High-resolution NMR Spectra of Crystalline Cyclohexanol

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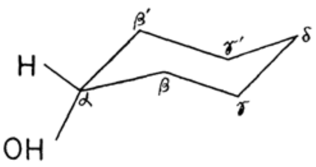
Usually, broad line NMR spectral study gives some important informations on the nature of molecular motion in the crystalline state by observing so-called motional narrowing. On the other hand, high-resolution NMR spectrometer has been generally applied to the study of chemical shift only when the samples are in their liquid or solution states.

We have been studying for a long time the behavior of molecular motion in the plastic crystals(1), mainly by use of X-ray and thermal methods(2). This kind of crystals has been known to exhibit self-diffusion phenomenon even at the temperatures considerably below their melting points(3). These things led us to expect strongly that the high-resolution NMR techniques would disclose their usefulness for investigating molecular motion in these crystals in more details and also for observing directly chemical shifts of the protons involved in the constituent molecule. We have chosen cyclohexanol crystal for the study of this purpose and found it was indeed the case.

Measurement were carried out with the Varian Associates Model V-4311 high-resolution NMR spectrometer. Comparison of the entropy of transition(4), $\Delta S_{tr}=7.44$ e. u. ($T_{tr}=263.5$°K), and entropy of fusion(4), $\Delta S_f=1.37$ e. u. ($T_f=297.0$°K) of the present material with the entropies of fusion of rare gases, such as argon: $\Delta S_f=3.4$ e. u.(5) and krypton: $\Delta S_f=3.38$ e. u.(6) and also broad line NMR study by Averbuch(7) below the transition point suggest strongly the possibility of occurrence of the self-diffusion above the transition point.



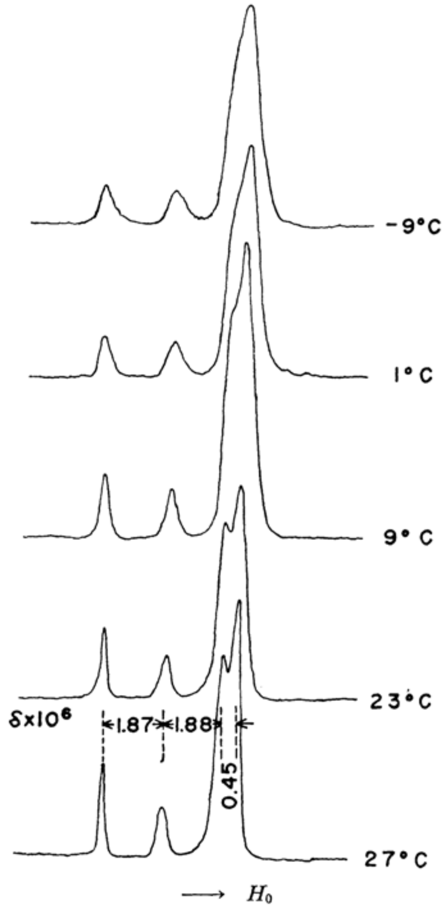


Fig. 1. Temperature variation of high-resolution NMR spectra of cyclohexanol.

As we have expected, the line width is sufficiently narrow to give well-separated peaks originated from different protons even just above the transition point. The area under the peaks stand roughly in the ratio 1 : 1 : 10, as would be expected if each peak in the order of increasing field corresponded to the chemically different OH, H_α and the other ring protons (see figure). As the temperature rises and the line width of each peak narrows by the self-diffusion process, the main peak gives a further splitting in the approximate intensity ratio 2 : 3. These two peaks may not be due to chemical shifts between the axial and the equatorial ring protons, since there are equal number of protons in each species, and rather may be interpreted as the chemical shift between H_β (or $H_{\beta'}$) and H_γ (or $H_{\gamma'}$) plus H_δ. The rate at which the change from one conformation to the other of the cyclohexanol isomers will be faster(8) than the inverse of the chemical shift

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1) J. Timmermans, *J. Phys. Chem. Solids*, **18**, 1 (1961).
2) I. Nitta, *Z. Krist.*, **112**, 234 (1959).
3) E. R. Andrew "Nuclear Magnetic Resonance", Cambridge Univ. Press, New York (1955); T. Yukitoshi, H. Suga, S. Seki and J. Itoh, *J. Phys. Soc. Japan*, **12**, 506 (1957).
4) K. K. Kelley, *J. Am. Chem. Soc.*, **51**, 1400 (1929).
5) P. Flubacher, A. J. Leadbetter and J. A. Morrison, *Proc. Phys. Soc. (London)*, **78**, 1449 (1961).
6) R. H. Beaumont, H. Chihara and J. A. Morrison, ibid., **78**, 1462 (1961).
7) P. Averbuch, *C. R. Acad. Sci. Paris*, **2**, 3147 (1957).
8) L. Reinisch, *Compt. rend.*, **243**, 1032 (1956).

difference between the axial and the equatorial protons attached to the same carbon atom. There is no discernible change in the line width at the melting point.

In conclusion, it was revealed that the high-resolution NMR spectrometers were also useful for investigating the molecular motions and also for detecting the chemical shifts in the plastic crystals. Similar results were also obtained for crystalline trimethylacetic acid⁽⁹⁾. A full discussion will be published elsewhere in near future.

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9) H. Suga and S. Seki, *J. Phys. Chem. Solid.*, to be published.