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## Even-odd alternation of near-infrared spectra of alkane- $\alpha,\omega$ -diols in their solid states

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### ABSTRACT

Even-odd alternation of the melting points of  $\alpha,\omega$ -disubstituted linear alkanes such as alkane- $\alpha,\omega$ -diols, alkane- $\alpha,\omega$ -dinitriles and  $\alpha,\omega$ -diaminoalkanes is well known. Melting points for compounds with an even number of carbons in their alkyl chains are systematically higher than those for compounds with an odd number of carbons. In order to clarify the origin of this alternation, near-infrared absorption spectra of linear alkane- $\alpha,\omega$ -diols with 3 to 9 carbon atoms in their alkyl chains were measured in the liquid and solid states. The band due to the first overtone of the O—H stretching mode was investigated. The temperature-dependent spectra of all alkane- $\alpha,\omega$ -diols in their liquid states were found to be similar; no even-odd alternation was observed. In the solid state, however, spectra of alkane- $\alpha,\omega$ -diols with even and odd numbers of carbon atoms differed greatly. Spectra of alkane- $\alpha,\omega$ -diols with an odd number of carbon atoms in their solid states were similar to those in the liquid states, although the variation of spectra observed upon lowering the temperature of liquid seemed to continue when the liquids were frozen. In contrast, spectra of alkane- $\alpha,\omega$ -diols with an even number of carbon atoms in their liquid and solid states were found to be quite different. New bands appeared upon freezing. The observed even-odd alternation of the spectra observed for alkane- $\alpha,\omega$ -diols in their solid states is presumably caused by their even-odd alternation of crystal structures.

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### 1. Introduction

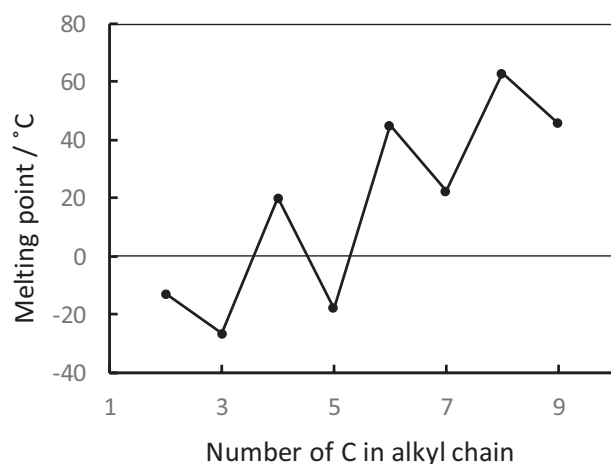
Even-odd alternations for melting points have been observed for linear alkane [1] and  $\alpha,\omega$ -disubstituted linear alkanes such as alkane- $\alpha,\omega$ -dicarboxylic acids [2,3], alkane- $\alpha,\omega$ -dithiols [4], alkane- $\alpha,\omega$ -diols [5–7], alkane- $\alpha,\omega$ -dinitriles [8], alkane- $\alpha,\omega$ -diamines [6,9], and alkane- $\alpha,\omega$ -diamides [10]. Here, “ $\alpha,\omega$ ” denotes the substituent groups at both ends of the linear alkyl chain. For each homologous series of compounds, the melting points of compounds with an even number of carbons in the alkyl chains are higher than those having an odd number of carbons, although the overall melting points for each homologous series rise as the carbon number increases. As an example, the melting points of alkane- $\alpha,\omega$ -diols are shown in Fig. 1, where the even-odd alternation for the melting points is clearly seen. Similar even-odd alternations are observed for the enthalpies and entropies of fusions and the temperatures of solid-to-solid phase transitions of these homologous series. However, since no alternation is observed for the boiling points of

these homologous series, the solid states are considered to be responsible for the variation. Crystal structures of the compounds with an even number of carbons differ from those with an odd number of carbons, as reported for alkanes [1] and alkane- $\alpha,\omega$ -diols [6,7]. The alternations for the melting points have been discussed in relation to the crystal structures, packing conditions in the crystals, and densities. The cause of the alternations, however, has not yet been clearly elucidated.

Observation of vibrational spectra of the crystals in addition to the analyses of crystal structures are expected to help in the elucidation of the alternation, although very few reports on the vibrational spectra of the compounds in solid states are found in the literature. In this study, near-infrared spectra of alkane- $\alpha,\omega$ -diols with 3 to 9 carbon atoms in the alkyl chains were collected in the solid state. Near-infrared spectroscopy, where overtones and combination tones of molecular vibrations are observed, is an appropriate technique to obtain vibrational spectra of solid materials because the absorption of near-infrared light by materials is much weaker than that of infrared light. Moreover, near-infrared spectra depend strongly on the condition of hydrogen bonding of the target molecules; precious information of intermolecular interactions of target molecules in the crystal state is thus expected to be obtained

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**Fig. 1.** Variation of the melting point of linear alkane- $\alpha,\omega$ -diols upon the change in the number of carbon atoms in the alkyl chain. The melting points shown in "Fate Pointers Search Module" by SRC, Inc. at <http://esc.syrres.com/fatepointer/search.asp> were employed.

by near-infrared spectroscopy. Here, we report the even-odd alternation of near-infrared spectra observed for alkane- $\alpha,\omega$ -diols.

## 2. Experimental

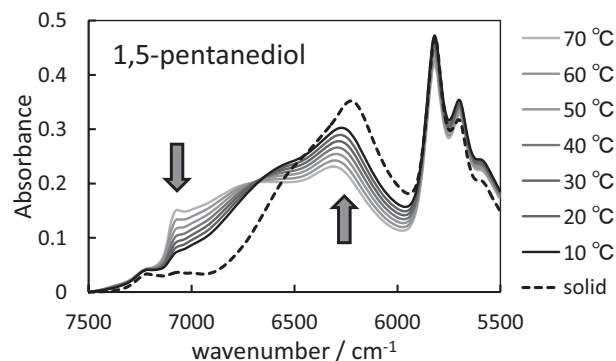
All reagents, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, and 1,9-nonanediol, of reagent grade were purchased from Tokyo Kasei, Co. Ltd., and used without further purification. Near-infrared absorption spectra of the reagents in their liquid and solid states were measured in the transmittance mode with an FT-NIR spectrophotometer (Bruker, MPA), whose resolution and number of accumulations were set at  $8\text{ cm}^{-1}$  and 16, respectively. The OPUS version 6.5.2 software (Bruker) was used for the spectral acquisition. A thermostat (Taitec, CTU-Mini), which is originally an aluminum block bath, was used to stabilize the temperature of the sample. The bath of the thermostat was exchanged with a home-made cell holder, which was set in the sample chamber of the spectrophotometer. A digital thermometer (Custom, CT-450WR) was set at the cell holder near the sample cell made of quartz with the optical path length of 1 mm. The thermostat was adjusted so that the digital thermometer shows the target temperature.

For each compound, the temperature was first set at  $70\text{ }^{\circ}\text{C}$  or  $80\text{ }^{\circ}\text{C}$  and its spectrum in the liquid state was measured. Next, the spectra were measured repeatedly while cooling the sample in  $10\text{ }^{\circ}\text{C}$  decrements until the temperature of the sample reached  $0\text{ }^{\circ}\text{C}$ . Some compounds were frozen before the temperature reached  $0\text{ }^{\circ}\text{C}$ . The compounds that were not frozen at  $0\text{ }^{\circ}\text{C}$  were frozen in a freezer (Sanyo, MDF-U338) at  $-30\text{ }^{\circ}\text{C}$  or in liquid nitrogen. Spectra of the frozen samples were measured quickly after removal from the freezer or liquid nitrogen. The mist on the outside of the cold cell did not affect the spectral measurements.

The measurements were repeated several times (twice to five times) over some days for each compound to check the reproducibility. Although the observed spectrum changed somewhat depending on how to freeze the sample, the change was found to be so small that it does not affect the conclusion shown below.

## 3. Results and Discussion

**Fig. 2** shows near-infrared absorption spectra of 1,5-pentanediol in the liquid state measured at various temperatures and in the solid state. Solid lines correspond to the spectra of liquid 1,5-pentanediol, where the spectra plotted with darker lines were measured at lower temperatures and the dashed line corresponds to the spectrum of the



**Fig. 2.** Near-infrared absorption spectra of 1,5-pentanediol in the liquid state measured at various temperatures (solid lines) and in the solid state (dashed line). The spectra shown with darker lines were measured at lower temperatures.

solid compound. Since the melting point of 1,5-pentanediol is  $-18\text{ }^{\circ}\text{C}$ , which cannot be achieved with our thermostat, solid 1,5-pentanediol was obtained by freezing in liquid nitrogen. An accurate temperature of the sample at the time of measurement, therefore, was not known.

The spectrum of solid 1,5-pentanediol was observed with a high background tilted upwards against the lower wavenumber, which was caused by serious scattering of the measuring light by the solid sample. Therefore, **Fig. 2** shows the spectrum corrected by shifting and tilting such that the absorbance at  $7500\text{ cm}^{-1}$  where no absorption was observed becomes zero and the intensity of the peak around  $5800\text{ cm}^{-1}$  becomes nearly the same as those observed for the sample in the liquid state. The same corrections were performed for the spectra of other compounds observed in the solid state, which are shown later. Since the corrections were performed without a strict quantitative basis, only qualitative variations of spectra upon freezing of the samples are discussed here.

Absorption due to the overtone of the O—H stretching modes was observed in the spectral region of  $7200\text{--}6000\text{ cm}^{-1}$ , while in the region lower than  $6000\text{ cm}^{-1}$  the overtone bands of C—H stretching modes were observed [11]. No remarkable variation was observed for the features of the bands due to the overtones of the CH stretching upon changing the temperature and physical state. On the other hand, the features of the bands due to the overtones of the OH stretching varied greatly. Upon lowering the temperature in the liquid state, the absorbance in the higher wavenumber region decreased, while that in the lower wavenumber region increased, as shown by arrows and line shading in the figure. The absorption in the higher wavenumber region is due to non-hydrogen-bonded or weakly hydrogen-bonded OH groups. The small peak at  $7070\text{ cm}^{-1}$  is presumably assignable to the non-hydrogen-bonded OH. On the other hand, the absorption in the lower wavenumber region is due to strongly hydrogen-bonded OH groups. Therefore, the increase in the number of the hydrogen-bonded OH groups by lowering the temperature was clearly observed. An isosbestic point was observed for the variation of spectra upon changing the temperature in the liquid state. Isosbestic points like that seen here are typically observed for the variations of spectra of water and alcohols in the liquid state upon temperature change.

Upon freezing, the absorbance in the higher wavenumber region of the OH band became very weak. Simultaneously, a slight lowering in shift was observed for the peak in the lower wavenumber region. These variations can be reasonably explained by considering that most OH groups in the solid form strong hydrogen bonds.

**Fig. 3** shows near-infrared absorption spectra of 1,6-hexanediol. Here again, the solid lines are spectra measured in the liquid state at different temperatures, and the dashed line is the spectrum measured in the solid state at  $0\text{ }^{\circ}\text{C}$ . Although the melting point of 1,6-hexanediol is around  $40\text{ }^{\circ}\text{C}$ , a spectrum of supercooled liquid 1,6-hexanediol was obtained at  $30\text{ }^{\circ}\text{C}$ .

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