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Proton Resonance in Single Crystals of Thiourea

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Résumé.

Nous avons enregistré les spectres de résonance des protons dans des monocrystaux de thiourée à la température ordinaire pour diverses orientations autour des axes $[a]$ et $[b]$. Les spectres s'interprètent en admettant que la molécule de thiourée (plane ou presque plane) subit une rotation générée autour de la liaison carbone-soufre.

Cette réorientation a pour effet de transformer la molécule en son image optique, le plan du miroir étant perpendiculaire à l'axe $[b]$ et contenant l'axe de rotation C-S.

The proton magnetic resonance spectrum of polycrystalline thiourea shows a line-width transition between 220° and 260° K during which the second moment of the spectrum is reduced from 18.9 to 9.8 gauss² [1]. The magnitude of this change is of interest with respect to the possibility of reorientation of the NH₂ group about the C-N bond in amides [2]. By the term reorientation, we refer either to hindered rotation or tunnelling between at least two potential minima for a complete rotation about the C-N bond (apart from the improbable case of free rotation). If the potential function had at least three minima, such motion would reduce the second moment of the powder by a factor of about $\frac{1}{4}$ ($3 \cos^2 \gamma_{jk} - 1$)² in which γ_{jk} is the angle that the interproton vector jk makes with the axis of reorientation, and we neglect the small effects of the slightly different reduction factors for the intermolecular contributions; in the simplified case when γ_{jk} equals 90° for all vectors, the second moment reduction factor is close to $\frac{1}{4}$. A factor of this order would be expected in thiourea for this form of motion of the NH₂ groups since the axis of reorientation is at 90° to the shortest interproton vector; in fact, we observe a factor of about $\frac{1}{2}$, which suggests that the transition cannot be explained in this way. These

measurements have been extended recently to single crystals of thiourea and we discuss in this article our present conclusions about the nature of the nuclear resonance transition.

Two crystals, each weighing about one gram, were used [3] and the proton resonance spectra were recorded with a twin-T *rf* bridge apparatus described previously [4]. One crystal was mounted with the *a*-axis perpendicular to the applied magnetic field H_0 and spectra were obtained at various values of the azimuthal angle Φ with respect to [b]. The second was mounted about the *b*-axis and studied at various values of the azimuthal angle with respect to [a]. Measurements were made at 180° and 298° K, that is below and above the principal nuclear resonance transition. Figures 1 and 2 show the results obtained at 298° (open circles) for the second moment over a range of 90° of the azimuthal angle Φ .

Crystalline thiourea at room temperature is orthorhombic, space group *Pnma* (No. 62) with $a = 7.68$, $b = 8.57$, and $c = 5.50$ Å. The X-ray structure analysis [5] has shown that the four heavy atoms lie in a plane which is inclined at $26^\circ 36'$ to (100). Since the hydrogen atoms were undetected by the X-ray analysis, we have had to assume a model based on a preliminary analysis of the results obtained at 180° K. In this model, the hydrogen nuclei lie in the plane of the heavy atoms such that the N-H distance is 1.06 Å, the HNH angle 119° , and their relative configuration conforms to the symmetry of the space group *Pnma*. A projection of this structure down the *a*-axis is shown in Fig. 3. These values are uncorrected for the effects of molecular vibrations and torsional oscillations [6], but they are used here principally to elucidate the mechanism of the transition.

It can now be shown that the single crystal data are not explained by a mechanism which involves reorientation of the NH_2 groups about the C-N bond. Firstly we consider the effect of rotation about an *n*-fold potential barrier for which $n \geq 3$; the Van Vleck equation [7] for the averaged second moment then contains terms which are proportional to

$$(3 \cos^2 \theta'_{12} - 1)^2 (3 \cos^2 \gamma_{12} - 1)^2 r_{12}^{-6}$$

for the vector $\text{H}_1 \text{H}_2$, in which θ'_{12} is the angle between the C-NH₁ H₂ bond and H_0 and γ_{12} is the angle between the interproton vector r_{12} and the C-N bond. There are similar terms for H₃ H₄ and the N-H vectors, but

we assume that the averaged values of the $H_2 H_3$ and $H_1 H_4$ terms can be neglected for the purposes of this discussion. The curves labelled A in Figs. 1 and 2 illustrate the result of applying these equations to thiourea.

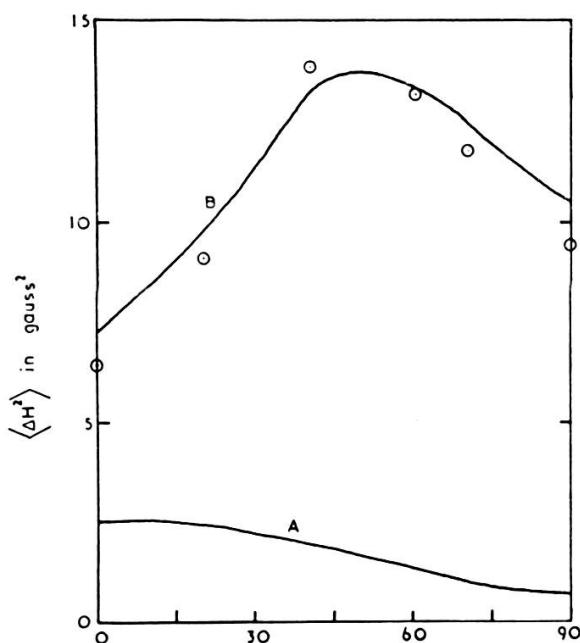


Fig. 1.
Variation of the second moment with Φ about the *a*-axis.

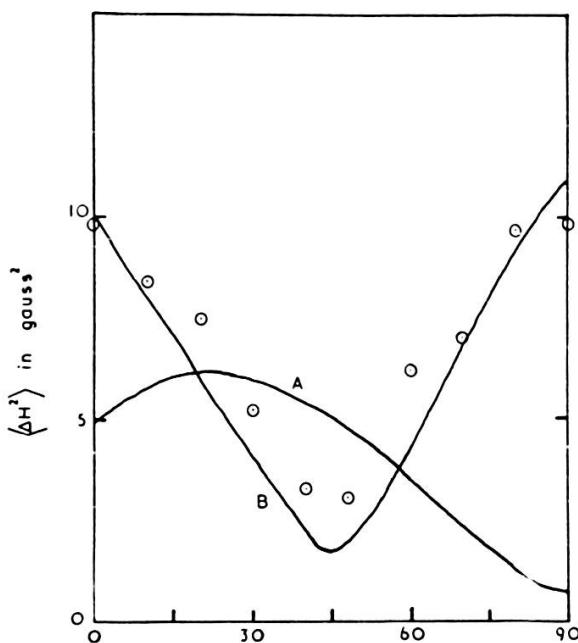


Fig. 2.
Variation of the second moment with Φ about the *b*-axis.

The summations were carried out only for those protons within the two independently oriented molecules in the unit cell, so that the intermolecular terms are missing. They are small and their inclusion would raise the curve as a whole by about 1 to 2 gauss², which would not alter the poor agreement with the experimental data. We conclude that this type of motion will not explain the transition.

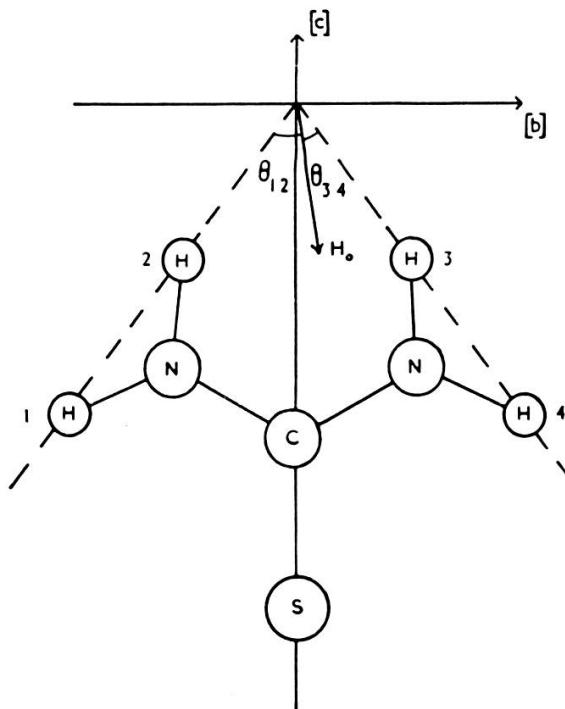


Fig. 3.

Projection of the thiourea molecule on (100);
the origin has been arbitrarily chosen.

It was observed that the line widths and second moments changed only slightly on passing through the transition when H_0 was along the a -, b -, or c -axes. For example, with H_0 parallel to $[b]$, the second moment is 14 gauss² at 180° and 10 at 298° K. At this orientation, the values of $(3 \cos^2 \theta_{12} - 1) = (3 \cos^2 \theta_{34} - 1)$ (in which θ_{12} is the angle between the interproton vector r_{12} and H_0) are nearly zero and the second moment is almost entirely due to the H_2 H_3 interaction. At 180° its magnitude is strong evidence for a planar or near-planar structure.

These observations can be explained if the transition is attributed predominantly to hindered rotation about the C-S bond; the molecule flips between the two planar or nearplanar configurations related by the mirror plane perpendicular to $[b]$. This plane is at right angles to that of Fig. 3

and is indicated by the continuous line passing through the carbon and sulphur atoms. The observed second moment at any orientation is now the average of two values, that of a molecule in the position shown in Fig. 3 and of a second configuration in which H_2 moves to H_3 and H_1 to H_4 ; the second moment of the $H_1 H_2$ term is now proportional to

$$\left[\frac{1}{2} (3 \cos^2 \theta_{12} - 1) + \frac{1}{2} (3 \cos^2 \theta_{34} - 1) \right]^2 r_{12}^{-6}$$

with similar expressions for the $H_1 H_3$, $H_2 H_4$, and the N-H terms, the $H_1 H_4$ and $H_2 H_3$ terms being unchanged. The curves labelled B in Figs. 1 and 2 show the results of applying this type of equation to all the intramolecular terms; a good fit to the experimental results (open circles) is found. This analysis does not exclude the possibility that the spectra might also be affected by hindered rotation of the NH_2 groups over a two-fold potential barrier about the C-N bond, in addition to the motion about the C-S bond. There would be a different reduction factor for the $H_2 H_3$ term according to whether the two NH_2 groups in the same molecule moved singly or together, but these calculations are not yet completed. When H_0 is parallel to $[a]$ or $[c]$, $\theta_{12} = \theta_{34}$ etc. and the intramolecular second moment should have almost the same value above the line-width transition as it has below, as is found experimentally. The intermolecular interactions are reduced by the motion, probably to less than 1 gauss², but accurate values have not yet been calculated.

With these qualifications, the results show that the proton resonance transition in thiourea is produced largely by hindered rotation of the molecule about the C-S bond between two planar or near-planar configurations.

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