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Polymorphism in Anthranilic Acid Crystals — Examination by DTA and DSC

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Abstract—Crystalline anthranilic acid in modifications I and II has been prepared from aqueous, ethanolic and non-polar solvents, and examined by DTA to determine transition and melting temperatures and by DSC to give associated enthalpy and entropy changes. The transition I → II occurs at 352.2 K at a zero extrapolated heating rate. An additional endotherm occurs with modification II when the acid is obtained from buffered aqueous solutions within a narrow pH range. The low transition enthalpy occurring under these conditions indicates that the modification has a lower degree of lattice order than II obtained under more acid conditions or from ethanolic solution. I and II were confirmed by X-ray powder photographs. The morphology of the forms obtained is discussed briefly.

Anthranilic acid (o-aminobenzoic acid) is known to exist in three different crystalline modifications.[1] All three can be obtained by crystallization from solution and form III is always obtained on crystallizing from the melt. The crystal structure of the form I, obtained as brown bi-pyramids from cold ethanol or colourless tablets from acetic acid, has been determined by Brown[2] and shown most probably to consist of two crystallographically non-equivalent molecules, a neutral anthranilic acid molecule $C_6H_4.NH_2.COOH$ and a zwitterion of formula $C_6H_4.NH_3^+.COO^-$. This form undergoes a solid state transition to form II at 81 °C observable by hot-stage microscopy. Thermal analysis techniques used to study this transition[3] have only been applied qualitatively and it is our purpose to examine this transition and fusion in more quantitative detail by DTA/DSC methods.

1. Experimental

Material

The initial stock sample of anthranilic acid, analytical reagent grade, was purified by repeated recrystallization from 96 % ethanol to constant m.p. followed by sublimation at 373 K at a pressure of 0.1 Torr. The sublimate was recrystallized from hot ethanol to give fine white needles of anthranilic acid, form II, with a m.p. 419.0 K as determined by calibrated hot-stage microscope (C. Reichert, Optische Werke A.E. Wein, Austria).

Apparatus

A DuPont 900 Thermal Analyzer fitted with scanning calorimeter and previously calibrated over the temperature range 313–593 K was used throughout. Samples were heated in uncoated aluminium containers hermetically sealed under atmospheric conditions and areas under curves determined to within an accuracy of ± 1.0 % using a Stanley Allbrit planimeter. Since enthalpies were found independent of heating rate, the latter was fixed at 15 K min^{-1} with a y-axis sensitivity of 0.1 K in^{-1} for all quantitative data. Transition and melting temperatures were more accurately determined by operating the instrument in the DTA mode. Under these conditions peak temperatures are dependent on rate of heating. Temperatures of transition and fusion were therefore extrapolated to a zero heating rate on the basis of at least five determinations carried out over the range 2–30 K min^{-1}.

Transitions were confirmed by X-ray diffraction powder photographs using CuKα radiation and a specimen-film distance of 5.73 cm.

Preparation of Modifications of Anthranilic Acid

Different crystalline modifications were obtained by two main methods. These were recrystallization from (a) water or organic solvents and (b) from aqueous solutions under different pH conditions. In the former method, crystals were prepared by slowly cooling nearly saturated aqueous or benzene solutions over a period of 48 h and secondly by the slow exaporation at room temperature

of an ethanolic saturated solution. In addition crystals were obtained by sublimation as described previously.

In the second method (b) crystals were obtained by slowly cooling solutions of anthranilic acid made up in a buffer of 0.04 M orthophosphoric acid, 0.04 M acetic acid and 0.04 M boric acid and adjusting to the desired pH with 0.20 M caustic soda. The pH range of these solutions was from 3.70 to 5.29. The values are the arithmetic mean of the pH of solution just prior to crystallization and the pH of the filtrate after crystallizing. In no case did the difference exceed 0.02 pH units. Above pH 5.29 crystallization did not occur. For an ionic strength < 0.05 the pK_2 value for anthranilic acid can be equated with the pH of the aqueous solution. This was found to be 4.96 (± 0.03) in good agreement with the value of 4.95 determined by Kilpi and Harjanne.[4]

2. Results and Discussion

Anthranilic acid recrystallized from water as long brown needles and from ethanol as brown truncated bi-pyramids. Sublimation at 373 K under reduced pressure gave very small colourless needles and recrystallization from slowly cooled benzene solutions gave colourless hexagonal plates. Both the brown needles and bi-pyramids show endothermic transitions in addition to melting peaks by DTA. The values of transition and melting temperatures given in Table 1 are those extrapolated to zero heating rate. Melting temperatures are compared with those obtained by hot-stage microscopy.

TABLE 1 Extrapolated Transition and Melting Temperatures of Anthranilic Acid

Sample	Transition temp. K	Melting temp. K	Microscopic melting temp. K
Brown needles	352.2($\pm$0.5)	419.9($\pm$0.3)	418.8($\pm$0.3)
Brown bi-pyramids	347.2($\pm$0.5)	420.0($\pm$0.3)	418.8($\pm$0.3)
Colourless needles	—	419.7($\pm$0.3)	418.7($\pm$0.3)
Hexagonal plates	—	419.7($\pm$0.3)	418.7($\pm$0.3)

At positive heating rates the transitions show double peaks which merge as the heating rate is reduced. This effect is shown in Fig. 1 for the brown bi-pyramids obtained from ethanol.

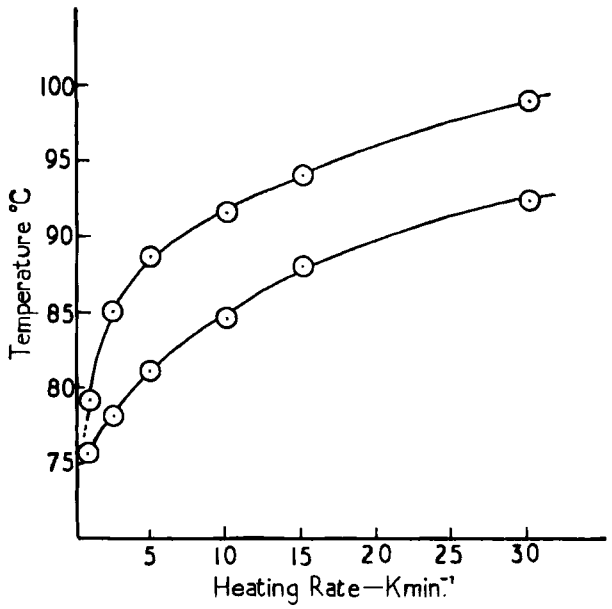


Figure 1. Merging of transition peaks—brown bi-pyramids of anthranilic acid.

The total enthalpy and entropy changes of transition and fusion are given in Table 2. The enthalpy change ΔH_i was determined (using DSC) by measuring endothermic peak areas at 15 K min^{-1} to within an accuracy of $\pm 1.0\,\%$. ΔS_i was calculated according to $\Delta H_i/TK$ where suffix i represents transition or fusion. For comparison with published data enthalpies are given in kcal.mol^{-1} and entropies in cal.mol^{-1} K^{-1}. To convert to S.I. units, 1 cal = 4.184 J. Both brown needles and pyramidal crystals exhibit identical X-ray powder diffraction patterns and show non-reversible or only slowly

TABLE 2 Enthalpies and Entropies of Transition and Fusion; Modifications of Anthranilic Acid

Sample	ΔH_t kcal. mol^{-1}	ΔS_t cal. mol^{-1} K^{-1}	ΔH_f kcal. mol^{-1}	ΔS_f cal. mol^{-1} K^{-1}
Brown needles	1.59($\pm$0.3)	4.52($\pm$0.85)	5.41($\pm$0.20)	12.89($\pm$0.49)
Brown bi-pyramids	1.24($\pm$0.3)	3.57($\pm$0.87)	5.25($\pm$0.23)	12.50($\pm$0.55)
Colourless needles	—	—	5.25($\pm$0.20)	12.51($\pm$0.49)
Hexagonal plates	—	—	5.22($\pm$0.17)	12.44($\pm$0.41)

reversible transitions, I → II, on heating at 352.2 and 347.2 K respectively. Diffraction patterns for the hexagonal plates are considerably different, possessing fewer reflections. On heating above the transition temperature and cooling, both brown needles and bi-pyramids show additional reflections of low intensity, whereas the patterns for the hexagonal crystals show no change on heating and cooling. The lower enthalpy change of transition for the bi-pyramids may be due simply to a lower degree of lattice order and may not indicate a difference in lattice structure. Independent determinations of heat capacity, using the DSC method show that below the onset of transition the value for the pyramidal crystal is smaller by 8.7 cal.mole^{-1} deg^{-1} indicating that the difference in enthalpy change may be due to a difference in the degree of lattice order.

The transition I → II can be detected by hot-stage microscopy as a change in colour from transparent brownish yellow to opaque white caused by the formation of striations and possible voids oriented perpendicularly to the long axis of the acicular crystals.

Values for the enthalpy of fusion of the different crystals cannot be differentiated in view of the experimental error involved. The mean value of modification II is 5.24 kcal.mol^{-1}. In addition, modification III, obtained by recrystallization from the melt fuses at 418.7 K with an attendant enthalpy change of 4.76(± 0.20) kcal. mol^{-1}. This value agrees with an exothermic heat of crystallization of − 4.87 kcal.mol^{-1} determined previously by Andrews.[5] Since the enthalpy of fusion of crystal II, obtained when brown bi-pyramids are heated above 347.2 K, is 5.25 kcal.mol^{-1} the mean enthalpy of the transition II → III, by difference is 0.48(± 0.20) kcal.mol^{-1}. It must be emphasized that this transition has not been observed, its enthalpy value being theoretically calculated.

Growth forms of anthranilic acid crystals obtained from aqueous buffered solutions over the pH range 3.7–5.2 were irregularly shaped and plate-like. Their transition temperatures and enthalpies of transition, determined by DSC at a heating rate of 15 K min^{-1} are given in Table 3. Within a narrow range of pH from 4.90 to 5.05 the enthalpy of transition decreases almost to zero. This effect is best observed in Fig. 2 which shows the variation of enthalpy with acidity of crystallizing solution.

TABLE 3: Transition Temperatures and Enthalpies of Growth Forms of Anthranilic Acid

Solution pH	Transition temperature K	ΔH_t kcal. mol^{-1}	ΔS_t cal. mol^{-1} K^{-1}
3.70	370.9	1.51(±0.03)	4.07(±0.08)
3.95	372.4	1.50(±0.02)	4.03(±0.06)
4.89	366.2; 371.2	1.51(±0.03)	—
4.98	372.4; 379.0	1.33(±0.01)	—
5.03	367.6	0.14(±0.05)	0.38(±0.14)
5.05	368.7	0.04(±0.01)	0.11(±0.03)
5.10	365.9	1.60(±0.08)	4.37(±0.22)
5.19	370.2	1.44(±0.04)	3.89(±0.11)
5.21	366.2	1.38(±0.02)	3.77(±0.05)
5.23	370.2	1.58(±0.06)	4.27(±0.16)
5.29	377.8	1.27(±0.04)	3.43(±0.11)

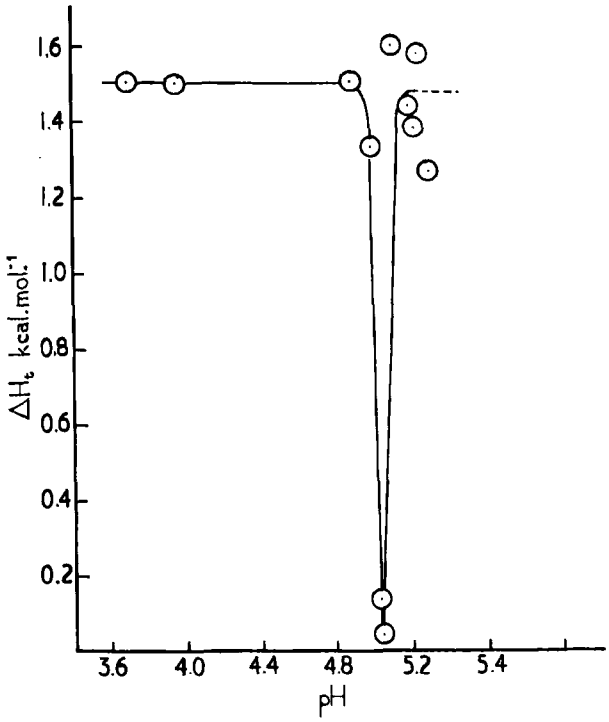


Figure 2. Changes in enthalpy of transition with pH of crystallizing solution.

The low enthalpy changes approximate to those pH conditions in which the zwitterion and anion are in equilibrium, which, for an ionic strength of less than 0.05 has been found to occur at pH 4.96. It is noticeable also that crystals obtained in this narrow region exhibit a double overlapping endothermic peak and since the same observation has been made for crystals obtained from binary aqueous solutions the presence of buffer ions has no major effect on crystal structure. This is confirmed by the similarity of X-ray Debye Scherrer diagrams for the two crystalline samples. For anthranilic acid obtained at pH <4.8 and >5.1 line spacings at d 5.5 Å of moderate to weak intensity, present in the diagrams of modification I are missing.

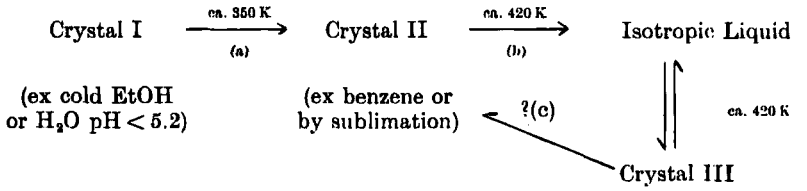
3. Conclusions

The results obtained by the DSC method confirmed by X-ray diffraction, illustrate well that the crystals of anthranilic acid obtained from aqueous and ethanolic solutions, although morphologically different, have the same internal lattice arrangement. The growth of bi-pyramids from ethanol solution by seeding with the orthorhombic modification obtained previously from aqueous solution gives a bi-pyramid with a predominant {211} face and the {110} is small.[6] The bi-pyramids obtained in the present work whilst showing a prominent {211} face also possess a residual {010} face leading to a truncated shape.

Crystals obtained from benzene or by sublimation are hexagonal prismatic. They do not undergo any transitions on heating from room temperature to the melting point, in contrast with the behaviour of the orthorhombic form, I, and with which they may be visually confused. Crystal II, obtained by heating I above its transition temperature, does not show any reversible change to I on cooling. X-ray diffraction patterns of II are identical with those obtained from crystals prepared from a non-polar (benzene) or solvent-free (sublimed) environment. It may be concluded that the form I, previously referred to as the low temperature stable form (2) may not be as thermally stable as II. Determination of the vapour pressures of both forms below the transition temperature of I may provide a more definite answer.

The presence of buffers, such as a mixture of orthophosphoric, acetic and boric acids, in the solution appears not to affect the crystal structure of modification I obtained under aqueous conditions, but within a narrow pH range (4.8–5.1) reduces the degree of lattice order, thereby lowering the energy barrier in the thermal transition I → II. The presence of an overlapping endothermic peak for some crystals of anthranilic acid obtained within this range cannot be explained without further investigation but appears to indicate a more complex transition mechanism than that anticipated.

In summary the transitions may be represented by the following scheme:



The reversibility of steps (a) and (b) has not been observed and step (c) is possible but has also not been observed.

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