CHEMISTRY LETTERS, pp. 1411-1412, 1979.

RAMAN AND INFRARED SPECTROSCOPIC STUDIES ON CONFORMATIONAL POLYMORPHISM OF N-PROPYL ACETATE

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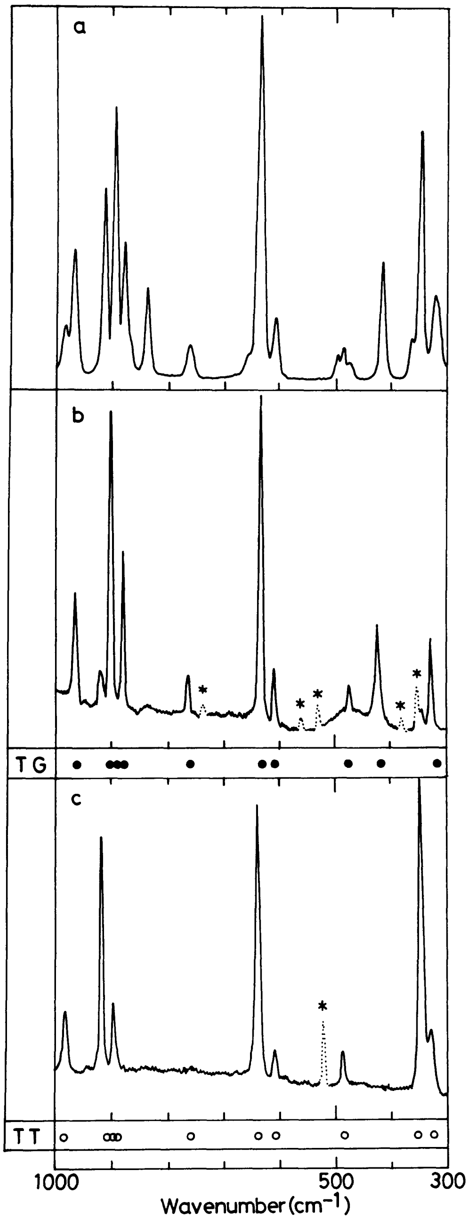
The Raman and infrared spectra of n-propyl acetate were observed at low temperatures and the results were analysed on the basis of normal-coordinate calculations. In two crystal modifications the molecules assume different conformations, namely, the *trans-gauche* form with respect to the two axes $CH_3(CO)O-CH_2-CH_2CH_3$ in Crystal I and the *trans-trans* form in Crystal II.

In a previous letter[1)] we reported on the conformational polymorphism of 1-bromopentane. A similar phenomenon has been found to occur for n-propyl acetate and will be described here.

The Raman spectra were recorded on a JEOL JRS-400D spectrometer with a Coherent Radiation CR-3 argon-ion laser (488.0- or 514.5-nm line, about 200 mW at the sample point). The infrared spectra were recorded on a Hitachi EPI-G2 and EPI-L spectrophotometers. Normal-coordinate calculations were performed using the program NCTB[2)] and a HITAC 8800/8700 system at the Computer Centre of the University of Tokyo. The force constants used were determined by treating not only n-propyl acetate but also other esters. The numerical values of force constants will be published elsewhere.

Transparent glassy samples obtained by rapid cooling or by depositing on the cooled KRS-5 plate transformed into white crystalline solids (Crystal I) when the temperature was raised to about 133 K. Crystal I is so unstable that its spectrum could not be obtained unless it was cooled down to the liquid-nitrogen temperature immediately after the crystallization. When Crystal I was warmed, the transformation from Crystal I to another form (Crystal II) occurred and the sample consisted completely of Crystal II at about 160 K. The Raman spectra of the glassy and two crystalline states in the region of 1000-300 cm^{-1} are shown in Fig. 1 and the corresponding infrared spectra in Fig. 2. The transformation from Crystal I to II could be easily followed by observing either the Raman or infrared bands in the region below 500 cm^{-1} arising from skeletal deformation vibrations. The inverse transformation from Crystal II to I did not occur when the temperature was again lowered to the liquid-nitrogen temperature. Crystal II showed no spectral change until it melted at about 178 K.

As is obviously seen in Figs. 1 and 2 the spectra of Crystal I and II are greatly different from each other, indicating that the molecules in the two crystal modifications have different conformations. Since no empirical rule is established for esters as to the relationship between conformations and spectra, normal-coordinate



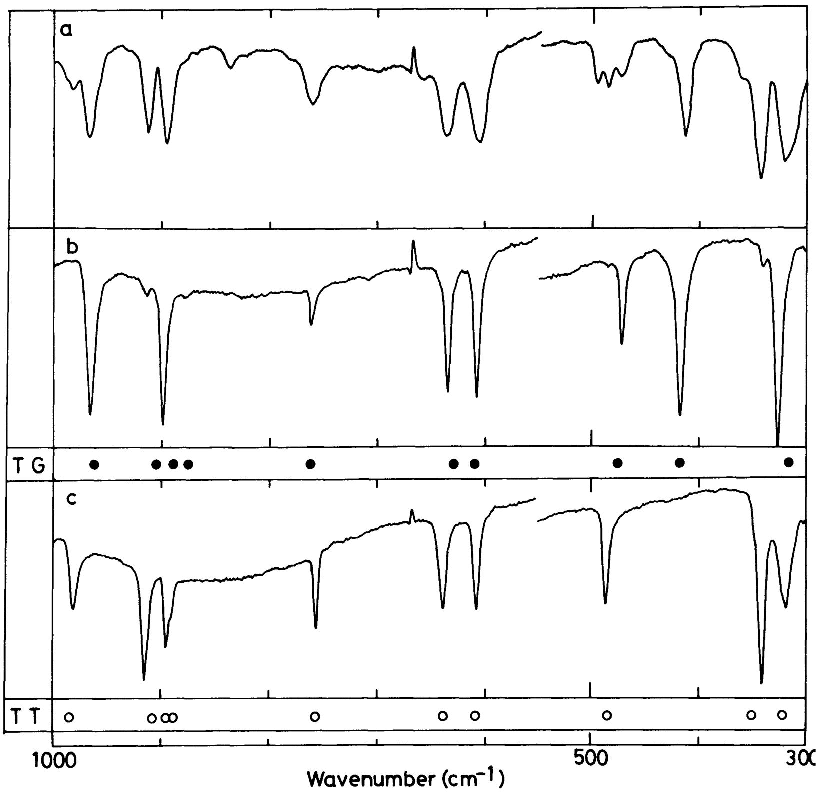


Fig. 1. (left) Observed Raman spectra and calculated frequencies (circles).
a, Glass; b, Crystal I; c, Crystal II. The peaks with * are due to the emission lines of Ar-ion laser.

Fig. 2. (right) Observed infrared spectra and calculated frequencies (circles).
a, Glass; b, Crystal I; c, Crystal II.

calculations for various model conformations were necessary in order to identify the conformations present in Crystals I and II. The calculated frequencies are given with the filled and open circles in Figs. 1 and 2. From the compariosn of the observed data and the calculated frequencies the conformation in Crystal I can be identified as the *trans-gauche* (TG) form with respect to the two axes $CH_3(CO)O-CH_2-CH_2CH_3$ and that in Crystal II as the *trans-trans* (TT) form. In the spectrum of the glassy state most bands correspond to the bands of either Crystal I or II. However, there are also a few weaker bands which suggest the presence of some conformations other than the TG and TT forms. The detailed assignments of all the observed bands will be reported in a separate paper.

References

1) Y. Ogawa and M. Tasumi, Chem. Lett., 947(1978).
2) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, J. Phys. Chem. Ref. Data 7, 1323(1978).

(Received September 14, 1979)