Journal of Thermal Analysis, Vol. 53 (1998) 317-322

POLYMORPHIC TRANSITIONS IN CRYSTALLINE *E*- AND *Z*-α-PHENYLCINNAMIC ACIDS FOLLOWED BY DSC

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(Received June 6, 1997)

Abstract

Polymorphic transitions of α-phenylcinnamic acid stereoisomers crystallized from various solvents ($CHCl_3$, ethanol, diethyl ether), precipitated with different acids (acetic acid or HCl) or sublimed have been studied by differential scanning calorimetry (DSC). Measurements were also supplemented by powder X-ray diffractometry (XRD). Polymorphic transitions were not found for any of the *E* isomer samples irrespective of the method of treatment. However, in heating-cooling cycles reversible transitions could be detected for the *Z* isomer. On heating an exothermic peak was registered on samples sublimed, crystallized from ethanol or diethyl ether before melting, while samples precipitated by HCl or crystallized from chloroform exhibited more complex transitions. Here, endothermic effects were also observed. Enthalpy values for transformations (either for melting or polymorphic and other transitions) are also given.

Keywords: α-phenylcinnamic acid, DSC, polymorphic transitions, stereoisomers

Introduction

Cinnamic acid derivatives are important intermediates in the shikimic acid metabolic pathway of higher plants [1]. They also are much studied as building blocks in crystal engineering [2]. In fact they were the models for the detailed investigations of Schmidt leading to the discovery of topotactic rules, which govern the photochemical dimerization and oligomerization reactions of these and related compounds [3]. Based on their reactivities and the products obtained in the dimerization of *E*-ethoxycinnamic acid, he could identify three polymorphs. In

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1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordecht

each polymorph the olefinic double bonds are parallel to each other. In the α form the phenyl and carboxylic groups lie antiparallel, while in the β and γ forms they are situated parallel. The α and β polymorphs react in [2+2] cyclization on illumination with light of appropriate wavelength, while the γ form remains unreactive.

Given that the physical and chemical properties of polymorphs can be very different and that polymorphism is quite general among organic crystals as revealed in CSD (Cambridge Structural Database) [4], studying their formation and giving, if possible, thermodynamic data on polymorphic transitions are of significant importance.

In this study we remain in the cinnamic acid family and describe the behaviour of stereoisomeric α-phenylcinnamic acids crystallized from various solvents or precipitated by different acids on heat treatment, seeking polymorphic transitions. To the best of our knowledge, this pair of compounds has never been the object of similar investigations. Although the single crystal structure of many cinnamic acid derivatives were solved, curiously, the crystal structure of these compounds are not known. Powder patterns were not published and they are not available in CSD either, therefore we thought that taking the powder X-ray diffractograms would supplement the thermal study.

Experimental

Materials

The stereoisomeric pairs were prepared following the recipe of Fieser [5]. It involved heating a mixture of benzaldehyde (6 cm^3), phenylacetic acid (5 g), acetic anhydride (4 cm^3), and triethylamine (4 cm^3) for 35 min. The mixture of products was precipitated with cc. HCl. The solid material was dissolved in diethyl ether then was washed with 3% NaOH until the aqueous solution became alkaline (about pH 10). The two isomers from the alkaline solution were obtained by selective precipitation. Acidifying with acetic acid to pH 5 afforded the *E* isomer, further lowering the pH to 1 with cc. HCl provided with the *Z* isomer. Portions if these crude products were used in measurements (precipitated samples), while other portions were recrystallized from ethanol, diethyl ether and chloroform or sublimed. The reactants, the acids and the solvents were the products of Aldrich Chemical Co. They were of high purity and were used as received.

Differential scanning calorimetry (DSC)

A Perkin-Elmer Electrothermal 9100 differential scanning calorimeter equipped with intercooler was used to measure transition heats. At least two independent samples of around 4 mg were taken in a sealed Al container and at

least seven successive heating and cooling cycles were applied between 298 and 473 K for each of the independent samples. The rates of heating and cooling were 10 K min^{-1}. The first heating periods were omitted from the calculations. The sample space was purged with dry nitrogen. Metallic indium was used as standard to calibrate the temperature and enthalpy scales.

Powder X-ray diffractometry

The X-ray spectra were measured on a Siemens D5000 Kristallofex spectrometer. Depending on the quantities of the materials either a normal sample holder or a Si-film was used. Measurements were performed in the 2–40° range using CuK_α source. The stepsize was 0.01°, reflections were collected for 2 s at each step. In order to facilitate comparison, the differences in angle scales due to the two sample holder types were corrected and the spectra were smoothed.

Results and discussion

The thermal behaviour the E acid and the powder X-ray patterns

For the *E* isomer there was no measurable heat effect before melting either for the precipitated or sublimed samples or for samples recrystallized from diethyl ether or chloroform. The sample recrystallized from ethanol gave an endothermic effect in the first cycle, but on repeating the heating-cooling procedure the peak disappeared. A 8% mass decrease after the first cycle could also be observed. Melting points for the first three samples measured by the DSC method were 449 K, close to the literature value. The last sample (recrystallized from ethanol) melted at 436 K in the first cycle, but at 446 K in the repeated cycles.

The anomalous behaviour of the sample crystallized from ethanol is probably due to the inclusion of ethanol molecules into the crystal structure of the acid.

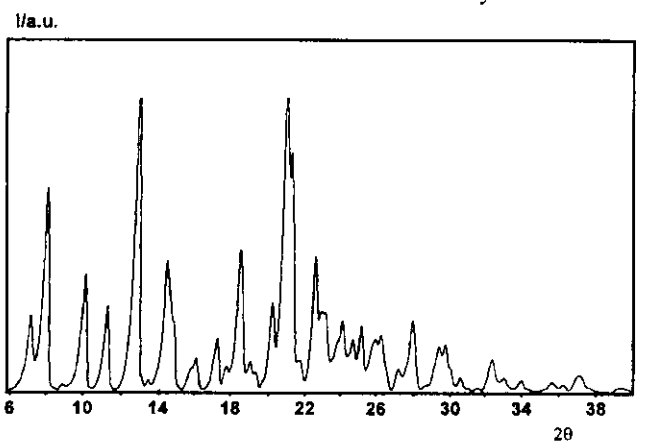

Fig. 1 The powder X-ray spectrum of the *E* isomer crystallized from diethyl ether

This inclusion is not reversible, the solvent molecules cannot reenter the structure on cooling. The possible reason of ethanol inclusion is its ability of forming hydrogen bonds with the acid.

The enthalpies of melting were also calculated for samples sublimed (2.01 kJ mol^{-1}) or recrystallized from chloroform (2.03 kJ mol^{-1}), diethyl ether (1.9 kJ mol^{-1}) and acetic acid (2.07 kJ mol^{-1}). They are in close agreement.

A powder X-ray pattern for the sample crystallized from diethyl ether is to be seen in Fig. 1.

X-ray diffractograms for the other samples are very similar. New reflections were not found for the sample crystallized from ethanol either. Here, small shifts in the position of some peaks were only observed indicating a change in the unit volume of the crystal.

The thermal behaviour the Z acid and the powder X-ray patterns

Melting point as well as DSC measurements revealed that samples sublimed or recrystallized from the same solvents as the *E* isomer were clean, they melted between 408–410 K in the region of the literature value. The sample prepared by precipitation melted somewhat lower, probably because of some coprecipitated *E* isomer as unavoidable contaminant.

For the sublimed and recrystallized samples the DSC spectra are similar in that before melting an exothermic peak appears. Its minimum is at 335 K for samples sublimed or crystallized from diethyl ether or ethanol. It is at 377 K for the precipitated sample and for the sample recrystallized from chloroform it is

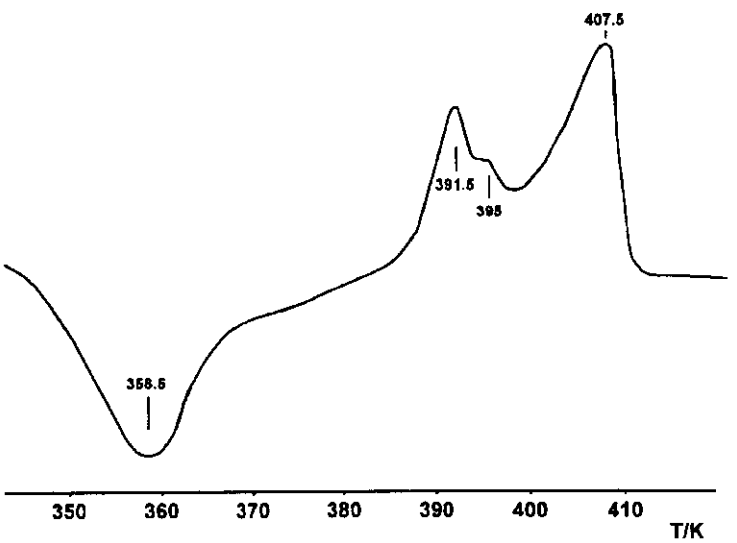

Fig. 2 The DSC spectrum of the Z isomer crystallized from chloroform

found at 358.5 K. These exothermic peaks indicate polymorphic transformations. The transitions are reversible, since they were observed in each heating-cooling cycle and neither the position of the peaks nor the area of the peaks changed. After the phase transition the sublimed material and the samples crystallized from diethyl ether and ethanol melted at 410 K. The other two samples underwent another, now endothermic transition before melting. The endothermic transition for the sample crystallized from chloroform is rather complex. It can be described by two intersecting curves with two extremes (Fig. 2).

Table 1 Enthalpy values measured during the heat treatment of the *Z* isomer

	HCl (precipitated)	$CHCl_3$	sublimed	diEt-ether	ethanol
Exothermic transition	–0.7	–6.9	–1.1	–0.9	–1.3
Endothermic process I	0.3	1.2	–	–	–
Endothermic process II	–	0.9	–	–	–
Melting	0.5	2.6	2.0	2.5	1.8

The values of the observed heat effects were also calculated and are summarized in Table 1. The melting enthalpy data are close to 2 kJ mol^{-1} (resembling that of the other isomer) except that of the precipitated sample, which has been already mentioned to contain traces of the isomer as contaminant.

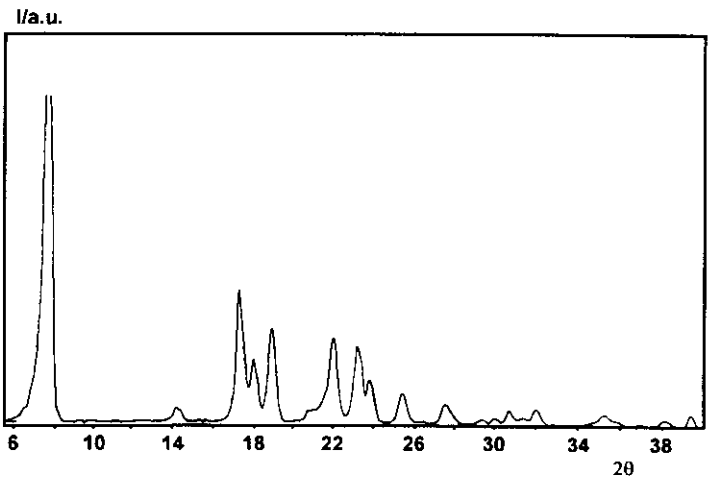

Fig. 3 The powder X-ray spectrum of the *Z* isomer crystallized from diethyl ether

Since the X-ray diffractograms for the samples do not differ, we only show one to make a visual comparison with that of the other isomer possible (Fig. 3).

Conclusions

DSC measurements revealed that *E*-α-phenylcinnamic acid samples do not undergo polymorphic phase transition on heat treatment, while the *Z* isomer samples crystallized from various solvents do. The transformations are found to be reversible.

In the case of the *E* isomer crystallized from ethanol, some of the solvent molecules were trapped in the crystal structure but could be irreversibly removed during the first heating-cooling cycle.

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Financial support provided for this work by the National Science Foundation of Hungary is highly appreciated.

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