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1961

SovietRxiv

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Abstract

Full Text

CRYSTALLOGRAPHY

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ON THE MECHANISM OF THE FERROELECTRIC PHASE TRANSITION IN THIOUREA AT 133°K

(Presented by Academician N. V. Belov, 29 IV 1961)

The structure of thiourea CS $(NH_2)_2$ has continually attracted the attention of researchers (^{1}-^{6}). It is of interest from the standpoint of elucidating the nature of the C–S bond and from the standpoint of the presence of hydrogen bonds. Until very recently the question remained unclear whether the thiourea molecule is planar (taking the hydrogen atoms into account). Finally, interest in thiourea increased again after the discovery in it of ferroelectric properties at low temperatures (^{7}). X-ray studies of the high-temperature phase of thiourea were carried out by Wyckoff and Corey (^{1}), Zvonkov and Tashpulatov (^{2}), and Kungur and Truter (^{3}). An electron-diffraction study of the high-temperature phase of thiourea (^{4}) essentially confirmed the results of the X-ray work. By the electron-diffraction method it was possible to localize the hydrogen atoms in this phase. It was found that the atoms S, C, N, and H_I lie in one plane, while the atom H_{II} deviates slightly from this plane. We have electron-diffractionally revealed the presence of a phase transition and the existence of the high-temperature phase of thiourea at a temperature of 133°K, determined the dimensions of the unit cell, the space group, and the nature of the displacement of molecules in this phase (^{5}).

Fig. 1. Scheme of the structure of the high-temperature phase V of thiourea. Two layers of molecules, *A* and *B*, are shown respectively by thick and thin lines.

Independently of us, in the USA Goldsmith and White (^{6}) carried out the same investigation by X-ray methods in the same year, establishing the positions of

Fig. 2

Figure 2: Fig. 2

the "heavy" atoms S, C, N in the low-temperature phase and investigating the physical properties of thiourea at low temperatures. According to the data of Goldsmith and White (^{6}), five phases are observed in thiourea, with the following transition points between them:

$$\begin{gathered}\text{I}-\text{ferroelectric} \underset{180^\circ\text{K}}{\overset{169^\circ\text{K}}{\rightleftarrows}} \text{II}-\text{antiferroelectric} \underset{201^\circ\text{K}}{\overset{176^\circ\text{K}}{\rightleftarrows}} \\ \rightleftarrows \text{III}-\text{ferroelectric} \rightleftarrows \text{IV}-\text{antiferroelectric} \rightleftarrows \\ \rightleftarrows \text{V}-\text{antiferroelectric.}\end{gathered}$$

In these designations the high-temperature phase is phase V, while the low-temperature phase studied by us, and also in work (^{6}), at a temperature of 133°K is phase I.

A scheme of the structure of the high-temperature phase V is given in Fig. 1. The molecules are arranged in two layers A and B, separated from one another by $c/2$, and are connected with one another by hydrogen bonds. The molecules superposed on one another in projection along the c axis are symmetrically equivalent owing to the presence of a twofold

of the screw axis 2_1. The dipole moments of each such pair of molecules in projection onto the b axis are equal and opposite, which leads to their compensation and to the presence of antiferroelectric properties. The dimensions of the unit cell of the low-temperature phase I$^{(5,6)}$ differ only slightly from those for phase V$^{(1-4)}$; however, its symmetry is lowered from D_{2h}^{16} (V) to C_{2v}^{2}—with loss of the center of symmetry and of the above-mentioned double screw axis.

Electronographic structural analysis of phase I at a temperature of 133° K$^{(7)}$ showed the following. About 250 reflections were recorded on electron diffraction patterns of the oblique-texture type. A dynamical correction was introduced and $|\Phi_{\text{exp}}|$ were found. The amplitude phases were found by calculating Φ_{theor} by successive approximations (taking H atoms into account), with an anisotropic temperature factor

$B_{hkl} = 1.7 + A\cos^2\varphi$,

where φ is the angle between the reciprocal-lattice vectors $\mathbf{H}_{hkl}$ and $\mathbf{H}_{0k0}$. For A of the various atoms the following values were adopted: $A_S = 0.52$ Å^2, $A_N = 1.64$ Å^2, $A_C = 1.34$ Å^2, and $A_H = 2.2$ Å^2. The structures were determined by the Fourier-potential synthesis method.

Fig. 2. Difference three-dimensional syntheses of the potential of the high-temperature phase V (a) and the low-temperature phase I (b) of thiourea, giving the positions of the hydrogen atoms. The positions of the calculated heavy

atoms S, C, N are indicated by dots. The contour lines are drawn at intervals of 5 V.

For a more accurate localization of the hydrogen atoms in the high-temperature and low-temperature phases of thiourea, difference three-dimensional syntheses were constructed. The set of two-dimensional sections of the difference three-dimensional series for the atoms H_{I}^{A}, H_{II}^{A}, H_{I}^{B}, H_{II}^{B} (the atoms S^{A}, S^{B}, N^{A}, N^{B}, C^{A}, and C^{B} having been removed) is shown in Fig. 2.

The "heavy" atoms S, C, N in all cases, within the limits of error, are located in one plane. The atom H_{II}, both in phase V and in phase I, according to our data, deviates slightly from this plane, as is evident from Fig. 2; moreover, in phase V molecule B is as it were turned with the atoms H_{II} to the other side. In molecule A of phase I the displacement of H_{II} from the plane is smaller, but it is nevertheless observed. On the average, according to our data, for phases I and V the deviation of H_{II} from the "planar" position is about 0.15 Å. The syntheses also show a very small displacement of the atoms H_{I} from the plane of the heavy atoms to the same side as the displacement of the atoms H_{II}—by 0.02-0.03 Å, which is less than the accuracy of localization of H atoms, approximately 0.05 Å.

The question of the non-coplanarity of H atoms with the heavy atoms is very interesting. It is known that in the structure of urea $CO(NH_2)_2$(8−10) non-coplanarity is observed, although, incidentally, no one has discussed the possibility of a "mixture" of two mirror-equivalent orientations of a non-coplanar molecule. On the other hand, for the similar molecule formamide, displacements of H atoms from the plane have been found(11). The same, according to infrared spectra, occurs for the urea molecule in the complex compound $CO(NH_2)_2{\cdot}H_2O_2$(12). Pyramidal bonding of nitrogen (and displacement of H from the plane is precisely such pyramidality) has been found in the structure of tetramethylurea $CO(NCH_3)_2$(13). In addition, X-ray and radiospectroscopic investigations of urea and thiourea(1−6, 8−10, 14, 15) invariably indicate an intense oscillation of H atoms about the C—N bond.

Thus, in addition to our data, a number of observations on similar molecules indicate the possibility of non-coplanarity of H atoms with the heavy atoms in the molecule $SC(NH_2)_2$. Most likely this is a property of the thiourea molecule as such. Conceivable, but less probable, is another explanation

of this phenomenon—as a consequence of the strong oscillation of the NH_2 group about the C—N bond and of the anisotropy of these vibrations in the force field of the crystal.

Thus, it may be assumed that the thiourea molecule as such exists in all phases I—V in one and the same form, nonplanar with respect to the H atoms. Of course, when the temperature changes, the parameters of the thermal vibrations change at the phase transition; the distances and angles may change somewhat owing to intermolecular interaction. This, as well as experimental errors, can account for certain insignificant differences in our (and also in the x-ray) data concerning

Fig. 3. Variants of the arrangement of nonplanar molecules in different phases of thiourea (projection along the c axis).

Figure 3: Fig. 3. Variants of the arrangement of nonplanar molecules in different phases of thiourea (projection along the c axis).

the intramolecular distances between the heavy atoms S, C, N in phases I and V, and also in our data concerning the magnitude of the displacement of the atom H_{II} from the plane SCN_2.

Let us now consider the character of the change in the structure of thiourea at the ferroelectric phase transition.

As is seen from Fig. 2, molecules A and B (as well as the layer as a whole), which are crystallographically equivalent in phase V, lose this equivalence in the low-temperature phase I. The molecules in layer B retain approximately the same position as at high temperature, whereas the molecules of layer A are displaced—their inclination relative to the axes a and b changes. The difference in the inclination of the molecules and in the orientation of the atoms H_{II} in them now does not allow their dipole moments to be compensated in projection on the b axis. It is along this direction that the ferroelectric properties of phase I are observed. The distances H_{II} ...S, which determine the mutual arrangement of layers A and B, in phase V are equal to 2.61 Å, while in the low-temperature phase I $H_{II}^A \ldots S^B = 2.39$ Å and $H_{II}^B \ldots S^A = 2.19$ Å. (The sum of the intermolecular radii of sulfur and hydrogen is 3.0 Å.) As is seen from these distances, the hydrogen bonds NH...S in the low-temperature phase I are considerably stronger than in phase V. The difference between these bonds determines the difference in the inclination and orientation of molecules A and B. The strongest bond is the one of 2.19 Å. As is seen from Fig. 2b, for this bond the condition that the atom S lie on the continuation of the N–H_{II} bond, which is a criterion of a strong hydrogen bond, is best satisfied.

Fig. 3. Variants of the arrangement of nonplanar molecules in different phases of thiourea (projection along the c axis).

Thus, the crystal-chemical mechanism of the ferroelectric properties of phase I of thiourea consists in the nonplanarity of its molecule and in the appearance of strong hydrogen bonds at low temperatures, which give an arrangement of the molecules less symmetrical than in the high-temperature phase V. The presence of a dipole moment of the molecule as such is apparently connected with ionization of the H atoms, the external manifestation of which is also the formation of hydrogen bonds (16).

Irrespective of the data of our investigation presented above, comparison of the structures of phases I and V, as well as the abundance of phase transitions, also leads to the supposition that the molecule is nonplanar. Indeed, how else can one explain the crystallographic inequivalence of molecules A and B of phase I, the structure of which is almost identical with the more symmetrical structure of phase V, where the molecules are crystallographically equivalent?

In conclusion, let us dwell on possible variants of the structure of phases II, III, IV of thiourea. If one proceeds from the fact that the molecules are nonplanar, then three variants of their mutual arrangement in neighboring layers are possible, shown in Fig. 3 as "back to back," "face to face," and "face to back." Electron-diffraction data for phase V testify in favor of variant 1; on the other hand, intense thermal motion in the direction of the *b* axis may be a slight "admixture" to it of state 2. In the low-temperature phase I, variant $3(3')$ is realized. In phase IV,

different from V, but also antiferroelectric, variant 2 is possible, or else a superstructure made up of pairs of types 3 and $3'$. In the latter case the layering will lead to compensation of the dipole moments of the molecules in projection onto the direction [010] and must be accompanied by at least a doubling of the period *c*. With respect to phase II, the same assumptions are possible as with respect to IV. In the ferroelectric phase III, a structure of type I is conceivable, or else a superstructure made up of 3 and $3'$, but without compensation of the dipole moments.

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Received
24 IV 1961

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