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RAMAN SPECTROSCOPIC STUDIES ON CONFORMATIONAL POLYMORPHISM OF 1-BROMOPENTANE

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Two crystal modifications of 1-bromopentane gave entirely different Raman spectra,which undoubtedly indicated simultaneous occurrence of a crystal transformation and a conformational change of molecules in the crystal. The molecular conformation is *trans-trans-trans* (TTT) in one crystal modification (Crystal I) and *trans-trans-gauche* (TTG) in the other (Crystal II). The polymorphism of 1-iodopentane, which presents a contrast to the case of 1-bromopentane, is also described.

Recently increasing interest is directed toward the study of a special case of polymorphism where molecules adopt significantly different conformations in various crystal modifications[1-5]. 'Conformational' polymorphism is a relatively new term to specify this kind of polymorphism. In this letter we wish to show the usefulness and sensitivity of Raman spectroscopy for studying the conformational dimorphism of 1-bromopentane, and the results are compared with the case of 1-iodopentane which shows 'simple' polymorphism.

1-Bromopentane and 1-iodopentane purchased from Tokyo Kasei Kogyo Co., Ltd. were distilled prior to Raman measurements. The Raman spectra were recorded on a JEOL JRS-400D spectrometer with a Coherent Radiation CR-3 argon ion laser (488.0 nm line, *ca.* 200 mW at the sample point). A glassy state was obtained by immersing the liquid sample contained in an ampoule into liquid nitrogen. Crystalline states were obtained by either annealing the glassy state or cooling the liquid sample slowly with liquid nitrogen. A thermocouple in contact with the ampoule was used for temperature measurements. All spectra were observed at the liquid-nitrogen temperature.

Normal frequencies were calculated with a computer program NCTB2[6] using a HITAC 8800/8700 system at the Computer Centre of the University of Tokyo. The force constants reported in Ref. 7 were used without change.

The dimorphism of 1-bromopentane was first found by Skau and McCullough[8] and was confirmed in the present study. Transparent glass obtained by the rapid cooling transformed into a white crystalline solid (Crystal I) when the temperature was raised to about -140°C. By elevating the temperature further the transition from Crystal I to the other crystalline state (Crystal II) occurred at about -115°C. The Raman spectra of the glassy and two crystalline states are shown in Fig. 1. The transition from Crystal I to II could be easily monitored by measuring the Raman spectrum in the CBr stretching region (700-500 $\mathrm{cm^{-1}}$). The inverse transition from Crystal II to I did not take place when Crystal II was again cooled to the liquid-nitrogen temperature. Crystal II showed no spectral change until it melted at -90°C. The liquid

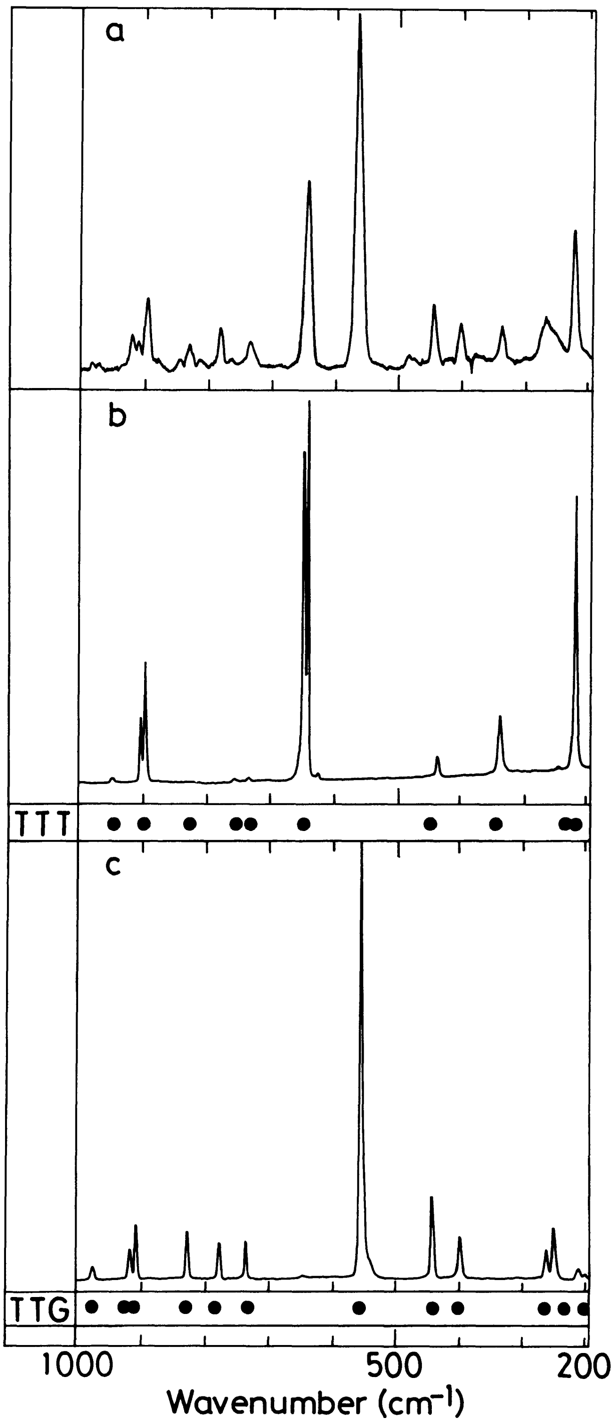

Fig. 1. Observed Raman spectra and calculated frequencies (dots) of 1-bromopentane in the region 1000-190 cm^{-1}.

a: Glass.
b: Crystal I.
c: Crystal II.

sample could be solidified into Crystal I by slow cooling.

It is well known that the carbon-halogen (CX) stretching frequency is a sensitive probe of the conformation about the CC single bond adjacent to CX[9]. The CX stretching frequency of the *trans* conformation is usually higher than that of the *gauche* conformation. In Fig. 1 the CBr stretching band is observed at about 650 cm^{-1} for Crystal I[10] and at 560 cm^{-1} for Crystal II. Therefore, the conformation about the CH_2CH_2-CH_2Br axis is *trans* in Crystal I, whereas it is *gauche* in Crystal II. For the other two axes, namely CH_3CH_2-CH_2CH_2 and CH_2CH_2-CH_2CH_2, there are no such empirical rules for discerning their conformations. To clarify this point normal coordinate treatments were carried out for various conformations. From the comparison of the calculated and observed frequencies it is easy to find that the conformation of $CH_3CH_2CH_2CH_2CH_2Br$ is *trans-trans-trans* (TTT) in Crystal I and *trans-trans-gauche* (TTG) in Crystal II (See Fig. 1). The glassy state mainly consists of these two conformers, but the presence of some weak bands not assignable to either of these two indicates the coexistense of other conformers.

By means of thermal and dielectric measurements several studies have been made on the dimorphism of 1-bromopentane [8,11-15]. These studies have established the presence of two crystalline modifications (an 'unstable' and a 'stable' forms melting at -94.6 and -87.9°C, respectively) and the monotropic exothermic transition from the unstable to the stable form occurring at -115°C in a heating process. These findings are consistent with the results of our study, and the unstable and stable forms correspond, respectively, to our Crystal I and II. The advantage of Raman spectroscopy over thermal and dielectric measurements lies in its power of elucidating the molecular conformation in each crystal form.

It is natural to ask what happens to similar halides, 1-chloropentane and 1-iodopentane in particular. As far as we know, there is no literature dealing with the polymorphism of these compounds. Only one crystalline state was found for 1-chloropentane by means of Raman spectroscopy. The molecular conformation of 1-chloropentane is TTT in the crystal$^{16)}$. By contrast, 1-iodopentane was found to have three crystal modifications, namely, Crystal A, B, and C. A glassy solid obtained by rapid cooling with liquid nitrogen transformed into Crystal A at about -170°C or sometimes into Crystal B at about -140°C. The former transformed into the latter at a temperature between -130 - -120°C. Crystal C was obtained directly when the liquid sample was slowly cooled. In Fig. 2 are shown the Raman spectra of these three crystal forms. These spectra show little difference in the region above 180 cm^{-1}, indicating clearly that the molecular conformation is invariably the same in all the crystal forms. This presents a striking contrast to the case of 1-bromopentane. The molecular conformation is identified as TTT by normal coordinate treatments. Spectral features in the region below 180 cm^{-1} reflect the differences in intermolecular interactions. Since nothing is known about the crystal structures, it is difficult to analyse the low-frequency Raman bands in detail.

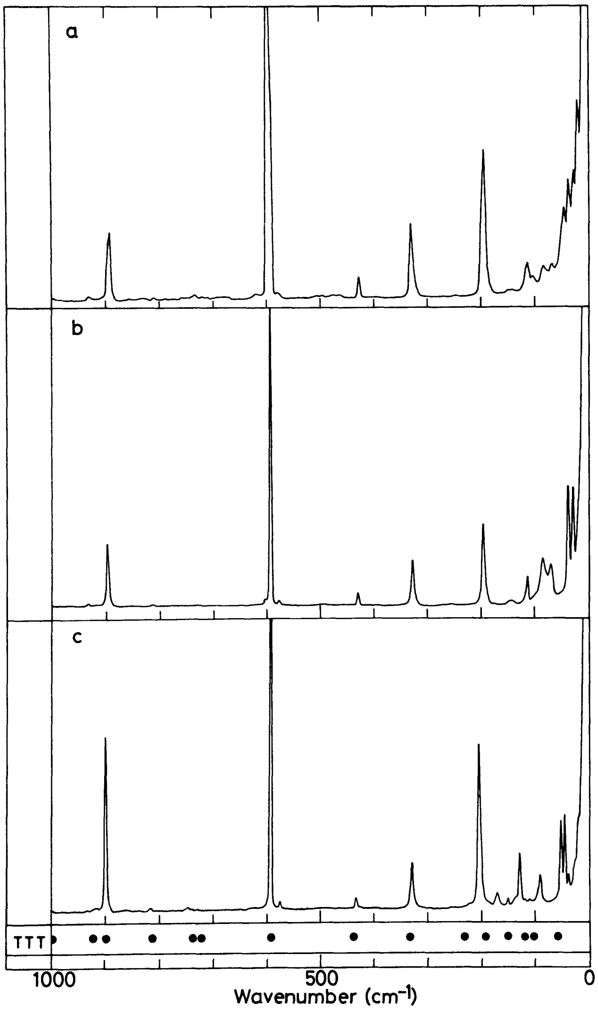

Fig. 2. Observed Raman spectra and calculated frequencies (dots) of 1-iodopentane in the region below 1000 cm^{-1}.

a: Crystal A.
b: Crystal B.
c: Crystal C.

In the present study Raman spectroscopy was shown to provide useful information on crystal polymorphism and molecular conformations in various crystal modifications. Studies on longer 1-halogenoalkanes are now in progress to clarify the conformational polymorphism of this class of compounds.

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