CCCLX.—*Studies in Polymorphism. Part II. Further Researches on* o-*Nitroaniline.*

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Mention has already been made (Part I; J., 1930, 729) of the slow development of dark brown patches in films of *o*-nitroaniline after the change from the " unstable " to the " stable " form is complete. This phenomenon has now been studied and is mainly due to a change into a third polymorph of still higher stability. We have therefore renamed the " unstable " and the " stable " form the α- and the β-form respectively, and have called the third variety the γ-form. The last we now identify with the form described crystallographically by von Jaeger (*Z. Krist.*, 1905, **40**, 114) and by Hermann and Burak (*ibid.*, 1928, **67**, 189).

The present paper records the m. p. and crystallographic properties of the γ-form and some additional crystallographic data for the other two forms. Also, our results are discussed in relation to the work of the above authors.

γ-Form.—Four slides were prepared from a specimen of *o*-nitroaniline which had been recrystallised five times from absolute alcohol, dried by a current of dry air, and then placed over phosphoric oxide until the β-form gave a constant m. p. of 70·15°. (The methods used to clean and manipulate the slides and cover-slips and to determine the m. p.'s were as described in Part I.) Two of these slides were placed with calcium chloride in a stoppered tube maintained at 60° by a thermostat, the object being to accelerate the formation of the dark brown patches which it was desired to study. The nitroaniline was prevented from evaporating by sealing on the cover-slips with glycerol–litharge cement. This was not applied, however, until some evaporation round the edges had occurred, so that it was not in contact with the nitroaniline. The two remaining slides were placed in a desiccator (calcium chloride) at room temperature.

The heated slides were examined from day to day with a polarising microscope, with the following results. All the α-form had disappeared by the end of the first day, and the films consisted mainly of the original spherulites of the β-form and large single crystals with irregular outlines, formed apparently by the recrystallisation of small β-crystals. In addition, however, there were patches of material which, between crossed Nicols, proved to be multiply twinned crystals, the laminæ of which possessed an oblique extinction of 7° (in sodium light) with reference to the trace of the twinning planes, and marked extinction dispersion in white light, shown by the fact that they did not extinguish perfectly but gave, instead, a dark green colour. These twinned crystals gradually increased in size at the expense of the surrounding β-crystals, and at the end of 3 weeks they occupied the greater part of the films. After a month a m. p. determination on one of the slides gave the values, β-form 69·95°,* twinned crystals 71·2°.

The two slides kept at room temperature were also examined from time to time under the microscope. The changes occurring in them were naturally much slower than those in the heated slides. After about a fortnight the films consisted of β-spherulites, and large irregular β-crystals, formed presumably by recrystallisation from small β-crystals as in the case of the heated slides. After about a month, dark brown patches had started to develop. These showed a very confused structure under the microscope, and between crossed Nicols they gave dark greens and reds instead of extinguishing perfectly. At the end of 3 months one slide had been entirely converted into this material, but the other still preserved some of the original β-crystals. A m. p. determination on the latter slide gave : β-form 70·15—70·2°, dark brown patches 71·15°.

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* The crystals observed were at the edge of the slide, so possibly water from the glycerol–litharge cement was responsible for this slight depression of the normal value.

The m. p.'s of the twinned patches on the heated slides and the dark brown patches on the unheated slides, taken in conjunction with their optical properties, showed that they were composed of the same material, which was different from, and of higher stability than, either the α- or the β-form. This γ-form appears to be the most stable variety of *o*-nitroaniline, for specimens which we have had under observation for over 18 months have shown no change. Its oblique extinction and extinction dispersion show that it is not orthorhombic.

Crystals of *o*-nitroaniline obtained by other methods, given in Table I, in the course of experiments on the purification of the substance and on its preparation in a form suitable for the goniometer, were also proved by their m. p.'s to be the γ-form. To determine the latter in such cases, the crystals were powdered in a carefully dried agate mortar and a little of the powder was spread between a slide and a cover-slip held together by fine cotton-covered wire. The slide was then inserted in the m. p. apparatus previously described.

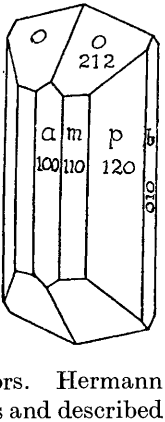
TABLE I.

M. p.'s of γ-o-nitroaniline from various sources.

Method of preparation.	M. p.
1. Transformation of β- to γ-form on slides	(i) 71·2° (ii) 71·15
2. 5 Recrystallisations from alcohol–water,* then slow sublimation in a vacuum	71·2
3. 10 Recrystallisations from alcohol–water	(i) 71·2 (ii) 71·25
4. 12 Recrystallisations from alcohol–water, then 1 recrystallisation from acetone–ligroin–carbon tetrachloride	(i) 71·3 (ii) 71·15—71·2 (iii) 71·2 (iv) 71·25—71·3

* In all cases equal volumes of each of the solvents in a mixture were used.

FIG. 1.



o-Nitroaniline was first described crystallographically by von Jaeger (*loc. cit.*) as orthorhombic, bipyramidal, the crystals (obtained from a solution of the substance in a mixture of acetone, ligroin, and carbon tetrachloride) being elongated in the direction of the vertical axis and showing the forms *a*(100), *b*(010), *p*(110), *m*(210), and *o*(414). Von Groth (*Chem. Krist.*, Vol. IV, 1917, p. 180), taking von Jaeger's measurements, renamed the *p*, *m*, and *o* faces thus: *p*(120), *m*(110), and *o*(212), and gave the axial ratios $a : b : c = 0{\cdot}6834 : 1 : 0{\cdot}5792$. Fig. 1 shows *o*-nitroaniline according to these authors. Hermann and Burak (*loc. cit.*) examined the substance by *X*-rays and described it as orthorhombic, holohedral, space group V_h^{17}, having spacings

$a : b : c = 10{\cdot}09 : 29{\cdot}44 : 8{\cdot}52$ Å., equivalent to axial ratios of $0{\cdot}3427 : 1 : 0{\cdot}2894$, these being nearly half the values given by von Groth. They crystallised their material from the same solvent as that used by von Jaeger.

The first crystals obtained in our work which were measurable on the goniometer were those formed as in Preparation 2 (Table I), and with the exception that the forms $a(100)$ and $m(110)$ (von Groth's nomenclature) appeared to be very rarely developed, the angular values agreed closely with von Jaeger's. A complete examination was not possible owing to the poor development of the end faces. Our results are given in Table II, cols. 2 and 3, the corresponding values of von Jaeger being in the last column.

TABLE II.

Angular measurements of γ-crystals.

	Sublimed crystals.		Crystals from solution.		
	No. of readings.	Mean value.	No. of readings.	Mean value.	Von Jaeger.
$a : o = (110) : (212)$	—	—	—	—	50° 51′*
$b : p = (010) : (120)$	11	36° 15′	32	36° 11′*	36 11·5*
$m : m = (110) : (1\bar{1}0)$	—	—	12	68 46	—
$p : m = (120) : (110)$	—	—	40	19 27	19 23
$m : a = (110) : (100)$	—	—	6	34 24	34 22
$o : m = (212) : (110)$	—	—	9	49 38*	48 59
$b : o = (010) : (212)$	6	77 22	3	77 29	77 20·5
$o : o = (212) : (2\bar{1}2)$	3	25 22	—	—	25 19
$o : o = (212) : (\bar{2}12)$	—	—	2	78 18·5	78 18·5

* Fundamental angles.

After many trials, measurable crystals from solution were obtained, using von Jaeger's solvent (Table I, Preparation 4). No details being given by him, we used equal volumes of the ingredients, and ligroin of b. p. 40—60°. The best crystals were grown by the slow evaporation of solvent from a saturated solution. The angles of these crystals showed no appreciable deviations from the values of von Jaeger, with the exception of $o : m$ and, to a less serious extent, $b : o$ (Table II, cols. 4, 5, and 6). Von Jaeger calculated these two angles to be 48° 9′ and 77° 23′, but we find that his calculation was incorrect and make them 50° 1′ and 77° 32·5′ respectively. His observed values differ considerably from these, particularly in the former case, and our own $o : m$ value does not agree with this calculation either. To investigate these discrepancies it would have been desirable to repeat the measurement of von Jaeger's fundamental angle $a : o$, but we were unable to get any acceptable readings from it at all. Using instead our value of $o : m$ (in preference to $b : o$, on the grounds of better reflexions and more concordant readings) and, with von Jaeger, $b : p$ as our fundamental angles, we calculate that the angle $b : o$ should be 77° 27′. This is in good agreement with our observed value and in fair agreement with that for the sublimed crystals (col. 3). Our results therefore agree better amongst themselves than do von Jaeger's. The axial ratios calculated from our fundamental angles are $a : b : c = 0{\cdot}6834 : 1 : 0{\cdot}5867$, but in view of the small number of readings obtained on end faces, we do not regard the c ratio as definitive.

This goniometric study confirmed the orthorhombic symmetry of the crystals. Their m. p.'s [Table I, Preparation 4, (i) and (iii)], however, were the same as the m. p.'s of the multiply twinned crystals on the slides, which, from their optical properties, were undoubtedly not orthorhombic. Further, although many of the former crystals appeared to give straight extinction in all positions round the prism zone, in agreement with their orthorhombic symmetry (an exact determination was impossible owing to the thickness and shape of the crystals), they showed, in certain positions, the green dispersion colour characteristic of the crystals on the slides. Our explanation of these apparent anomalies is based on the following observations.

Some of the crystals deposited from the ternary solvent were found by microscopic examination to be twinned. Their m. p.'s [Table I, Preparation 4, (ii) and (iv)] were the same as those of other crystals from this solvent. Typical examples are illustrated in Fig. 2. Types (i) and (ii) had a central striated portion which probably consisted of fine multiple twins, on each side of which appeared larger individuals which possessed a maximum oblique extinction of about 7° with reference to the vertical edge, and marked extinction dispersion similar to that given by the multiple twins on the slides. In some cases [Type (i)] the individuals were similarly orientated optically and appeared to form complementary parts of a single monoclinic crystal, as inspection of the edge angles (measured under the microscope) given in the figure will show. In others [Type (ii)] the optical and geometrical orientation was opposite. Crystals of Type (iii) were simple twins essentially like those of Type (ii) but of acicular habit and without the central striated portion. With all three types, straight extinction was observed at right angles to the direction of maximum extinction.* The crystals were therefore monoclinic and twinned by rotation about the clino-axis. They were not perfect enough to give good goniometric measurements and so no complete examination was possible, the prism faces being often curved and the end faces as a rule merely indicated. A few

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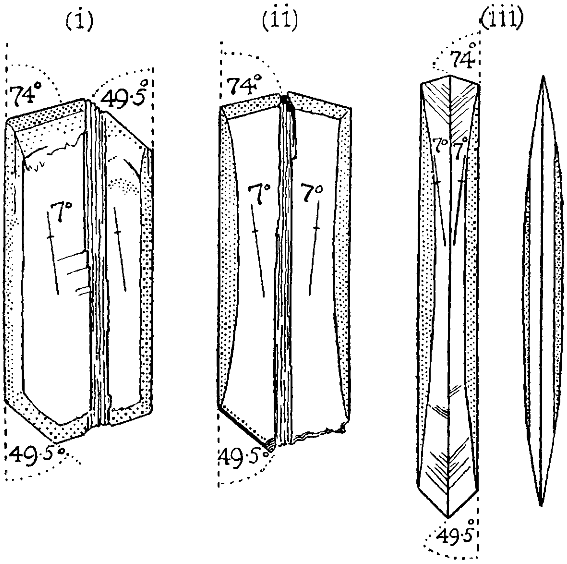
* Straight extinction was also observed with some of the γ-crystals on the slides, and these showed no dispersion of the extinction position. This confirms the monoclinic symmetry of this form.

acceptable measurements round the prism zone gave the following angular values in order : 34° 33′, 19° 22′, 36° 18′; these are very near to those of *m* : *a*, *p* : *m*, and *b* : *p* respectively of the orthorhombic type given in Table II.

From the above observations we have been led to suggest that the orthorhombic crystals are composed of submicroscopic monoclinic laminæ twinned, probably by rotation about the clino-axis, in such a way as to give pseudo-orthorhombic symmetry. The marked tendency towards multiple twinning, sometimes very fine, shown by the γ-form on microscope slides lends support to this hypothesis.

Fig. 2.



It should be remarked that, if this is so, the optical properties of the monoclinic laminæ show that their *b* or ortho-axis is the *a* axis of the pseudo-orthorhombic crystal. It is to be expected that *X*-ray measurements would reveal the truly monoclinic nature of the crystals, and the fact that the work of Hermann and Burak (*loc. cit.*) did not do so is, of course, at variance with our explanation.* We hope shortly to carry out a re-examination of the substance by *X*-rays.

The following optical data about the γ-form, in addition to those recorded above, have been obtained on the polarising microscope : Pleochroism, X = orange, Y = yellow, Z = orange; optical axial

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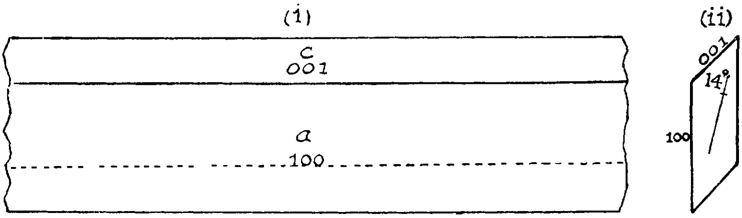
* It is assumed that Hermann and Burak were dealing with the same form as von Jaeger, since they used the same solvent.

plane and Z (for sodium light) normal to the face giving the maximum extinction; 2V near 90°, sign doubtful.

β-*Form.*—In the course of our attempts to prepare suitable material for the goniometer, we tried separating the crystals from a partially solidified melt of *o*-nitroaniline, by rapidly pouring off the liquid—on the principle of the well-known method of preparing monoclinic sulphur. The following procedure was found to be satisfactory. About 2 g. of the substance, recrystallised 10—12 times from alcohol–water and dried over phosphoric oxide for several weeks, were sealed in a thick-walled glass tube about 4″ long and $\frac{3}{4}''$ wide, which had previously been carefully cleaned and dried. The tube was then immersed in a large beaker of water, being held in an upright position by means of a special kind of clamp which could be rotated *in situ*, thus inverting the tube without removing it from the beaker. The water was heated to melt the nitroaniline, and was then allowed to cool very slowly. When a suitable quantity of solid had formed, the tube was inverted, and the liquid allowed to drain off completely from the crystals, which always remained stuck to the walls of the tube at the end where they had formed. The tube was then removed from the bath, dried, cut in halves, and the best crystals were picked out. Examination on the polarising microscope showed them invariably to have the optical properties of the β-form, and this was confirmed by the following m. p.'s of different specimens: 70 2—70·35°, 70·15°, 70·2°. When doing these m. p. determinations, it was often observed that, after the crystals had melted, they started to solidify with still rising temperature, showing that the substance was undergoing transformation to the γ-form, a fact confirmed by subsequent microscopic examination.

FIG. 3.



The best crystals obtained in this way were elongated plates (Fig. 3), the faces parallel to the direction of elongation being often well formed. The end faces, however, were usually non-existent and were never good enough to give reflexions on the goniometer. These crystals gave straight extinction and no dispersion in all directions normal to the axis of elongation. When lying on one of the broad faces, they gave an obtuse bisectrix figure tilted slightly in a direction normal to the optic axial plane. After much difficulty we succeeded in preparing a few end sections [Fig. 3, (ii)] by cutting the crystals into short lengths with a razor. (Any form of grinding seems to be quite out of the question with the substance.) These sections gave an oblique extinction of 14° (in sodium light) with reference to the longer edge (see figure), and dispersion in white light. The β-form is therefore not orthorhombic as stated in Part I, but monoclinic, the reason for this mistake being that at that time the only material available was that on slides, on which the crystals always lie so as to give straight extinction, being elongated along the *b* axis.

The faces developed were referred to the (100) : (001) zone and the angle $a : c = (100) : (001)$ gave the value 42° 35′ (mean of 19 readings). Since, as stated above, no end faces were developed, further examination was impossible. The pleochroism was X = light orange, Y = yellow, Z = dark orange; 2E probably small, sign negative; optic axial plane and X normal to the end section.

α-*Form.*—We have not attempted to prepare the α-form otherwise than on microscope slides, but have been able to obtain it in larger crystals than those hitherto described, by using *o*-nitroaniline distilled on to the slides (see Part I, p. 728), the low stabilisation rate of such specimens enabling us to crystallise the α-form at a higher temperature, and therefore more slowly than is usually possible. The crystals were commonly simply twinned and occasionally multiply twinned. The maximum oblique extinction was 21° (this replaces our approximate value of 24° given in Part I), but some crystals presented faces showing straight extinction. The α-form is therefore monoclinic. There was a considerable degree of dispersion, but the extinction position was not dispersed. The faces showing straight extinction gave in sodium light what appeared to be an inclined optic normal figure, and those having the maximum oblique extinction a Z bisectrix figure, which was probably obtuse but may have been given by a very large acute angle. The optic axial plane and Z are therefore normal to the monoclinic symmetry plane. The pleochroism is X = pale yellow, Y = yellow, Z = orange.

It is significant that the m. p.'s of *o*-nitroaniline recorded in the literature cover a range of temperature, *viz.*, 68° to 71·5°, which almost coincides with that covered by the m. p.'s of the three polymorphs. The m. p. determined by the ordinary capillary-tube method must depend upon whether unstable forms are present or not, which in turn depends upon the age and method of preparation of the specimen, and these factors no doubt influenced some of the previous determinations. The fact that the highest m. p. which we have observed for the γ-form, *viz.*, 71·3°, is below the upper limit of these determinations is, we think, due to our apparatus enabling us to detect the commencement of melting at a lower temperature than is possible in the ordinary method. The extensive recrystallisation of the substance, in the final stages of which specially purified alcohol was used (details of the procedure will be published later), the prolonged drying of the final product, and our use of a carefully standardised thermometer, make it unlikely that either the purity of our material or the measurement of our temperatures was at fault.

Our discovery that the β-form is deposited from a melt has a bearing on any attempt to determine the f. p. of *o*-nitroaniline. Preliminary experiments on this property were mentioned in Part I, and a further study is in progress in the light of the facts now recorded.

Summary.

1. In addition to the two polymorphs, α and β, previously described, a third, γ, has been identified, which is apparently the most stable form of *o*-nitroaniline. It is the same form as that studied crystallographically by von Jaeger and by Hermann and Burak, and has been prepared by the stabilisation of the β-form on microscope slides, by slow sublimation in a vacuum, and by recrystallisation from aqueous alcohol, or from acetone–ligroin–carbon tetrachloride.

2. The m. p. of the γ-form is 71·2—71·3°. It is monoclinic but, presumably by fine multiple twinning, can assume a pseudo-orthorhombic habit. Some of its optical properties have been determined.

3. The β-form is monoclinic, but in thin films it is always elongated in the direction of the *b* axis, and thus under the microscope appears to be orthorhombic.

4. Some additional optical properties of the α- and the β-form are recorded. The former is monoclinic.

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