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PHASE TRANSITION IN *TRANS* AND *CIS*-1,2-CYCLOHEXANEDIOL STUDIED BY INFRARED SPECTROSCOPY

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Abstract

The study of *trans*- and *cis*-1,2-cyclohexanediol by infrared spectroscopy was performed. The variation of the maximum frequency and of the bandwidth of the OH stretching vibration give evidence of the role played by hydrogen bonding in the solid and liquid phases of both isomers and allows to follow the phase transitions. A solid rotator phase is shown for the *cis* compound.

Keywords: cyclohexanediol, infrared spectroscopy, isomerism, phase transitions, solid rotator phase

Introduction

It has been shown previously by differential scanning calorimetry that *trans*-1,2-cyclohexanediol exhibits no phase transition but fusion at 99.2°C, in the temperature range –80 to 120°C, while *cis*-1,2-cyclohexanediol gives rise to a solid transition phase before fusion [1]. Indeed for this isomer the crystalline form at lower temperature (phase II) is transformed into phase I at 87.3°C which in turn melts at 98.5°C. The high entropy observed for phase II – phase I transition and the low value of this function for fusion lead to the conclusion that phase I is a disordered state known as rotator phase, denomination coined for the first time by Müller [2, 3]. As many solids in this state are soft and waxy, that is, some molecular translational motion is observed, they were called by Timmerman plastic crystals [4]. Both denominations are often employed without any distinction.

Many organic compounds, namely cyclic hydrocarbons and their derivatives, show a disordered state preceding fusion. Because the molecules of both cyclohexanediol isomers under study are alike, a different behaviour between them was not expected and, therefore, the knowledge of their structures is indubitably a subsidy for understanding the formation of solid rotator phases.

The crystal structure of these two isomers was studied by X-ray [5, 6] giving evidence for the role played by hydrogen bonding in the crystal engineering of both

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compounds. Since vibrational spectroscopy is a sensitive method for studying hydrogen bonding the application of this technique to the systems under consideration can provide valuable information about the structure of the phases.

The target of this paper is, therefore, to obtain information on the structure of the phases and on phase transitions from temperature-dependent infrared spectra. The OH stretching vibration band of *cis* and *trans* isomers of 1,2-cyclohexanediol, recorded at temperatures between 50 and 120°C, are presented.

Materials and spectroscopic measurements

Trans-(lR,2R)-1,2-cyclohexanediol, *trans*-(lS,2S)-1,2-cyclohexanediol and *cis*-1,2-cyclohexanediol obtained from Aldrich Chemical Co., were used in this study. These substances labelled as »99% pure, were used without any further purification. Handling was carried out under conditions avoiding, as much as possible, moisture contamination from air.

The spectra were performed with FTIR Philips PU 9800 using a cell assembly and a temperature control device supplied by Grasely Specac. In order to avoid condensation especially at low temperature, the cell was connected to a vacuum line. The temperature control inside the cell ±0.05°C. Water vapour and carbon dioxide were purged off the spectrometer by dried air, flowing through an absorption column.

A certain amount of fine powder of the substance to be studied was put into a CaF_2 cell and to obtain a better distribution of the sample a few drops of CCl_4 were added. The temperature of the cell was then raised to 110°C in order to ensure evaporation of the liquid and, via melting, to get a uniform film of the sample. It was proved before, by calorimetric measurements, that phase transition features of the cyclohexanediols are reproducible after several heating and cooling cycles [1]. Thus, fusion can be used in the preparation of the sample, fearless of producing irreversible changes in the properties of the compounds.

In order to evaluate the spectroscopic effects due to intermolecular forces in the condensed state the spectra of cyclohexanediols in an inert solvent were performed. Dilute solutions of CCl_4 (0.004 M) were used as reference. These spectra were recorded using a variable pathway sodium chloride cell.

Results

This study is based on the analysis of OH stretching vibration absorption band. A peak fitting program commercialised by Jandel Scientific Software, Germany, was used for a more accurate determination of important spectral features and for the characterisation of hidden peaks. With this program, fitting of the spectra using Gaussian or Lorentzian line shapes is achieved and the absorption maximum frequency, ν_{max}, the bandwidth at half-height, $\Delta\nu_{1/2}$, and the areas of hidden peaks are obtained.

Table 1 Maximum frequency and half-width of OH-stretching vibration spectra for *cis*- and *trans*-1,2-cyclohexanediol

	Cis-1,2-cyclohexanediol				*Trans*-1,2-cyclohexanediol	
	Lower frequency band		Higher frequency band			
T/°C	ν_{max}/cm^{-1}	$\Delta\nu_{1/2}$/cm^{-1}	ν_{max}/cm–1	$\Delta\nu_{1/2}$/cm^{-1}	ν_{max}/cm–1	$\Delta\nu_{1/2}$/cm^{-1}
50	3276	156	3402	58	–	–
60	3278	155	3404	62	3330	184
70	3280	157	3407	67	3340	186
80	3283	158	3410	70	3343	187
85	3285	158	3412	73	–	–
90	3285	165	3415	86	3345	190
93	3295	173	3420	120	–	–
95	3300	–	3423	190	3350	193
97	3315	–	3425	240	3370	210
100	3412	–	3425	278	–	–
105	–	–	3425	280	3420	252
110	–	–	3425	280	3425	253
120	–	–	–	–	3428	253

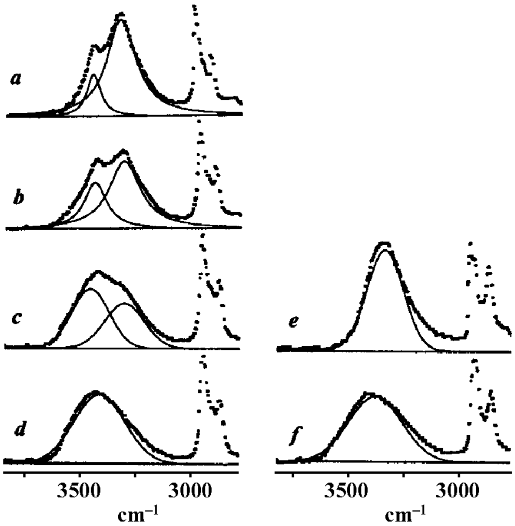

Fig. 1 Typical fundamental OH vibration at different temperatures for *cis*- and *trans*-1,2-cyclohexanediol;
cis-1,2-cyclohexanediol a – T<87.3°C; b – T=93°C; c – T=95°C; d – T>98.5°C;
trans-1,2-cyclohexanediol e – T<99.2°C; f – T>99.2°C

The spectra of the *cis* isomer in the solid state were separated in two Lorentzian bands while the spectra of this compound in liquid state and of the *trans* isomer are better described by a Gaussian function.

In Table l, ν_{max} and $\Delta\nu_{1/2}$ of the peaks for different temperatures are presented. No significant differences were observed between *R* and *S* enantiomers, so no specification is needed throughout the paper. Figure l illustrates typical absorption band patterns for the solid or liquid phases of both isomers. To follow the base line in the frequency range in which we are interested, CH stretching vibrations (2870–2950 cm^{-1}) were included. The spectra for *trans*- and *cis*-1,2-cyclohexanediol in CCl_4 at 298.15 K are shown in Fig. 2.

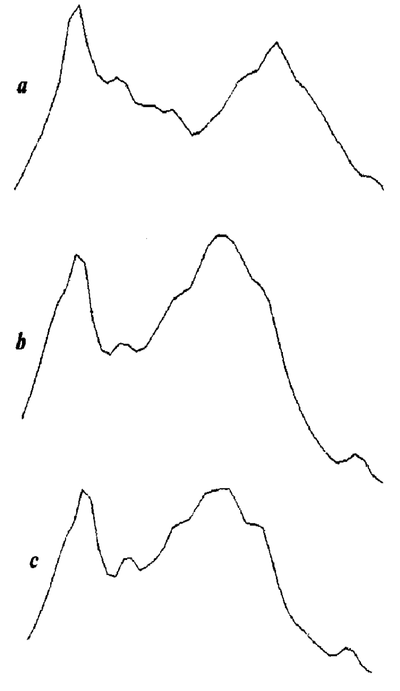

Fig. 2 OH-stretching band in CCl_4 solution; a – *cis*-1,2-cyclohexanediol; b – *trans*-lR,2R-cyclohexanediol; c – *trans*-lS,2S-cyclohexanediol

The uncertainty corresponding to a confidence level of 95% is ±2 cm^{-1} for ν_{max} and ±6 cm^{-1} for $\Delta\nu_{1/2}$. The fitting correlation coefficient is better than 0.99.

Discussion

The effect on the stretching vibration frequency of the free A–H group due a hydrogen bond established between this group and a hydrogen-bond acceptor, *B*, giving rise to (A–H···B) complex, can provide valuable information on phase structure and phase transitions. As a consequence of the perturbation on the potential energy function of A–H, the A–H stretching vibration moves toward lower frequencies, the absorption band becomes wider and its energy decreases. These effects are well known, have been reviewed in books and journals and used in studies carried out by infrared techniques [7–11]. In this work attention is concentrated mainly on the shift of frequency maximum, $\Delta\nu_{max}$, and half-height width of the OH stretching fundamental band, $\Delta\nu_{1/2}$. The OH stretching band of hydrogen bonded molecules exhibits large bandwidth and is very likely much more intense than the band of the corresponding free OH group [7, 8, 12]. It will be very sensitive to molecular interactions for the systems under study.

The spectra of *cis*- and *trans*-cyclohexanediol in CCl_4 show two maxima, one at 3628 cm^{-1} observed for both isomers and the other at 3590 and 3596 cm^{-1} for *cis* and *trans* isomer, respectively. The higher frequency band has been ascribed to free OH and the lower frequency band to intramolecular bonded OH. These figures are in agreement with those given in the literature [13, 14]. For the calculation of $\Delta\nu_{max}$, 3628 cm^{-1} was always taken as a reference value.

In Figures 3 and 4 $\Delta\nu_{max}$ and $\Delta\nu_{1/2}$ for *cis* and *trans* isomers are plotted against temperature. Before any detailed analysis it should be noted that both isomers in solid or liquid phases show OH vibration ν_{max} localised in the frequency range assigned to hydrogen bonding. No free OH group is observed.

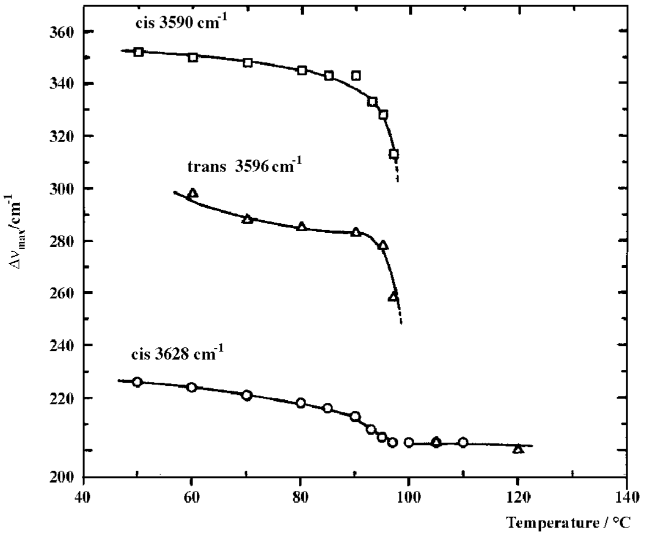

Fig. 3 OH-stretching vibration shift as a function of temperature for *cis*- and *trans*-1,2-cyclohexanediol

The $\Delta\nu_{max}$ *vs. T* curve of the *cis* compound shows a slope variation with temperature especially of the lower frequency band. As the temperature reaches a value around 85°C a decrease of $\Delta\nu_{max}$, was observed for the higher frequency band becoming almost constant above 100°C. The lower frequency band exhibits a slight decrease of $\Delta\nu_{max}$ up to about 85°C being the decrease more and more pronounced to about 99°C, value at which only one band is observed. These findings show that in the temperature range between 85 and 99°C, the stronger hydrogen bonding system collapses and the other is becoming slightly weaker till reaching the liquid pattern. The disruption of the stronger bonding group gives rise to an orientational disordered state allowing molecular rotation before translational freedom takes place.

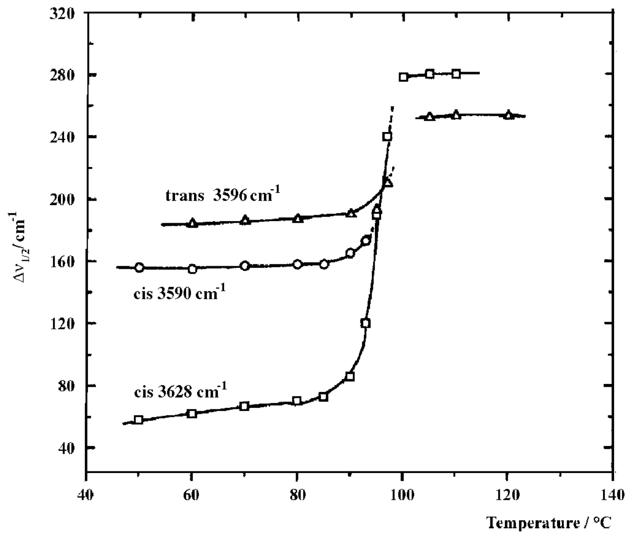

Fig. 4 Bandwidth of OH stretching vibration band as a function of temperature for *cis*- and *trans*-1,2-cyclohexanediol

The temperature effect on hydrogen bonding of *cis*-cyclohexanediol can also be followed through the variation of $\Delta\nu_{1/2}$. As expected, the half-width is a very sensitive spectral feature for the characterisation of intermolecular forces in the three phases described for this compound and to follow the transformations in which they are involved.

The *trans* isomer does not show any intermediate state between crystal and liquid phase. The crystalline phase shows a unique hydrogen bonding system characterised by a broad band whose maximum are localised in a wavenumber range between the two systems assigned to the *cis* form. Fusion occurring at about 100°C, is followed by a sudden variation of the slope of ν_{max} or $\Delta\nu_{1/2}$ *vs.* T curves. The values for the temperature at which the fusion of both isomers takes place or that at which phase II–phase I transition in *cis* isomer occurs determined by infrared measurements are in agreement with those determined by DSC. Naturally, the accuracy for transition temperatures is higher in DSC technique than in infrared due to the discontinuous way for obtaining spectroscopic data for different temperatures.

The only data we have about infrared spectra of *cis*- and *trans*-1,2-cyclohexanediol in solid phase were obtained by Kuhn at room temperature and published in

1952 [13]. He observed that OH stretching vibration gives two bands for *cis* and one band for the *trans* compound.

In liquid phase no appreciable differences are observed between *cis* and *trans* isomers. In this state no free OH is present that means that all molecules and both OH groups are involved. No free rotation exists even in the liquid state.

An important question is to know whether hydrogen bonds are of inter or intramolecular type. It has been admitted that intramolecular hydrogen bonding takes place in liquid polyalcohols [7, 15]. On the other hand self-association of monoalcohols in solution or in liquid state was proved by a large number [9, 16–19].

Intermolecular bonding suits the spectral data presented above better. In fact the values obtained for OH stretching vibration frequency are much lower than those observed for intramolecular bonding of the monomers in CCl_4. Also the values of the maximum frequency of the OH vibration band are in the range assigned to polymeric species of monoalcohols.

Cis- and *trans*-1,2-cyclohexanediol differ one from the other by the conformation of the OH groups. In the *cis* structure one OH is equatorial and the other axial in relation to the cyclohexane ring while in *trans* both OH groups are equatorial. According to X-ray diffraction data both crystallize in the orthorhombic space group with the same number of molecules in the unit cell and for both a structure of layers of dimers bonded by interdimeric hydrogen bonds were proposed [5, 6]. However, the different conformation gives rise to different densities, angles and interatomic distances which make the rotational barrier in *trans*-1,2-cyclohexanediol higher than in *cis*-1,2-cyclohexanediol, hence the possibility of the existence of orientation disordered phase preceding fusion in *cis*- and not in *tran*s-1,2-cyclohexanediol.

Conclusions

From the data presented above one can appraise the far-reaching procedure in the study of solid and liquid phases by complementing thermodynamics with methods more directly related to molecular structure. When hydrogen bonding accounts for the intermolecular forces, infrared spectroscopy is a valuable technique for this purpose.

The information that can be obtained from infrared spectroscopy in the characterisation of the structure of the phases and their transformations is worth emphasising.

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