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Rotational Isomers in Two Crystalline Phases of *N*-Methylchloroacetamide

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In a previous investigation by Mizushima *et al.*¹⁾ the internal rotation about the $\text{CH}_2\text{-CO}$

bond was studied for *N*-methylchloroacetamide, $\text{ClCH}_2\text{-CONHCH}_3$, a model molecule of polypeptide chains. The infrared and Raman spectra and dipole moments were measured and the *trans* and *gauche* isomers (see Fig. 1 of Ref. 1) were found to coexist in the liquid phase.

1) S. Mizushima, T. Shimanouchi, I. Ichishima, T. Miyazawa, I. Nakagawa and T. Araki, *J. Am. Chem. Soc.*, **78**, 2038 (1956).

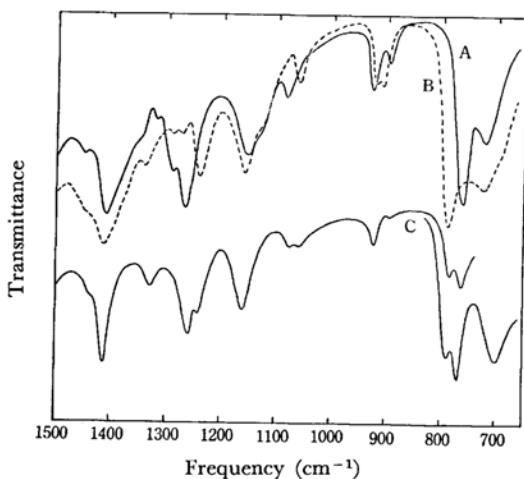


Fig. 1. Infrared spectra of solid films (at 20°C), (A) slowly cooled from the melt, (B) rapidly cooled from the melt, and liquid film (C) at 60°C. A Baird Infrared Spectrophotometer was used for absorption measurements.

In the present infrared study, however, two different spectra were obtained, one (A) for the solid film slowly cooled from the melt and the other one (B) for the solid film rapidly cooled from

the melt (C). As seen in Fig. 1, these solid films A and B exhibit the infrared bands of the *gauche* (763 cm^{-1}) and *trans* isomer (786 cm^{-1}), respectively, of *N*-methylchloroacetamide. Apparently, the solid film A (with the *gauche* isomer) is stable at room temperature, while the solid film B (with the *trans* isomer) is metastable after being quenched.

The temperature effect on the infrared absorption of *N*-methylchloroacetamide was carefully observed; a narrow spectral region 950–870 cm^{-1} was repeatedly scanned while the sample temperature was lowered from 65°C down to 9°C in 75 min and subsequently was raised back to 63°C in 65 min. Reversible spectral changes $(C) \rightleftharpoons (B) \rightleftharpoons (A)$ were observed and the transition point was found at about 38°C between the high-temperature phase (with the *trans* isomer) and the low-temperature phase (with the *gauche* isomer). Thus, *N*-methylchloroacetamide exhibits a new type of phase transition that is accompanied with the internal-rotation transition (*trans* \leftrightarrow *gauche*) of constituent molecules. The presence of the *gauche* molecules in the low-temperature phase was recently confirmed by an X-ray analysis of the crystal structure.²⁾

2) Y. Koyama, T. Shimanouchi and Y. Iitaka, Preprints for the 22nd Annual Meeting of the Chemical Society of Japan (Tokyo, April, 1969), 01602.