\sigma(U^o)$ ,  $S < 150$  and  $\theta < 25^\circ$  for satisfactory agreement ( $R$ ),  $U^o - U^c > 3\sigma(U^o)$  or  $S > 200$  or  $\theta > 30^\circ$  for unsatisfactory agreement ( $NR$ ), with a question mark for those atoms which fall into neither of the above categories) leads to column  $B$  in Table 6. From this classification it is clear that there is reasonable doubt as to the rigidity of the molecules, at both temperatures, despite the improvement in the  $\chi$  value at the lower temperature.

In the last column in Table 6 we have included an agreement factor,  $A$ , the root mean square value of  $(U_{\text{obs}} - U_{\text{calc}})/\delta U_{\text{obs}}$ , for each atom, and suggest that the agreement is satisfactory if  $A < 2$ , unsatisfactory if  $A > 3$  and questionable in between these values. In this case all the low temperature molecules are rigid, whereas the room temperature ones are unlikely to be rigid. The apparent disagreement between the two methods of classification is caused by the much lower accuracy of the thermal parameters at the lower temperature ( $\sim 20\%$  compared with  $5\%$ ), which has been included in our agreement level, but not to the same extent in

that of Burns *et al.* The conclusion we have therefore reached is that, within the accuracy of our measurements, the thiourea molecules vibrate rigidly at low temperature but are unlikely to do so at room temperature. This correlates well with the numerical values obtained for the  $T$  and  $\omega$  matrices. Before commenting on the results it is worth noting that correlation factors between 40 and 70% occur between  $T_{11}$  and  $\omega_{22}$ ,  $T_{11}$  and  $\omega_{33}$ ,  $T_{22}$  and  $\omega_{11}$ ,  $T_{33}$  and  $\omega_{11}$ , and  $T_{13}$  and  $\omega_{13}$ , so their numerical values must not be taken too literally.

At room temperature the results for both materials are very similar. The translation tensors correspond to vibrations in which the largest motion is between the  $x$  and  $z$  axes, at an angle  $\sim 60^\circ$  from the  $x$  axis, and in which the other two axes are approximately equal. Within the limits of error the molecule is rotating about its inertia axes, and has markedly different vibrations about the three axes;  $\pm 4^\circ$  about axis 1,  $\pm 11^\circ$  about 2 and  $\pm 7^\circ$  about 3. Calvo (1960) has deduced from the mirror plane symmetry and the good cleavage of the crystal perpendicular to the ferroelectric axis, that the largest vibration will be about axis 2. This rotation also corresponds to the predominant movement of the atoms during the ferroelectric transitions, and only involves the weak N-H-S bonds discussed in the previous section. The small rotation about axis 1 indicates that this motion is clamped. By considering the effect of this rotation on the N-H-S distances it is found that the strong, group I hydrogen bonds are responsible.

At low temperature a similar result is obtained for the  $\omega$  matrices, but all the vibrations are much smaller;  $\pm 3^\circ$  about axis 1,  $\pm 5\frac{1}{2}^\circ$  about axis 2, and  $\pm 4\frac{1}{2}^\circ$  about axis 3. The  $T$  matrices are more nearly isotropic and are not, therefore, so specifically oriented with respect to the crystallographic axes.

#### (e) Correction of bond lengths

Using the  $\omega$  matrices calculated in the previous section, we have calculated the intramolecular bond length corrections, using the formula given by Busing & Levy (1964) for rigid molecules. The uncorrected lengths and the calculated corrections are given in Table 7. At low

Table 5. Rotation and translation tensors describing the thermal vibrations of the thiourea molecules

(Standard deviations in brackets.)

Molecule	Translation tensors* ( $\text{\AA}^2 \times 10^4$ )				Rotation tensors* [(radians) $^2 \times 10^4$ ]				
	$T_{11}$	$T_{22}$	$T_{33}$	$T_{13}$	$\omega_{11}$	$\omega_{22}$	$\omega_{33}$	$\omega_{13}$	$\chi$
HT293	474 (73)	299 (49)	408 (50)	92 (47)	49 (21)	384 (59)	164 (41)	-10 (24)	4.21
DT293	537 (67)	442 (40)	448 (44)	109 (45)	41 (16)	394 (44)	133 (30)	-1 (19)	5.16
HT110,1	147 (37)	100 (17)	102 (17)	-16 (19)	23 (7)	89 (24)	77 (19)	-9 (10)	1.55
DT110,1	200 (40)	211 (20)	166 (21)	43 (23)	30 (8)	114 (18)	55 (16)	2 (10)	1.86
HT110,2	101 (25)	135 (18)	97 (16)	-6 (16)	28 (8)	90 (15)	69 (13)	-2 (9)	1.49
DT110,2	200 (25)	240 (16)	183 (15)	33 (16)	18 (6)	69 (10)	56 (11)	1 (7)	1.44

\*  $T_{12}, T_{23}, \omega_{12}, \omega_{23}$  are zero by symmetry

$$\chi = \left[ \frac{1}{(n-p)} \sum \left( \frac{U_o - U_c}{\delta U_o} \right)^2 \right]^{1/2}$$

where  $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ ,  $n$  = number of independent observations,  $p$  = number of non-zero parameters.

temperature, because of the small angular rotations, the corrections are all less than 0.7%. This is less than 2 standard deviations, so is barely a significant correction. At room temperature, because of the large rotation about axis 2, the corrections to the S-C and N-H(1) bonds are 2.2%. Since the molecules do not appear to be rigid at room temperature it is doubtful whether these corrections are accurate. However, if they are applied, the room temperature bond lengths agree statistically with those obtained at the lower temperature. Also included in Table 7 are the uncorrected intramolecular bond angles. We have not calculated any corrections for these angles, chiefly because at low temperature the corrections will be very small as the rotations about the three axes are not greatly different, and at room temperature the rigid molecule hypothesis is not very good.

#### 4. Ferroelectricity in thiourea

Since the first report of ferroelectricity in thiourea by Solomon (1956) the most comprehensive study of the structural and dielectric properties of thiourea and deuterated thiourea has been made by Goldsmith & White (1959). For hydrogen thiourea they found three major dielectric anomalies, at 169, 179 and 202°K,

and that the crystal was ferroelectric in two regions, below 169°K and between 173 and 179°K. Substitution of deuterium for hydrogen produced negligible changes in the polarization, dielectric constant, and coercive field, but caused the temperatures of the anomalies to rise by 16°, 16°, and 11° respectively. These results, coupled with their two-dimensional structure analysis at 120°K showed that the ferroelectricity in thiourea is not caused by single ionic displacements, as for example in  $\text{KH}_2\text{PO}_4$  (Bacon & Pease, 1955), but is associated with relative shifts of the entire molecules. This is confirmed by our results (previous section), which show that, apart from the non-planar hydrogen atoms, the dimensions of the thiourea molecule are independent of temperature. Assuming that the dipole moment of the thiourea molecules lies along the C-S bond, Goldsmith & White concluded that the spontaneous polarization originates from a non-cancellation of these molecular dipole moments along the ferroelectric axis.

Calvo (1960) has explained the observed temperature shifts of the anomalies on isotropic substitution solely in terms of the change of mass and moment of inertia of the molecules. He concluded that the upper transition is mainly translational, and that the lower transitions are predominantly rotational. However his attempt to explain the observed variation of the spon-

Table 6. Values used in assessing the rigidity of the thiourea molecules (terms described in text)

Molecule	Atom	$U^0[\sigma(U^0)]$ ( $\text{\AA}^2 \times 10^4$ )	$U^0 - U^c$ ( $\text{\AA}^2 \times 10^4$ )	$S$	$\theta$ ( $^\circ$ )	$B^*$	$A$
HT293	S	1329 (72)	-580	285	33.4	NR	6.53
	C	1200 (32)	-54	1	5.4	R	1.17
	N	2078 (27)	89	33	12.6	NR	3.47
	H(1)	3483 (100)	147	5	16.4	R	1.63
	H(2)	2166 (61)	-63	197	16.9	?	3.02
DT293	S	1545 (60)	-684	363	31.2	NR	8.73
	C	1463 (25)	-15	30	4.4	R	1.56
	N	2244 (20)	128	14	5.3	NR	3.86
	D(1)	3467 (46)	29	2	4.9	R	1.94
	D(2)	2170 (30)	-104	6	17.5	NR	2.98
HT110,1	S(1)	459 (85)	-80	182	23.6	?	1.15
	C(1)	362 (38)	-6	575	2.6	NR	1.27
	N(1)	598 (22)	-21	6	16.6	R	1.07
	H(1)	1179 (86)	205	12	11.6	?	1.15
	H(2)	1008 (66)	200	159	32.2	NR	1.67
DT110,1	S(1)	680 (96)	-165	1339	23.4	NR	1.84
	C(1)	610 (42)	16	94	14.5	R	0.84
	N(1)	793 (24)	-48	265	39.7	NR	2.04
	D(1)	1339 (47)	47	4	12.0	R	1.05
	D(2)	1044 (39)	71	130	20.3	R	1.58
HT110,2	S(2)	426 (74)	-107	380	38.7	NR	1.76
	C(2)	418 (37)	65	164	1.0	?	1.19
	N(2)	568 (20)	-37	48	9.3	R	1.16
	H(3)	1096 (68)	109	0	10.3	R	0.92
	H(4)	955 (64)	173	197	15.0	?	1.21
DT110,2	S(2)	621 (86)	-166	242	4.8	NR	1.23
	C(2)	633 (41)	-2	263	0.4	NR	1.19
	N(2)	795 (21)	-18	15	14.0	R	0.67
	D(3)	1109 (37)	25	22	20.6	R	1.58
	D(4)	1033 (42)	79	89	5.8	R	1.13

\* Rigidity classification according to the criteria of Burns *et al.* (1967).



taneous polarization with temperature in terms of a disordered structure appears to be unnecessarily complicated.

If  $\mu$  is the dipole moment along the C-S bond of a thiourea molecule then the spontaneous polarization,  $P$ , along the  $x$  axis is  $2\mu(\cos \theta_1 - \cos \theta_2)$ , where  $\theta_1(\theta_2)$  is the angle between the C-S bond of molecule one (two) and the  $x$  axis (Devonshire, 1963). If we express  $\theta_1$  and  $\theta_2$  as  $(\theta_0 + \theta)$  and  $(\theta_0 - \theta)$  and assume that  $\theta_0$  is independent of temperature in the lower ferroelectric region, (for our structures  $\theta_0 = 65.5$  for HT110 and  $65.3$  for DT110, and Goldsmith & White's determination gives  $\theta_0 = 65.5$  at  $120^\circ\text{K}$ ), then  $P = 4\mu \sin \theta_0 \sin \theta$ , so that for small angles  $P$  would be proportional to  $\theta$ . The observed temperature variation of  $P$  can then be explained if, at the transition temperature, the angle  $\theta$  makes a discontinuous jump of about  $7^\circ$  (the observed r.m.s. rotation at  $110^\circ\text{K}$  is approximately  $5\frac{1}{2}^\circ$ ), and then continues increasing more slowly as the temperature is lowered to zero, when  $\theta$  would be about  $10^\circ$ . This further rotation would strengthen the hydrogen bond which, it is suggested later, controls the ferroelectric state of the crystal. The coercive field would therefore increase as the temperature is lowered below the transition, and this is observed experimentally (Goldsmith & White, 1959).

Using the measured dipole moment of thiourea in a dioxane solution, 4.86 debyes (Kumler & Fohlen, 1942), our hydrogenous low temperature structure

gives a spontaneous polarization of  $2.3 \pm 0.1 \mu\text{C.cm}^{-1}$  compared with the observed value  $3.2 \pm 0.1 \mu\text{C.cm}^{-1}$ . Using the ionic model suggested by Calvo, in which each sulphur atom has a charge of 0.42 electron and each nitrogen has  $-0.21$  electron, we made preliminary calculations of the electric fields at the atom sites, using the Ewald transformation (Ewald, 1921), and obtained an average value of  $0.11 \times 10^6 \text{esu.cm}^{-2}$  for the field along the C-S bond. (This field disagrees with that given by Calvo who has only summed out to  $25 \text{\AA}$  and has not included charged atoms on the same molecule as the origin atom). If we assume that the difference between the observed and calculated polarization is induced by the action of the electric field on the C-S bond, a polarizability of the C-S bond in thiourea of  $(17 \pm 3)10^{-24} \text{cm}^3$  is obtained. This is of the correct order: Smythe (1955) gives a value of  $10.6 \times 10^{-24} \text{cm}^3$  for the electronic polarizability of C-S. However the polarizability of the thiourea molecule has not yet been measured experimentally.

Partly for simplicity, and partly because it is difficult to speculate on the intermediate structures, we have assumed that one transition occurs over a small temperature range, and contains both a translational and a rotational component. From the rigid vibration analysis at room temperature the largest motion of the centre of gravity is at an angle of  $60^\circ$  to  $+x$  and  $30^\circ$  to  $+z$ . It is therefore likely that the translational shift at the transition will be in this direction. However, on

Table 7. *Uncorrected intramolecular bond lengths and angles, and calculated corrections assuming rigid molecular vibrations, of the thiourea molecules*

(Standard deviation, in last d.p., in brackets)

Uncorrected bond lengths ( $\text{\AA}$ )				
	S-C	C-N	N-H (1)*	N-H (2)*
HT 293	1.709 (8)	1.333 (3)	0.991 (11)	1.010 (7)
DT 293	1.701 (7)	1.329 (2)	0.999 (3)	1.009 (3)
HT 110,1	1.732 (11)	1.334 (3)	1.000 (8)	1.006 (8)
DT 110,1	1.707 (13)	1.330 (4)	1.017 (5)	1.008 (5)
HT 110,2	1.733 (11)	1.335 (4)	1.021 (8)	1.012 (10)
DT 110,2	1.740 (12)	1.326 (4)	1.025 (6)	1.012 (5)
Bond length corrections assuming rigid molecules ( $\text{\AA}$ ) (to be added to uncorrected bond lengths)				
	S-C	C-N	N-H (1)*	N-H (2)*
HT 293	0.037 (4)	0.016 (2)	0.021 (2)	0.012 (2)
DT 293	0.037 (5)	0.018 (3)	0.022 (3)	0.014 (2)
HT 110,1	0.010 (2)	0.007 (1)	0.006 (1)	0.005 (1)
DT 110,1	0.012 (2)	0.007 (1)	0.007 (1)	0.005 (1)
HT 110,2	0.010 (2)	0.007 (1)	0.006 (1)	0.005 (1)
DT 110,2	0.007 (1)	0.005 (1)	0.004 (1)	0.004 (1)
Uncorrected bond angles ( $^\circ$ )				
	S-C-N	C-N-H (1)	C-N-H (2)	H(1)-N-H(2)†
HT 293	121.67 (0.16)	118.30 (0.48)	120.14 (0.39)	121.26 (0.57)
DT 293	121.35 (0.13)	119.75 (0.27)	120.18 (0.24)	119.81 (0.31)
HT 110,1	121.40 (0.19)	119.81 (0.55)	120.44 (0.52)	119.66 (0.68)
DT 110,1	121.39 (0.20)	120.91 (0.40)	120.95 (0.37)	118.05 (0.45)
HT 110,2	120.88 (0.22)	118.82 (0.53)	120.71 (0.59)	119.96 (0.68)
DT 110,2	120.53 (0.24)	119.03 (0.41)	120.66 (0.40)	119.75 (0.45)

\* N-H(1) refers to this bond in any molecule, e.g. N(2)-D(3).

N-H(2) refers to this bond in any molecule, e.g. N(1)-D(2).

† Not an independent angle.

ferroelectric reversal, the molecules move in antiphase with respect to the centre of symmetry which relates the two low temperature structures. In the  $z$  direction half the molecules move towards  $+z$  and half towards  $-z$  so that no net shift of the centre of gravity of the unit cell in this direction results. However, along the  $x$  axis, the ferroelectric axis, all the molecules move the same amount in the same direction resulting in a net shift of the unit cell or, if the crystal consists of one domain, a net shift of the crystal. Since this is physically unrealistic the translational shift of the molecules at the transition must be parallel to the  $z$  axis. This cannot be confirmed from our structure results because the  $x$  coordinate of the origin of the space group  $P2_1ma$  is arbitrary. This shift would suggest that,

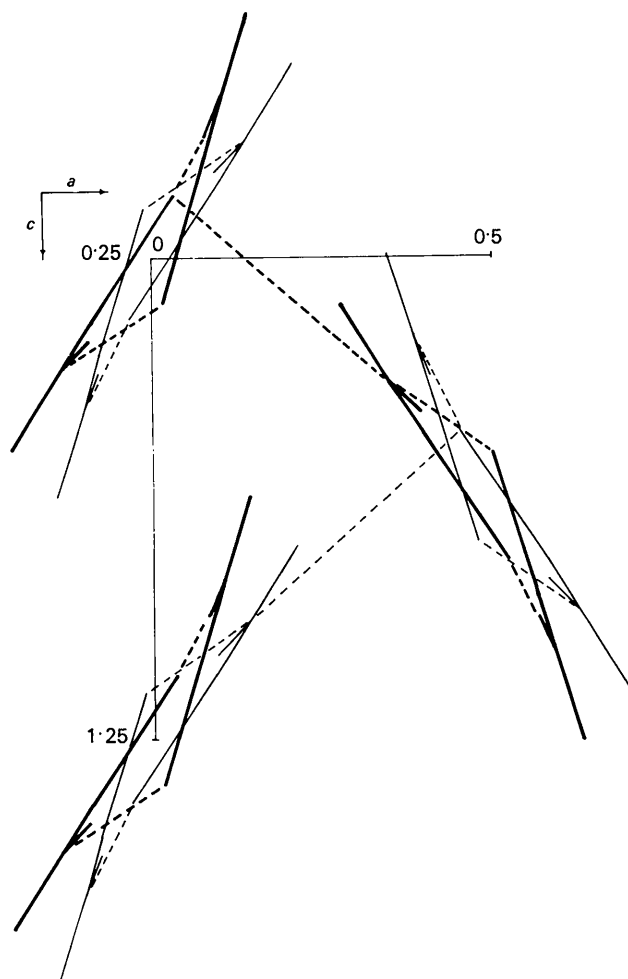


Fig. 4. A composite diagram indicating the structures of both of the ferroelectric states of thiourea (hydrogen or deuterium) at  $110^\circ\text{K}$ , projected on the  $x-z$  plane. The relative position of the two structures is such that the motion of the centres of gravity of the molecules during ferroelectric reversal is parallel to the  $z$  axis (see text).

as the crystal is cooled from room temperature, the orientation of the translational tensor will rotate from its room temperature orientation towards the  $z$  axis, and be parallel to the  $z$  axis at the transition.

In the previous section we have shown that at both temperatures the largest molecular vibration is about axis 2, and, as is confirmed by the structure analyses, this vibration correlates well with the observed structure change between room temperature and low temperature. As has already been pointed out by Calvo (1960) this vibration does not violate the mirror plane symmetry, and only involves the weak bonds indicated by the good cleavage of the crystal perpendicular to the ferroelectric axis. Using our results on the  $\text{N-H}\cdots\text{S}$  distances in the  $x-z$  plane we have confirmed Calvo's results.

However, Calvo assumed there were no hydrogen bonds in thiourea, whereas we have found that the molecules are linked together in infinite chains parallel to the  $y$  axis by hydrogen bonds which are independent of temperature. These bonds link the two sublattices at low temperature, and probably play an important part in the ferroelectric reversal process. (Sublattice 1 contains molecule 1, and sublattice 2, molecule 2.) This process is quite easily visualized if we assume that only one pair of bonds in the  $x-z$  plane,  $\text{N}(1)^*$ ,  $\text{H}(1)^*$ ,  $\text{S}(1)^*$  and  $\text{N}(2)^*$ ,  $\text{H}(3)^*$ ,  $\text{S}(2)$  in group II (Table 4) is the controlling factor. The former of these is in sublattice one and the latter in sublattice two. If, as with the structure coordinates given, the latter is the weak hydrogen bond, the former is not. This situation is reversed during the ferroelectric reversal.

When the reversing electric field is applied the force on the molecular dipoles tends to break this bond in one sublattice, and assist in its formation in the other. The process is further assisted by the group I hydrogen bonds for, when a molecule in sublattice one rotates to its new position it pulls its neighbouring molecules in sublattice two (at  $\pm y/2$ ) with it. This leads to a reversal mechanism which is very easily propagated through the crystal and in which the weak hydrogen bonds are transferred from one sublattice to the other. Fig. 4 shows the two low temperature structures superimposed. The shift of the centres of gravity of the molecules is parallel to the  $z$  axis, and the weak hydrogen bond in each sublattice is indicated.

## 5. Conclusion

The present neutron diffraction study of thiourea and deuterated thiourea at low temperatures has proved sufficiently accurate for conclusions to be reached about facts previously in doubt. The positions of the hydrogen atoms have been determined and, as had been suspected, they are basically coplanar with the SCNN group.  $\text{N-H}\cdots\text{S}$  hydrogen bonds, which are as strong at room temperature as they are at liquid nitrogen temperature, definitely occur in both thioureas. Deuteration produces no significant change in

these bonds, in the shape of the thiourea molecule, or in the spatial orientation of the molecules in the structure.

The analysis of the atomic thermal parameters in terms of rigid molecular vibrations has shown that the molecules are basically rigid at low temperatures, but that this rigidity is lost as the thermal vibration of the molecules increases. Despite this lack of rigidity, corrections to the bond lengths have been calculated assuming rigid molecules, and if these are applied the intramolecular bond lengths in thiourea are independent of temperature. The large components of the thermal vibrations at room temperature correlate very well with the observed structure change between room temperature and the lower ferroelectric state.

Elucidation of the structures of the intermediate phases which occur over a range of 35° above the lowest, major dielectric anomaly awaits further structure determinations in each phase. This is probably amenable to X-ray studies, where good low temperature control is now readily available, with refinements on molecular positions, and orientations, as suggested by Pawley (1963).

The most interesting field of study upon which our results have shed new light is the basic nature of ferroelectricity and the ferroelectric reversal mechanism in thiourea. The qualitative theory we have proposed can explain very simply the observed temperature variation of the spontaneous polarization and coercive field, and further work is in progress to put this theory on a quantitative basis, along the lines used by Devonshire (1949, 1951, 1954) for barium titanate. The actual driving force behind the transition is unknown. However, as the temperature increases from zero, the increased thermal vibrations must lead to a weakening of the controlling hydrogen bond, and it is suggested that the transition will occur when the r.m.s. molecular rotation about the axis **2** of the molecules exceeds the angle required to jump to the symmetric structure. A similar situation has been found in the  $\alpha$ - $\beta$  transition in quartz where Young (1962) has shown that the transition occurs when the r.m.s. thermal vibration of the oxygen atoms just exceeds the jump required to the more symmetrical  $\beta$  structure.

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