

A study of the phase transformation in anthranilic acid single crystals

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Abstract

The electrical properties (resistance, dielectric constant and pyroelectric current) as a function of temperature in the range $30^{\circ}\text{C} < T < 120^{\circ}\text{C}$ of anthranilic acid single crystals (*o*-aminobenzoic acid, $\text{C}_6\text{H}_4\text{NH}_2\text{COOH}$), were accurately measured and correlated to the structural phase change that has been observed at 81°C . The activation energies of the two phases were determined. The recorded DTA thermogram supports this phase change. In addition, the mean molar susceptibility χ_M of the powdered sample was accurately determined in the same temperature range; the result indicates that the structural phase change takes place at 81°C .

INTRODUCTION

Anthranilic acid, (*o*-aminobenzoic acid, “*o*-ABA”, $\text{C}_6\text{H}_4\text{NH}_2\text{COOH}$) exists in three modifications [1] and undergoes a polymorphic transition at 81°C [2]. The crystal structure of the low temperature form, **I**, which is stable up to 81°C , has been determined [3]: the crystals are orthorhombic, the unit cell parameters being $a = 12.868 \text{ \AA}$, $b = 10.772 \text{ \AA}$, $c = 9.325 \text{ \AA}$, $z = 8$ and the space group is $P2_1ca$. The general feature of this structure is that there are two non-equivalent molecules (A and B) per symmetric unit cell. The molecule A is neutral, i.e. $\text{C}_6\text{H}_4\text{NH}_2\text{COOH}$, while the molecule B is a zwitterion, $\text{C}_6\text{H}_4\text{NH}_3^+\text{COO}^-$.

The crystal structure of the second modification, anthranilic acid **II**, (stable above 81°C), the high temperature form, has been investigated by Boone et al. [4]: the crystals are also orthorhombic but the unit cell constants are $a = 15.978 \text{ \AA}$, $b = 11.605 \text{ \AA}$, $c = 7.162 \text{ \AA}$, $z = 8$ and the space group is $Pbca$. In modification **II**, all the molecules are in the non-zwitterionic form, i.e. neutral. Furthermore, modification **II** shows the familiar linkage of carboxylic groups by two hydrogen bonds of cyclic-dimer type across the centre of symmetry, whereas anthranilic acid **I** has only single $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. In both modifications, $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds join the molecules in networks, although the rather long $\text{N} \cdots \text{O}$ distance (3.122 \AA) in anthranilic acid **II** indicates only a weak bond.

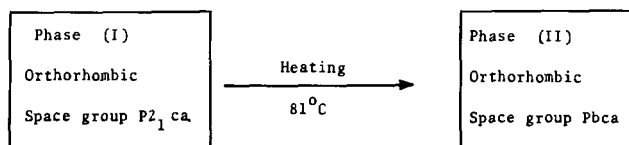


Fig. 1. The phase transformation in anthranilic acid single crystals.

The mean molar susceptibility χ_M , the crystal susceptibilities, χ_a , χ_b and χ_c and the principal molecular susceptibilities, K_1 , K_2 and K_3 , as well as the anisotropy δK of the low temperature form, anthranilic acid I, have been measured before [5].

We decided to study the electrical properties as a function of the temperature of the single crystals of the two phases, as well as the mean molar susceptibilities, χ_M , of the powdered samples. All these parameters strongly support the structural phase transition (see Fig. 1).

EXPERIMENTAL

Some previous crystal-growth experiments have shown that the form of the crystals is very susceptible to slight changes in the conditions of the crystallization i.e. temperature, solvent, pH etc. In the present work, the commercial materials were purified by recrystallization from absolute ethanol and then dissolved again in absolute ethanol. By slow evaporation of the saturated solution at room temperature (about 25°C) we obtained, after two attempts, large single crystals in the form of brown bipyramids, suitable for the electrical measurements. These crystal were coated with silver paste and were then connected to the two electrodes.

The electrical resistance was measured using a digital electrometer. A thermocouple was used to determine the temperature to $\pm 1^\circ\text{C}$. The dielectric constant was determined with a digital RLC bridge of the Keithley type, and the pyroelectric current was measured with a picoammeter. The mean molar susceptibility χ_M was determined by the well-known Gouy method. The details of this method have been given elsewhere [6].

RESULTS AND DISCUSSION

The DTA of anthranilic acid single crystals was performed over a wide temperature range, from room temperature to 130°C, with a heating rate of $10^\circ\text{C min}^{-1}$ and a ΔT sensitivity of 10 mV cm^{-1} . The DTA thermogram obtained from this thermal analysis process is shown in Fig. 2. The curve indicates clearly the occurrence of an endothermic phase transition, I \rightarrow II, starting at about 78°C on heating. The sudden sharp changes in the differential temperature, ΔT , suggest that the phase transition is a first-order reaction.



Fig. 2. The DTA thermogram.

The height of the peak, ΔT_{max} , was taken as a measure of the endothermicity and exothermicity, and of the rate of the transition. The location of the peak along the temperature axis was related to the activation energy provided. The thermal analysis was extended to calculate the enthalpy of transformation, ΔH , using the sharp DTA signal obtained [7-9]. The calculations yielded the values listed in Table 1.

TABLE 1

Results of the thermal analysis

ΔH^a (J g^{-1})	T_p^b ($^{\circ}\text{C}$)	T_i^c ($^{\circ}\text{C}$)
4.6	82	78

^a Heat of transformation.

^b Peak temperature of the DTA signal.

^c Initiation temperature.

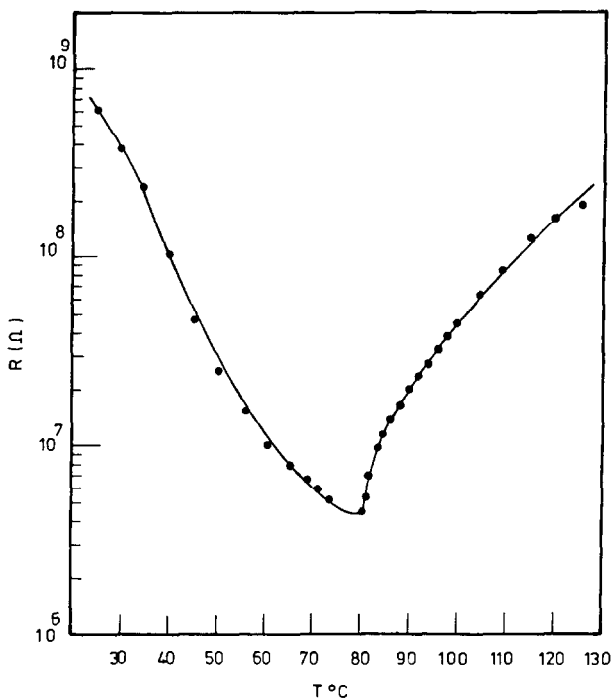


Fig. 3. Relation between the d.c. resistance and temperature T (°C).

The relation between R (on a logarithmic scale) and the temperature in the range $30^\circ\text{C} < T < 120^\circ\text{C}$, is presented in Fig. 3. We can observe that the values of the resistance are very sensitive to the variation in the temperature (except for the phase transformation region). In other words, as the temperature increases gradually from 30 to 70°C , the value of R decreases rapidly. The variation of R with temperature near the transition temperature, i.e. $70 < T < 80$, however, is somewhat small. As the temperature exceeds 85°C , the value of R increases again, but at a slow rate compared with the low temperature phase.

To account for this behaviour of R we have calculated the activation energies of the two phases (I and II). The values obtained are $E_1 = 1.02$ eV and $E_2 = -0.82$ eV.

In the low temperature phase, the molecules of the crystals are disordered; this is clear from the high value of E_1 compared with that of E_2 and from crystal structure considerations. As discussed above, the molecules are arranged with only single $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. This is not the case for most carboxylic acids, where the molecules are usually arranged in the form of dimers [10]. Furthermore, for the low temperature form, I, one molecule is neutral ($\text{C}_6\text{H}_4\text{NH}_2\text{COOH}$) and the other is zwitterionic i.e. charged or non-neutral ($\text{C}_6\text{H}_4\text{NH}_3^+\text{COO}^-$). In other words, 50% of the molecules inside the crystals are charged. Thus we can say that the COOH

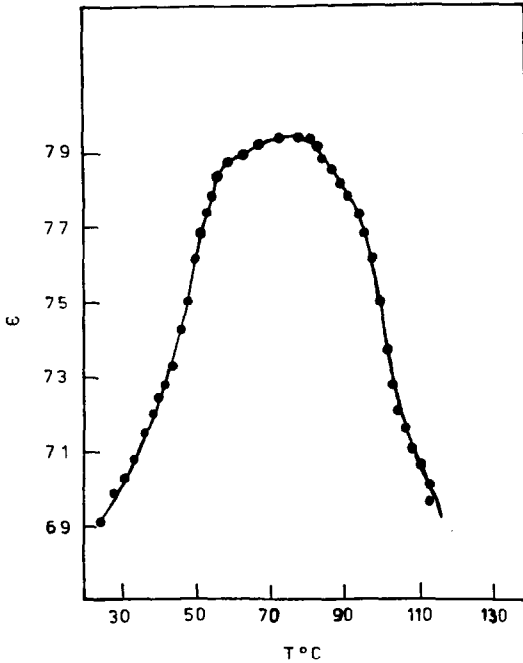


Fig. 4. Variation of the dielectric constant ϵ and the temperature T ($^{\circ}\text{C}$).

groups are somewhat disordered, i.e. the presence of these charges increases the conductivity of the molecules and hence of the crystals as the temperature increases. Therefore, the resistance decreases with increasing temperature, as was observed.

At a certain temperature (81°C), the energy is enough to rotate (to packing) the COOH groups such that the molecules in the crystals are arranged to form dimers, i.e. double $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, as in most carboxylic acids. In this phase the high temperature phase, all the molecules are in the neutral form.

Figure 4 shows the relation between the dielectric constant ϵ and the temperature T in the same range, i.e. $30^{\circ}\text{C} < T < 120^{\circ}\text{C}$ (at 1 kHz).

As the temperature gradually increases from 30°C to about 70°C , the values of ϵ increase at nearly a constant rate. In the temperature range $70^{\circ}\text{C} < T < 80^{\circ}\text{C}$, the rate of increase in ϵ with T is very small, i.e. we have a fairly broad peak.

As the temperature exceeds the transition, i.e. $T \approx 83^{\circ}\text{C}$, the values of ϵ decrease with increasing temperature. This behaviour of the dielectric constant in the temperature range studied is to be expected, especially if we compare this behaviour with that of the resistance.

To support our work, we have also studied the pyroelectric current of the crystal. Figure 5 shows the relation between the pyroelectric current (nA) and the temperature in the range $30^{\circ}\text{C} < T < 120^{\circ}\text{C}$.

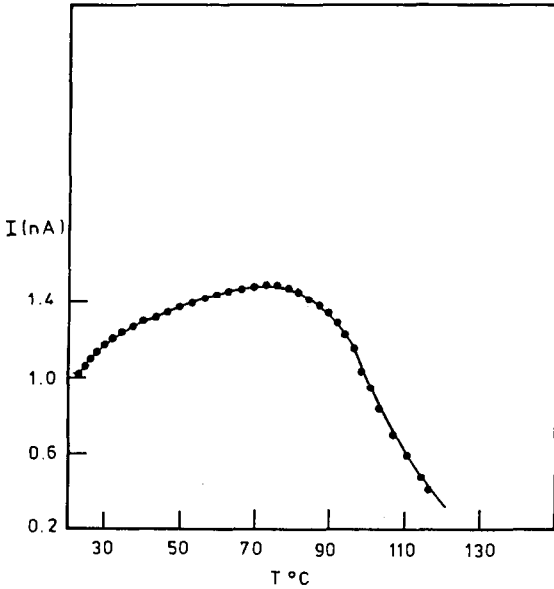


Fig. 5. Pyroelectric current I vs. temperature T (°C).

The curve in Fig. 5 can be explained by the same principle. Again there is a gradual increase in I with increasing temperature T . This is perhaps due to polarization of the charges of non-neutral molecules. The value of I reaches a maximum at about 81–82°C, and then decreases at a somewhat faster rate with increasing temperature.

Figure 6 shows the relation between χ_M , the mean molar susceptibility, and the temperature T in the same temperature range: 30°C < T < 120°C.

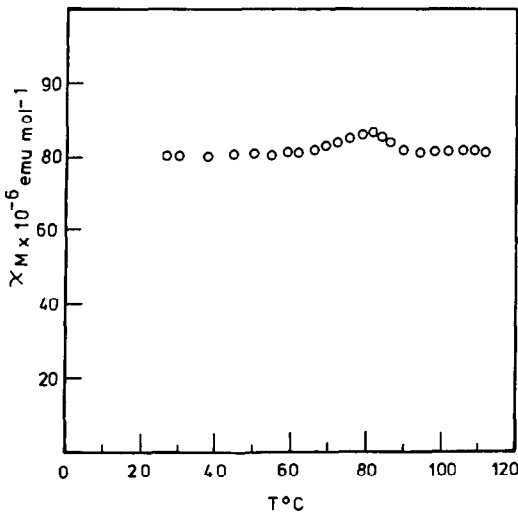


Fig. 6. Relation between χ_M (molar susceptibility) and the temperature T (°C).

It is clear from this figure that there is an anomalous or broad peak centred at about $T = 80-82^{\circ}\text{C}$. This can be taken to indicate the structural phase change.

In conclusion, all these properties confirm the occurrence of a phase change that has been observed at 81°C . However, the electrical properties are a much more sensitive probe than the magnetic susceptibility.

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