Structural Changes of Thiourea in Connection with its Phase Transitions: Reappraisal of Rigidity and Libration of the Molecule

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Abstract

Crystal structures of $SC(NH_2)_2$ in the paraelectric and ferroelectric phases have been refined at several different temperatures. Details of structural changes through successive phase transitions have been obtained $\{Pbnm$ $[T > T_i$ $(= 202$ K$)]$, $Pb2_1m$ $[T < T_c$ $(= 169$ K$)]$, $Z = 4$, $M_r = 76 \cdot 12$, $\mu = 6 \cdot 3$ cm^{-1} (295 K), $F(000) = 160$, Mo $K\alpha$, $\lambda = 0 \cdot 71073$ Å$\}$. Typical crystal data are the following: at 295 K, $R = 0 \cdot 042$, ND (number of reflections) $= 433$, $a = 5 \cdot 488$ (3), $b = 7 \cdot 663$ (4), $c = 8 \cdot 564$ (4) Å, $V = 360 \cdot 2$ (6) Å^3, $D_x = 1 \cdot 404$ g cm^{-3}; at 119 K, $R = 0 \cdot 034$, $ND = 1133$, $a = 5 \cdot 464$ (4), $b = 7 \cdot 500$ (5), $c = 8 \cdot 535$ (5) Å, $V = 349 \cdot 8$ (7) Å^3, $D_x = 1 \cdot 445$ g cm^{-3}. Contrary to previous results [Elcombe & Taylor (1968). *Acta Cryst.* A24, 410–420], rigidity of the molecule has been confirmed by thermal motion analysis. It has also been shown that the center of librational motion deviates from the center of mass of the molecule. A good relationship has been noticed between the static displacement of the molecule in the incommensurate phase and the largest component of the librational motion in the non-modulated phases. Evidence of hydrogen bonding is discussed.

Introduction

Thiourea is a well known ferroelectric which exhibits many interesting higher order commensurate and incommensurate (IC) phases between the paraelectric (P) and ferroelectric (F) phases. Such a complex phase diagram is considered to be the result of a delicate balance of several kinds of intermolecular interactions (Dénoyer & Currat, 1986).

The structure of the modulated phases has been studied by many workers (Shiozaki, 1971; McKenzie 1975; Takahashi, Onodera & Shiozaki, 1987, 1988; Gao, Gajhede, Mallinson, Petricek & Coppens, 1988; Tanisaki, Mashiyama & Hasebe, 1988; Simonson, Dénoyer, Currat & Vettier, 1988; Zuñiga, Madariaga, Paciorek, Pérez-Mato, Ezpeleta & Etxebarria, 1989). In the works of McKenzie (1975), Takahashi *et al.* (1987, 1988), Gao *et al.* (1988) and Simonson *et al.* (1988), the molecule of thiourea is

assumed to behave as a rigid body, on the basis of the structure analysis of the P and F phases.

According to Elcombe & Taylor (1968), the molecule in the P phase at room temperature has almost the same shape as that in the F phase at 110 K. On the other hand, the results obtained from their vibration analysis based on the method given by Cruickshank (1956) showed that the molecules do not vibrate rigidly. In order to understand the mechanism of the successive phase transitions on an atomic scale, it is necessary to investigate the vibrational state of the molecule not only at some particular temperature but also throughout the whole temperature range from the P phase to the F phase.

The present authors have pointed out the importance of the short-range interactions between the molecules in the modulated structure (Takahashi *et al.*, 1987, 1988). As an important short-range interaction the S···H—N type hydrogen bond has been considered. Although there have been several studies on this problem (Takahashi, Schrader, Meier & Gottlieb, 1967; Elcombe & Taylor, 1968; Dove & Lynden-Bell, 1986), its properties have not been fully understood yet. In this study, we also discuss hydrogen bonding in the light of the present data.

Experimental

A spherical specimen of radius 0·19 mm was mounted on a four-circle diffractometer (Rigaku AFC6) with graphite-monochromated Mo $K\alpha$ radiation. The specimen was cooled by using a cold nitrogen gas flow system with a stability better than 0·5 K

Integrated Bragg intensities were collected by a θ–2θ scanning mode (295, 159, 139 and 119 K: $0 < \sin\theta/\lambda < 1 \cdot 0$ Å^{-1}, $0 \leq h \leq 10$, $0 \leq k \leq 14$, $0 \leq l \leq 16$; 257, 221 and 149 K: $0 < \sin\theta/\lambda < 0 \cdot 9$ Å^{-1}, $0 \leq h \leq 9$, $0 \leq k \leq 13$, $0 \leq l \leq 15$). Standard reflections 400, 020 and 008 were monitored after every 100 reflections, but no serious variation was observed. The reflections with $|F_o| < 3\sigma$ were omitted in the refinements. Correction to the observed intensities was made for Lorentz–polarization, but not for absorption. Lattice parameters calculated from the observed 2θ values of

Table 1. *Refinement details*

Temperature (K)	119	139	149	159	221	257	295
Number of reflections measured	2065	2076	1537	2082	1556	1611	2204
Number of unique reflections observed [$|F| > 3\sigma(F)$]	1133	1073	847	962	549	477	433
Space group	$Pb2_1m$	$Pb2_1m$	$Pb2_1m$	$Pb2_1m$	$Pbnm$	$Pbnm$	$Pbnm$
a (Å)	5·464 (4)	5·468 (3)	5·465 (3)	5·468 (3)	5·464 (2)	5·472 (3)	5·488 (3)
b (Å)	7·500 (5)	7·524 (3)	7·527 (4)	7·540 (4)	7·593 (3)	7·633 (5)	7·663 (4)
c (Å)	8·535 (5)	8·538 (4)	8·542 (4)	8·537 (5)	8·553 (3)	8·565 (6)	8·564 (4)
Number of parameters refined	59	59	59	59	31	31	31
R	0·034	0·037	0·029	0·036	0·036	0·036	0·042
R (before TDS correction)	0·036	0·040	0·032	0·040	0·040	0·040	0·047
wR	0·034	0·036	0·029	0·036	0·036	0·036	0·041
wR (before TDS correction)	0·036	0·039	0·031	0·040	0·038	0·038	0·046
S	1·22	1·28	1·31	1·26	1·62	1·65	1·53
g	24 (3)	24 (3)	22 (3)	24 (3)	39 (4)	50 (4)	66 (5)
$(\Delta/\sigma)_{max}$	0·0006	0·0001	0·0009	0·0009	0·0032	0·0006	0·0005
$\Delta\rho$ (e Å^{-3})	−0·4–0·5	−0·4–0·4	−0·3–0·3	−0·3–0·5	−0·3–0·3	−0·3–0·2	−0·2–0·3

Table 2. *Positional parameters and isotropic thermal parameters* (Å^2) *at* 295 *and* 119 K *with their e.s.d.'s in parentheses*

$y_{N(1)}$ is fixed to be 0·1. U_{eq} for non-H atoms is defined as $\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{eq}(\times 10^4)$
295 K				
S	0·1142 (1)	−0·0075 (1)	0·25	551 (4)
C	−0·1616 (6)	0·0904 (4)	0·25	514 (16)
N	−0·2748 (5)	0·1311 (3)	0·3822 (2)	762 (14)
H(1)	−0·430 (6)	0·182 (4)	0·381 (3)	657 (93)
H(2)	−0·218 (5)	0·097 (3)	0·468 (3)	393 (67)
119 K				
S(1)	0·3466 (1)	0·0036 (3)	0·0	208 (2)
C(1)	0·0487 (4)	0·0734 (4)	0·0	187 (7)
N(1)	−0·0715 (3)	0·1	0·1335 (2)	267 (6)
H(11)	−0·225 (4)	0·129 (4)	0·131 (3)	133 (61)
H(12)	−0·002 (5)	0·078 (4)	0·228 (2)	30 (43)
S(4)	0·1230 (1)	0·0230 (3)	0·5	195 (2)
C(4)	0·3866 (4)	−0·0994 (4)	0·5	185 (7)
N(4)	0·4923 (3)	−0·1486 (3)	0·3659 (1)	255 (5)
H(41)	0·626 (4)	−0·206 (3)	0·368 (3)	82 (60)
H(42)	0·434 (4)	−0·110 (3)	0·283 (3)	77 (56)

21 reflections ($32 < 2\theta < 50°$) at each temperature are listed in Table 1 together with other refinement details.

As initial values of the positional parameters those reported by Elcombe & Taylor (1968) were used, except for H. After the refinements of these parameters, positions of H were found by difference Fourier syntheses, and were refined with isotropic thermal parameters. An isotropic secondary-extinction correction was made with the use of *MOLLY5* (Hansen & Coppens, 1978) in which a full-matrix least-squares calculation is performed by minimizing the functions $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(|F_o|) + (a|F_o|)^2$; $a = 0\cdot010-0\cdot014$. The atomic scattering factors and anomalous-scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Since the effect of thermal diffuse scattering (TDS) was observed on the higher order reflections, TDS correction was made for each data set by the program *TDS2* (Stevens, 1974). The elastic

constants were obtained by interpolations of the values given by Haussühl & Pahl (1986). After correcting for TDS, all the structure refinements were repeated. Ripples in the difference Fourier map obtained by this treatment were reduced, and R factors were improved (Table 1). The parameters at 295 K were used as initial ones for the refinements at other temperatures. The final parameters at 295 and 119 K are given in Table 2.*

Discussion

Structural parameters

The temperature dependence of the lattice parameters qualitatively agrees with that previously reported (Futama, 1962). The increase in a at T_c with decreasing temperature seems to reflect the condensation of the TO mode along the a axis which belongs to the B_{2u} irreducible representation (Takahashi *et al.*, 1987). The expansion coefficient of the b axis $[(1/b)db/dT]$ is larger than those of the other axes. It is understood that this is due to the gradual change of the orientation of the molecule; the angle between the a axis and the molecular plane decreases with decreasing temperature ($\sim 0\cdot01° $K^{-1} in the P phase).

The positional parameters at room temperature are in agreement with those given by Elcombe & Taylor (1968) within about three times the e.s.d.'s. By contrast, all the diagonal components of the thermal parameters are larger than the values of Elcombe & Taylor (1968), representing the effects of neglecting a TDS correction in their analysis. The

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* Lists of parameters at other temperatures, anisotropic thermal parameters, bond lengths and angles involving S, C and N in the molecule, structure factors, and results of rigid vibration analysis have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53204 (68 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

disagreements between the present positional parameters at 119 K and theirs at 110 K are somewhat large, which is due to the difference in the temperature.

The temperature dependence of the bond lengths and angles among S, C and N in the molecule is found to be zero within the e.s.d.'s. This result seems to support the validity of the rigid molecule model sufficiently. However, as pointed out by Elcombe & Taylor (1968), it is necessary to analyze the thermal motion of the molecule at each temperature for a more rigorous understanding of the rigidity of the molecule.

The temperature dependence of the thermal parameters of the non-H atoms is a linear function with temperature as shown in Fig. 1, where that of S is indicated. It is noticed that the slopes in the P phase are larger than those in the F phase. All the lines in the P phase can be extrapolated to negative values at 0 K, although thermal parameters in the F phase approach zero with decreasing temperture. Such an upward deviation in the P phase may be attributed to anharmonic vibration.

Libration and rigidity of the molecule

A rigid vibration analysis was performed at each temperature (*RSMV*4; Sakurai, 1967); translation and libration matrices were refined by using the anisotropic thermal parameters in the molecular unit. Contrary to the model proposed by Elcombe & Taylor (1968), the center of libration was searched for so as to find the most plausible solution. Furthermore, the H atoms were ignored in the calculation, because they are the lightest atoms and seem to be loosely bonded in the molecule. The weights in the
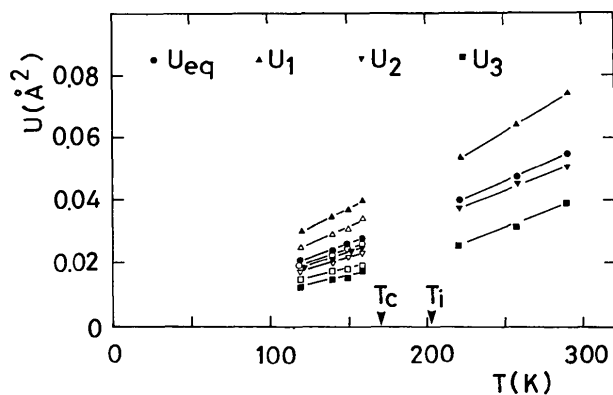
Table 3. *Center of libration and discrepancy factors* R_U *and* R_U^G

R_U's are defined as $\{[\Sigma(U_{\text{obs}} - U_{\text{calc}})^2]/(\Sigma U_{\text{obs}}^2)\}^{1/2}$. R_U^G is obtained by fixing the center of libration on the center of mass of the molecule.

T (K)	Coordinates of the center of libration	R_U	R_U^G
295	(−0·06, 0·02, 0·25)	0·021	0·102
257	(−0·06, 0·01, 0·25)	0·030	0·106
221	(−0·06, 0·01, 0·25)	0·020	0·112
159 (mol. 1)	(0·16, 0·02, 0·00)	0·036	0·079
159 (mol. 4)	(0·30, −0·03, 0·50)	0·030	0·079
149 (mol. 1)	(0·17, 0·02, 0·00)	0·029	0·069
149 (mol. 4)	(0·29, −0·03, 0·50)	0·035	0·081
139 (mol. 1)	(0·16, 0·02, 0·00)	0·021	0·069
139 (mol. 4)	(0·30, −0·03, 0·50)	0·030	0·077
119 (mol. 1)	(0·16, 0·02, 0·00)	0·027	0·070
119 (mol. 4)	(0·29, −0·03, 0·50)	0·031	0·077

least-squares calculation were chosen to be unity for each atom.

The discrepancy factors R_U are found to be much improved by choosing an adequate center of libration, compared with the case where the center of mass of the molecule is chosen as the center of libration (Table 3). R_U's are sufficiently small to assert the rigidity of the molecule. Schematic representation of the center of libration and that of mass is shown in Fig. 2.

The present analysis manifests the relation between the thermal motion of the molecule and the successive phase transitions. According to the results, the direction of the principal axis of the largest libration is along the c axis in both phases, which

Fig. 1. Temperature dependence of the thermal parameters of S. U_{eq} and U_i ($i = 1$, 2 and 3) represent the isotropic and diagonalized thermal parameters, respectively. Directions of the principal axes are nearly along the b axis ($i = 1$), rigorously along the c axis ($i = 2$), and nearly along the a axis ($i = 3$). Open and closed symbols in the F phase correspond to molecules 4 and 1, respectively.
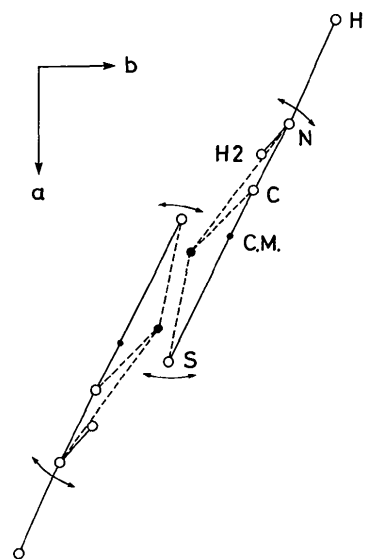

Fig. 2. Projection of molecules 1 and 4 viewed along the c axis. The closed circle represents the center of libration at 295 K. It does not change significantly with temperature. The center of mass of the molecule is shown by the closed circle denoted as C.M.

corresponds to the polarization of the soft B_{2u} mode. If the largest libration is regarded as a superposition of the coupled rotational vibration around the center of mass and the translational vibration in the ab plane, we can see that the correlated thermal motion almost corresponds to the static displacements in the IC phase. That is, the frozen phase difference between the R_c mode and the T_a mode in the IC phase is conserved in the thermal motion in the non-modulated phases (McKenzie, 1975). Fig. 3 represents the temperature dependence of the mean square of the libration along the c axis.*

Hydrogen bonds along the c axis

Evidence of hydrogen bonds along the c axis should be discussed. The distance between the two electronegative S and N atoms is found to be nearly the sum of the van der Waals radii (~ 3.4 Å). Thus, the presence of the hydrogen bond is a subtle problem in the present case and it would be weak even if it exists (Pauling, 1960).

Truter (1967) suggested its existence by pointing out the fact that the thermal parameter of H(2) was somewhat smaller than that of H(1) at room temperature. Elcombe & Taylor (1968) also concluded the existence of the S⋯H—N bond by the interatomic distance between S and N and by the location of H(2): they found that the positions of H(12) and

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* In the case where the center of libration is kept on the center of mass, the obtained principal axis of the largest libration is always along the S=C bonding, which is irrelevant to the soft mode. However, Elcombe & Taylor (1968) reported that the largest libration around the center of mass is along the c axis. Their result seems to be affected by the 'rigid' H atoms which increase the moment of inertia along the S=C direction.

H(42) are kept between and aligned with S and N at 110 K. The above considerations still hold in the present study, although the accuracy of the parameters of H is rather low. It is a very important fact that the S—N distance is kept nearly constant through the successive phase transitions.

Recently an important role of the hydrogen-bonding network in the IC phase has been demonstrated by extensive computational work (Gao & Coppens, 1989).

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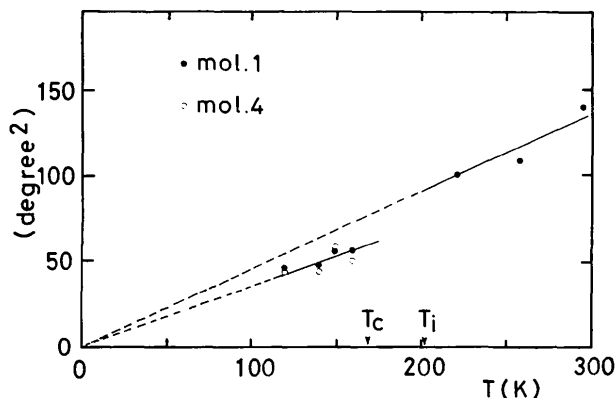
Fig. 3. Temperature dependence of the mean square of the principal value of the largest librational motion. Open circles in the F phase represent those for molecule 4.