Nuclear Magnetic Resonance Experiment of Diacetylhydrazine

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The X-ray difference electron-density contour map (D-map) of anhydrous diacetylhydrazine clearly shows peaks to be ascribed to hydrogen atoms of methyl groups as well as of amide groups[1]. This led us to the study of the proton nuclear magnetic resonance of this crystal in order to examine if the methyl groups really rest in the most stable potential minima or they are reoriented among equivalent positions.

Diacetylhydrazine was purified by repeated fractional sublimation in high vacuum, and powdered specimen was sealed in a thin glass tube in vacuo at above the dehydration temperature 82°C to assure the formation of no hydrate crystals.

The magnetic resonance was recorded with the equipment already reported elsewhere[2]. The results are given in the figures. The second moments (see Fig. 1) of the absorption at room temperature and down to $-180°C$ are nearly constant in rough agreement with the theoretical value based on a rotating methyl group (about its three-fold symmetry axis). At liquid nitrogen temperature the second moment approaches to that corresponding to the rigid-lattice value. Therefore, the hydrogen peaks in the D-map[1] must correspond to reorienting methyl groups. It is inferred that there would be rather severe requirements to be satisfied in order for such peaks to appear in the D-map. The fact that the C–C_{Me} bond length is very short (1.48 Å) for a normal single bond may possibly be responsible for that effect.

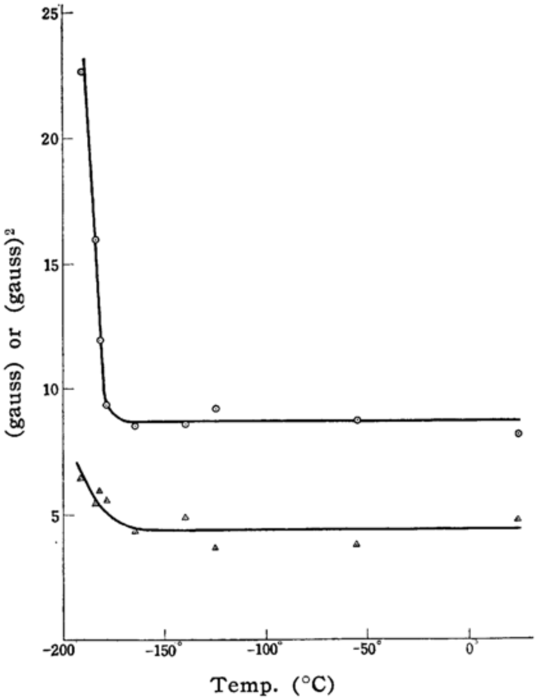

Fig. 1. The second moment and the line-width of proton nuclear reasonance absorption of diacetylhydrazine crystals.
⊙ Second moment in gauss^2
△ Width in gauss

The measurements of the spin-lattice relaxation time T_1 were then made with a hope of obtaining the barrier height hindering the internal rotation of the

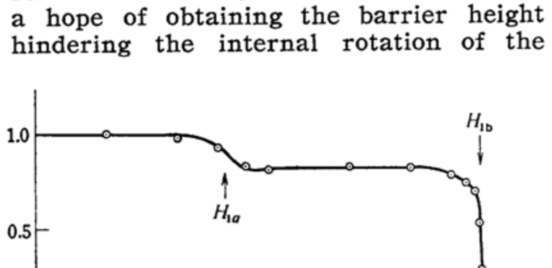

Fig. 2. A typical saturation curve at $-110°C$. The ordinate is in an arbitrary scale.

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[1] R. Shintani and I. Nitta, read before the 4th International Congress of Crystallography, July 1957 (Montreal, Canada).

[2] T. Yukitoshi, H. Suga, S. Seki and J. Itoh, *J. Phys. Soc. Japan*, **12**, 506 (1957).

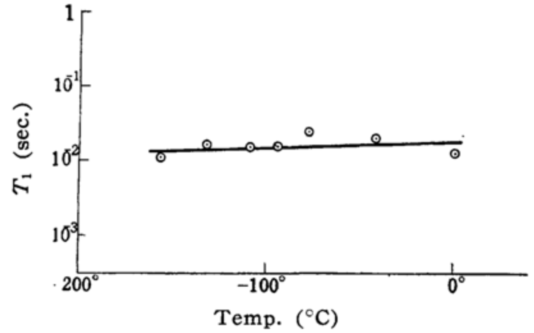

Fig. 3. The temperature dependence of the spin-lattice relaxation time T_1.

methyl groups. One of saturation curves is reproduced in Fig. 2, which has two horizontal portions with two knees at H_{1a} and H_{1b} followed by a monotonous decline. The first knee at H_{1a} was not so distinct at some other temperatures as the one reproduced here, owing to poor signal-to-noise ratio. The temperature dependence of T_1 in Fig. 3, obtained by correlating the oscillator output with the strength of the high-frequency field through calculation based on the coil dimensions and by using the portion of saturation curve at higher field than H_{1a} as the reference, was rather unusual in that T_1 (of the order of magnitude 2×10^{-2} sec.) was almost independent of the change in temperature. Although the magnitude of the T_1 values may be considered as reasonable for this type of crystal, it seems that the invariance of T_1 can hardly be accounted for by reorientation of methyl groups as dominating mechanism of nuclear relaxation. A trial of detecting possibly-present paramagnetic ingredients in the specimen by the electron-spin resonance was not successful[3]. Paramagnetic species does not exist, if any, in a greater concentration than 10^{-5} in mole fraction. Incidentally, it was found that the absorption line-width, measured by the separation between points of maximum positive and negative slope, also depends on the strength of the high-frequency field as is shown in Fig. 4. This type of experiment was conducted only at −183°C, but its precision was much greater than the measurements of the saturation curves. The absorption narrowed at an oscillator output coinciding approximately with H_{1a}. This means that the component of absorption having larger width is more readily saturated.

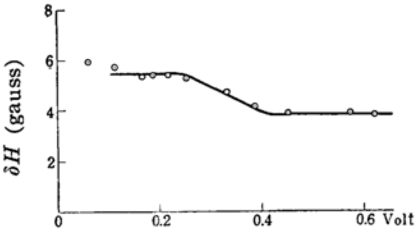

Fig. 4. Change of line-width with the strength of high-frequency field at −183°C.

An explanation was seeked which can account for the entire observation with consistency, but the present data seem to be insufficient to permit it. The role of the amide hydrogen atoms is not quite evident and substitution of deuterium for the hydrogen will provide us with further information. Inasmuch as we have no further attempt to attack this problem, satisfactory elucidation of the mechanism of the nuclear resonance in this crystal will be deferred until more data are accumulated as to the behavior of analogous substances.

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[3] The authors are grateful to Mr. K. Morigaki of Department of Physics, Osaka University for examination of the electron spin resonance of diacetylhydrazine.