CCCCXXXIII.—*The Crystalline Forms of 5-Nitrosalicylic Acid and of Related Compounds.*

By Frederick Daniel Chattaway and William Ryle Clifford Curjel.

When a hot saturated aqueous solution of 5-nitrosalicylic acid is cooled to the ordinary temperature, the acid separates as slender, hair-like, almost colourless needles, the whole liquid becoming a felted pulp. On separating these crystals, suspending them in a small quantity of the mother-liquor, and warming, compact crystals appear, and grow at the expense of the slender needles, which quickly dissolve and disappear. On allowing the compact crystals to remain in contact with the aqueous mother-liquor at the ordinary temperature, the hair-like form reappears and grows slowly at the expense of the compact crystals, which in their turn dissolve and finally disappear.

When the hair-like crystals are separated from the aqueous mother-liquor and placed in a little alcohol or acetone at the ordinary temperature, compact crystals, identical with those obtained by heating in aqueous suspension, make their appearance and grow at the expense of the needle-shaped form, which, as before, dissolves and finally disappears.

These phenomena are due to the formation and decomposition of a hitherto unrecognised monohydrated form of the acid, which crystallises in hair-like needles, the compact form being the anhydrous acid.

The hydrated form readily loses water on exposure to the air, and, on account of the fine hair-like character of the crystals, great difficulty is experienced in drying them for analysis. This could only be done by exposing them for a long period to a current of air saturated with water-vapour at the equilibrium pressure of the system hydrate–anhydrous acid–vapour (compare Hill and Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 546).

The solubility of the acid in water over the temperature range 15—100° has been determined. The intersection of the respective solubility curves for the anhydrous acid and the monohydrate shows that the transition point lies in the immediate neighbourhood of 42·5°.

In the course of this work, crystals of the compact anhydrous form of 5-nitrosalicylic acid have been examined. Crystals of this acid have previously been examined by Fels (*Z. Kryst. Min.*, 1903, **37**, 486), who obtained them from solution in acetone. The crystals were described as monoclinic with axial elements $a : b : c =$

0·9692 : 1 : 1·1067; $\beta = 92° 5'$. No crystals corresponding to this description have been observed during the present examination.

Crystals of ethyl 5-nitrosalicylate have also been examined.

EXPERIMENTAL.

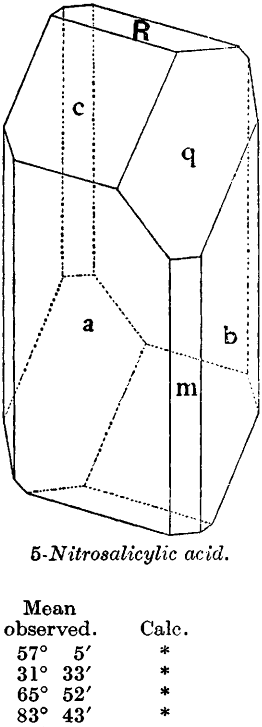
The 5-nitrosalicylic acid used was prepared by the direct nitration of salicyclic acid in acetic acid solution (compare Raiziss and Proskouriakoff, *J. Amer. Chem. Soc.*, 1922, **44**, 791), and was purified by repeated crystallisation from water.

Anhydrous 5-*Nitrosalicylic Acid.*—On account of the great solubility of the acid in all common organic solvents, it was difficult to obtain crystals suitable for measurement. Those used in this work were obtained by allowing solutions in acetic acid or in a mixture of acetone and ethyl acetate to cool during 3 days in a slow cooler.

The crystals belong to the holohedral class of the anorthic system. The axial elements are $a : b : c = 1·7456 : 1 : 1·0945$; $\alpha = 96° 16'$, $\beta = 114° 6'$, $\gamma = 88° 40'$.

The forms observed were $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $M\{\bar{1}10\}$, $R\{\bar{1}01\}$, and $q\{011\}$.

The interfacial angles (based on the three best crystals measured) are shown in the accompanying table.



5-*Nitrosalicylic acid.*

Angle.	No.	Limits.	Mean observed.	Calc.
100 : 110	6	56° 39′—57° 25′	57° 5′	*
110 : 010	6	31° 4′—31° 58′	31° 33′	*
100 : 001	6	65° 32′—66° 16′	65° 52′	*
001 : 010	6	83° 18′—84° 15′	83° 43′	*
001 : 011	4	41° 36′—42° 6′	41° 51′	*
$\bar{1}00 : \bar{1}10$	6	59° 1′—59° 32′	59° 18′	59° 3′
$\bar{1}10 : 010$	6	31° 19′—32° 20′	31° 53′	32° 19′
$001 : \bar{1}01$	6	37° 5′—37° 52′	37° 25′	37° 22′
110 : 011	2	38° 29′—38° 39′	38° 34′	39° 0′
$\bar{1}01 : 011$	2	53° 17′—53° 33′	53° 25′	53° 0′

There is a perfect cleavage parallel to $q\{011\}$. The resultant cleavage fragments show a biaxial interference figure, apparently symmetrical to the centre of the field. Strong crossed dispersion is shown. The double refraction is strong and negative. The axial angle is fairly wide. $\rho < v$.

Twin-crystals are frequently found, twinned on the plane {011}.

The density of the crystals is 1·654 at 18·5°.

Monohydrated 5-Nitrosalicylic Acid, $OH\cdot C_6H_3(NO_2)\cdot C(OH)_3$.—To obtain crystals of the hydrate as large as possible, an aqueous solution of 5-nitrosalicylic acid, saturated below the transition point at 40°, was allowed to cool to the ordinary temperature during 2 days in a slow cooler. The hydrated form separated in very slender, strongly doubly-refractive, elongated prisms. A biaxial interference figure of narrow axial angle is visible through one of the prism faces. The figure appears to be symmetrical, and is markedly different from that shown by the anhydrous acid.

The symmetrical appearance of this figure, together with the frequent occurrence of straight extinction on the prism faces of the smaller crystals, indicates that the crystals of the hydrate are probably orthorhombic, but it has not been found possible to confirm this definitely, since no measurable crystals could be obtained.

Analysis of the hydrate. The anhydrous acid did not lose weight on prolonged heating in an air-bath at 100—120°, and, consequently, the amount of water in the hydrate could be determined by heating a weighed quantity at this temperature.

The crystals of the hydrate were freed from adhering water in the way already mentioned and were apparently dry after about 7 hours' treatment. The passage of air was continued for a further 2 hours, and about half the hydrate was then transferred to a crucible, weighed, and dehydrated by heating in an air-bath at 100—120° to constant weight (Found : loss, 9·3%). The passage of air over the second half of the hydrate was continued for a further 6 hours; it was then similarly weighed and dehydrated (Found : loss, 9·1%).

In another experiment, a further quantity of hydrate was similarly dried for 2 days [Found : loss, 9·0%. $OH\cdot C_6H_3(NO_2)\cdot C(OH)_3$ requires loss, 8·95%].

Determination of the Transition Point between the Monohydrate and the Anhydrous Acid.—(a) *Dilatometric experiments.* A dilatometer was filled with an intimate mixture of the anhydrous acid and the monohydrate in presence of water, and the direction of any volume change occurring in the system noted at various constant temperatures. At all temperatures between 15° and 37°, a very slight progressive decrease of volume, and at temperatures above 46° a very slight progressive increase of volume, was observed. The transition point accordingly lay between these limits. The volume changes were, however, very slow and slight, and at temperatures between these limits were so slow as not to be perceptible.

(b) *Solubility measurements.* A number of experiments showed that aqueous and aqueous-alcoholic solutions of 5-nitrosalicylic acid could be evaporated to dryness at 100—120° without any loss of acid, the amount of which in such solutions could be determined by weighing the residue. Its slight solubility in water, however, necessitated the evaporation of inconveniently large volumes and it was found that the quantity dissolved could be ascertained with equal accuracy by titrating sufficiently diluted solutions with standard N/100-alkali, the end-point being shown by the appearance of a permanent distinctive yellow colour. The most consistent results are obtained with solutions containing not more than 0·15 g. of acid in 100 c.c. In stronger solutions, the faint yellow colour of the acid itself obscures the end-point.

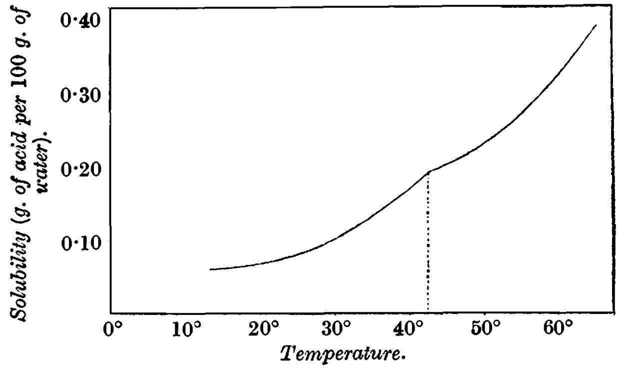
By either method small quantities of 5-nitrosalicylic acid can be estimated with a maximum error of 1%.

The saturated solutions, prepared by shaking tightly corked bottles containing water and excess of the hydrated acid for 3—4 hours in a thermostat, were aspirated into a weighing pipette through a plug of cotton wool. The amounts withdrawn, after weighing, were transferred to a calibrated flask and diluted to the uniform strength required for titration.

The results are given below; the solubility, *s*, is expressed as g. of acid per 100 g. of water. It was not found possible to determine metastable solubilities, since partial transformation always occurred.

Hydrated acid.				Anhydrous acid.			
Temp.	*s*.	Temp.	*s*.	Temp.	*s*.	Temp.	*s*.
14·95°	0·061	31·0°	0·103	45·0°	0·200	65·0°	0·391
17·5	0·064	33·0	0·115	50·1	0·228	72·0	0·501
20·5	0·068	35·0	0·125	55·2	0·273	74·1	0·528
25·0	0·078	36·6	0·139	60·0	0·325	99·5	1·505
29·0	0·093	40·1	0·169				

The change from the hydrated to the anhydrous form did not occur at 41°, but occurred at 43·5°. Hence the transition point lies between these limits. By plotting the solubility–temperature curve for each solid phase and prolonging the curves to their intersection,



it is seen that the transition point lies in the immediate neighbourhood of 42·5°.

Crystallographic Examination of Ethyl 5-Nitrosalicylate.—The ester was prepared by heating 5-nitrosalicylic acid with excess of ethyl alcohol in presence of a little concentrated sulphuric acid. The liquid was poured on to ice; the ester which separated crystallised from alcohol, in which it was readily soluble, in colourless, prismatic crystals, m. p. 96°.

Crystals were obtained for measurement by allowing a solution in carbon tetrachloride to cool during 3 days in a slow cooler. The crystals belong to the monoclinic system and are of prismatic habit. The axial elements are $a : b : c = 0·9530 : 1 : 0·4377$; $\beta = 122° 38'$. The forms observed were *a*{100}, *b*{010}, *c*{001}, *m*{110}, *n*{120}, and, less frequently, *q*{011}.

The interfacial angles are given in the accompanying table.

Angle.	No.	Limits.	Mean observed.	Calc.
100 : 120	6	57° 57′—58° 16′	58° 5′	*
100 : 001	6	57° 2′—57° 37′	57° 22′	*
001 : 011	2	20° 8′—20° 20′	20° 14′	*
100 : 110	6	38° 33′—39° 28′	39° 0′	38° 45′
120 : 001	6	73° 16′—73° 41′	73° 24′	73° 26′

Perfect cleavage is developed parallel to *n*{120}. Less perfect cleavage is developed parallel to *c*{001}. A cleavage fragment parallel to (120) shows one optic axis, the *b*-axis being the acute bisectrix of the axial angle. The double refraction is very strong and positive. $\rho < v$.

The density of the crystals is 1·429 at 19°.

The Polymorphic Forms of 5-Nitro-2-ethoxybenzaldehydesemicarbazone.—The semicarbazone of 5-nitro-2-ethoxybenzaldehyde (see this vol., p. 2721) exists in two monotropic polymorphic modifications. It is very sparingly soluble in boiling alcohol, acetic acid, or acetone, and on rapidly cooling a solution in any of these solvents a labile form separates in clusters of almost colourless, prismatic crystals. These, in contact with the mother-liquor at the ordinary temperature, slowly change into a stable form consisting of small, brilliant yellow crystals. This form is also obtained on allowing an alcoholic solution, saturated at the boiling point, to cool during 3 days in a slow cooler.

The crystals of the labile form, which are not suitable for measurement, are of slender prismatic habit and strongly doubly-refractive. The extinction on all the prism faces examined is oblique with the interfacial edges.

The crystals of the stable form belong to the monoclinic system. The axial elements are $a : b : c = 1·3963 : 1 : 2·1269$; $\beta = 104° 26'$.

The forms observed were *a*{100}, *l*{210}, *m*{110}, *c*{001}, and, less frequently, *R*{$\bar{1}$01}.

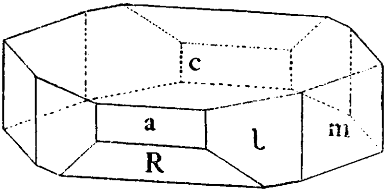
The interfacial angles are given in the accompanying table.

Angle.	No.	Limits.	Mean observed.	Calc.
100 : 001	4	75° 0′—75° 49′	75° 34′	*
100 : 210	12	33° 50′—34° 20′	34° 4′	*
001 : $\bar{1}$01	4	66° 57′—67° 38′	67° 11′	*
110 : 210	12	19° 10′—19° 37′	19° 22′	19° 27′
001 : 210	4	78° 19′—78° 32′	78° 26′	78° 5′

Fair cleavage occurs parallel to *c*{001}. The density of the crystals of the stable form at 18·5° is 1·437.

At 20°, 100 g. of alcohol, of chloroform, and of acetone dissolve 0·10 g., 0·05 g., and 0·30 g., respectively, of the stable form.

The very slight solubility of the semicarbazone in all solvents, together with the fact that, on shaking in the thermostat, the transformation into the stable form is rapid, has prevented the solubility of the labile form from being determined.



Semicarbazone of 5-nitro-2-ethoxybenzaldehyde.

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