404. *Identification of Some Aromatic Nitro-compounds by Optical Crystallographic Methods.*

By E. SYDNEY DAVIES and NORMAN H. HARTSHORNE.

THE identification of an organic compound by ordinary methods is sometimes difficult or tedious, as, *e.g.*, when it is present in a mixture, or has an indefinite m. p., or especially when it may be associated with isomeric or closely related compounds from which it cannot be sharply differentiated by simple tests. Under such conditions, however, it can often be readily identified by its characteristic optical crystallographic properties (or, if it is a liquid, by those of one of its solid derivatives), determined by means of the polarising microscope. With the object of demonstrating this method and furnishing the necessary data, optical crystallographic studies on the following series of compounds have been undertaken in recent years: α- and β-naphthylamine salts of naphthalene-mono- and -di-sulphonic acids (Ambler, *Ind. Eng. Chem.*, 1920, **12**, 1081); hydrochloride and naphthalene-mono- and -di-sulphonates of benzyl-ψ-thiourea (Hann and Keenan, *J. Physical Chem.*, 1927, **31**, 1082); amino-acids (Keenan, *J. Biol. Chem.*, 1924, **62**, 163; 1929, **83**, 137); 3 : 5-dinitrobenzoates of alcohols, and 2 : 4-dinitrophenylhydrazones of aldehydes (Bryant, *J. Amer. Chem. Soc.*, 1932, **54**, 3758; 1933, **55**, 3201); sugars (Wherry, *J. Washington Acad. Sci.*, 1928, **18**, 302; *J. Amer. Chem. Soc.*, 1918, **40**, 1858; 1920, **42**, 125; Keenan, *J. Washington Acad. Sci.*, 1926, **16**, 433); pentosazones and hexosazones (Wright, *J. Amer. Chem. Soc.*, 1916, **38**, 1647); phenylosazones and other derivatives of sugars (Morris, *ibid.*, 1932, **54**, 2843); heptitols (Wherry, *J. Biol. Chem.*, 1920, **42**, 377); alkaloids (Wright, *loc. cit.*; Wherry, *U.S. Dept. Agr. Bull.*, No. 679, 1918; Wherry and Yanovsky, *J. Amer. Chem. Soc.*, 1918, **40**, 1063; Poe and Sellars, *ibid.*, 1932, **54**, 249; *Ind. Eng. Chem., Anal.*, 1932, **4**, 69).

In the majority of these studies, the most distinctive optical characters of the compounds have been embodied in a table of systematic tests, called a determinative table. These tests consist mainly in mounting the crystals to be identified in one liquid after another until a refractive index is matched, *e.g.*, with elongated crystals, the index for light vibrating along their length. Their identity is then usually confirmed by some other characteristic index, *e.g.*, that commonly shown for light vibrating across their length, or by some prominent property such as abnormal polarisation colours.

It is clear that tests of this kind, depending largely as they do upon the assumption that the crystals lie preferentially upon certain faces, may be ineffective if applied to crystals of a different habit, which orientate themselves on a slide in some other way. It is therefore very important that every such table be accompanied by details of the conditions under which the specimens were crystallised; other solvents, *e.g.*, may not only affect the habits but form solvates. This information is lacking from some of the earlier determinative tables, and their general applicability is therefore doubtful; this, however, does not detract from the value of the optical data (principal refractive indices, size of optic axial angle, etc.) which usually accompany such tables.

The present work was undertaken to examine the possibilities of the optical method of identification in a series of *o*-, *m*-, and *p*-isomerides of benzenoid compounds. The following compounds were studied: *m*- and *p*-nitroanilines (the *o*-compound had already been described; Dippy and Hartshorne, J., 1930, 726; Hartshorne and Stuart, J., 1931, 2583); *o*- and *p*-nitrobenzyl alcohols; *p*-nitrotoluene; *o*-, *m*-, and *p*-nitro-derivatives of phenols, benzoic acids, aldehydes, bromo- and chloro-benzenes. No attempt was made to examine the compounds completely, but the optical and morphological properties of the sections commonly presented by crystals grown under definite conditions were determined, since it was thought that these properties would be the most useful criteria for the purpose of identification. In addition, however, some observations were made on material taken straight from the stock bottle, and on " melted " slides (see below).

Optical data for many of these compounds appear in Groth's " Chemische Kristallographie," but are ancillary to goniometrical studies and mostly unsuitable as criteria for identifying the compounds under the microscope. Moreover, no refractive indices are given.

EXPERIMENTAL.

Apparatus.—The microscope used was a Swift " Lapidex," with the converging lens mounted in a slider on the rotating stage, thus allowing easy passage between parallel and convergent illumination; 1″ and ¼″ objectives sufficed for all the observations. The instrument having no Bertrand lens, interference figures were either viewed directly by removing the ocular, or focused by means of a Becke lens fitted over the ocular. For isolating the interference figures of small crystals, a rotating stop ocular supplied by Messrs. Swift and Son was used.

Monochromatic Light.—The approach work to the refractive indices of the crystals was carried out in white light, but, owing to the high dispersions encountered, the final stages demanded monochromatic light, as did the study of many of the interference figures. A " Neron " sodium vapour lamp (Bellingham and Stanley) satisfactorily served the purpose.

Immersion Media.—The refractive indices were determined by the Becke immersion method. For most of the substances the following immersion media sufficed: medicinal paraffin, α-bromonaphthalene, and methylene iodide, mixed in adjacent pairs in various proportions; solutions of sulphur, and of stannic, arsenious, and antimonious iodides in methylene iodide. Some substances, however, notably *p*-nitrotoluene, *o*- and *m*-bromonitrobenzenes, and *p*-chloronitrobenzene dissolved rapidly in these liquids, and in these cases aqueous glycerol solutions of potassium mercuric iodide (Wherry, *U.S. Dept. Agr. Bull.*, No. 679, 1918) were suitable, the only objection to these media being that their maximum index is 1·71.

All media of refractive index up to 1·70 were standardised on an Abbé refractometer, and a stock series with intervals of about 0·01 was made up. The final matching of crystal and liquid required in most cases the mixing of an adjacent pair in this series, the index of the mixture being determined, immediately after obtaining the match, on the refractometer, which was placed near the microscope. In this way it was ensured that the liquid was standardised at approximately the same temperature as that prevailing on the microscope stage. The results with these liquids are considered to be accurate to ± 0·0015.

Media of higher refractive index were standardised by comparison under the microscope with the following isotropic solids of known refractive index: ammonium iodide (1·701), ammonium bromide (1·715), magnesium oxide (1·736), arsenious oxide (1·755), sodium iodide (1·774), strontium oxide (1·87). Owing to the considerable intervals in this series, the refractive indices determined with these liquids are only given to 0·01. The most refractive medium used had a value of 1·78, and so indices falling above this are merely given as " $>$1·78."

Preparation and Mounting of Material.—The substances were supplied by British Drug Houses, with the exception of *m*- and *p*-nitroaniline, from Merck and Schuchardt respectively.

Preliminary observations were made on material as supplied, crushed to a suitable state of division; and also on " melted " slides, *i.e.*, mounts prepared by melting a little of the substances between a slide and a cover slip, and allowing it to crystallise by slow cooling. In the latter case, if excessive supercooling occurred, resulting in the sudden growth of crystals too small to examine satisfactorily, the substance was remelted except for a small portion to act as a nucleus, and the cooling repeated. These " melted " slides often yielded clearer interference figures than did other mounts, owing to the perfect plate-like form of the crystals, and so facilitated the determination of the optical sign and the optic axial angle.

The main observations were made on specimens prepared by recrystallisation from various solvents (see below), the solutions being mechanically stirred during crystallisation, thus ensuring that the crystals formed were small enough to mount directly. The apparatus for this purpose consisted of a large test-tube containing about 5 c.c. of the solution, and fitted with a cork carrying a rotating stirrer. Crystallisation was effected either by cooling a hot saturated solution, or by evaporating a cold one, the latter method being used for some substances of low m. p. which were prone to melt under the solvent. When the cooling method was adopted, the lower part of the test-tube was usually kept in a water-bath, by means of which the rate of cooling could be controlled. For the evaporation method, a stream of air was drawn over the solution through two tubes passing through the cork of the test-tube.

In a few cases these methods of recrystallisation were unsuccessful, and crystals were obtained by the slow evaporation of solution on a watch-glass, covered by a glass capsule.

Each substance was recrystallised from both a polar and a non-polar solvent, for it was thought possible that the polarity might influence the crystal habit. Alcohol and benzene were used in most cases, but where these gave unsatisfactory results, a selection was made from the following: water, chloroform, carbon tetrachloride, acetone, toluene. In all cases, however, the crystal habit was practically the same for all the solvents used.

The m. p.'s of all the specimens examined were determined in order to see whether solvates were formed or different polymorphic forms developed, but only in one case (possibly two) did polymorphism occur, and no solvates were found.

Results.

The results are described by means of Figs. 1—20 and the notes below. The diagrams refer to the recrystallised specimens, and show the edge angles and optical properties of the sections which they most commonly present when mounted on a slide. Only the simple outlines of the crystals are drawn, small secondary faces on edges and corners being omitted. In order to economise space, elongated crystals are shown considerably shortened. The vibration directions are denoted by double-headed arrows, and are marked with their refractive indices (*D* line) and, if the substance is pleochroic, the colours transmitted. Cleavage directions are indicated by broken lines. The interference figure (in the 45° position) is drawn inside the central circle and is orientated correctly with respect to the crystal outline. The numerical apertures of the objective and converger with which the figures were obtained were 0·8 and 1·0 respectively. Data obvious from the diagrams are not repeated in the notes unless they call for special mention.

As is well known, it is very difficult to distinguish an optic normal figure from an obtuse bisectrix figure when $2V$ is small, and also to distinguish an acute from an obtuse bisectrix figure when $2V$ is very large. Several such cases of uncertainty arose in the present work, and where it was impossible to make a definite decision, the most probable solution is given, and dependent properties, *viz.*, the optic sign and the identity of the indices (whether α, β, or γ), are followed by a query.

Groth's data (*op. cit.*), when available, are given in brackets immediately after the name of each compound.

Unless otherwise stated, recrystallised specimens were obtained from mechanically stirred solutions (see above).

m-*Nitroaniline* [rhombic bipyramidal with elongation along *c* and m. p. 109·9°], crystallised from alcohol and carbon tetrachloride (by cooling hot solutions), had m. p. 113·5—114°, and consisted of yellow hemimorphic plates (Fig. 1), which, though orthorhombic, were obviously not bipyramidal. The apex angle of the pointed end was near either 80° or 100°; β was found to be 1·72—1·74 by mounting the crystals in glass powder, whereby some were induced to stand on edge.

p-*Nitroaniline* [monoclinic prismatic with perfect cleavage along *c* (001), the axial plane being *b* (010)], crystallised from alcohol, benzene, and carbon tetrachloride (by cooling hot solutions), had m. p. 147°. The crystals consisted of yellow hexagonal plates (Fig. 2), the properties of which were in harmony with Groth's orientation of the axial plane. The curvature of the isogyre in the 45° position was difficult to observe with certainty, but probably $2V$ is about 80° and the optic sign +. Since the birefringence of this inclined optic axial section is $>0{\cdot}22$, that of the substance must be very large.

o-*Nitrophenol* [monoclinic prismatic with cleavage along, and the axial plane normal to, *b* (010), the acute bisectrix being at 5° to the *c* axis in the acute angle β], crystallised from alcohol and benzene (by cooling hot solutions), consisted of greenish elongated plates and blades (Fig. 3), m. p. 45·5°. The interference figure is probably an obtuse bisectrix; optic sign — (?).

m-*Nitrophenol* [monoclinic prismatic with perfect cleavage along *m* (110), and the axial plane normal to *b* (010) and nearly normal to *c*], crystallised from water and benzene (by cooling hot solutions), had m. p. 96°. The crystals consisted of pyramidal fragments, one end being usually imperfectly developed (Fig. 4), though occasional individuals with more or less rhombic outlines were observed. In specimens crystallised from water, some elongated crystals with straight extinction and presumed optic normal interference figures were also seen. " Melted " slides showed very clearly characteristic abnormal polarisation colours on either side of the extinction position, *viz.*, lavender ⟷ grey (imperfect extinction) ⟷ fawn. $2V$ *ca.* 60°; optic sign +.

p-*Nitrophenol* [two modifications, both monoclinic prismatic], according to Barker, has transition temperature 63°, above which the α-form (almost colourless), and below which the β-form (yellow), is stable. A " melted " slide allowed to crystallise above 63° yielded both colourless and pale yellow crystals. The former, presumed to be the α-form, showed the following properties: cleavage along the direction of elongation; bright polarisation colours of purple, blue, green, and gold; extinction angle 30·5°; elongation —; interference figure, obtuse bisectrix (presumed); optic sign + (?). The pale yellow crystals were similar to those obtained as below, which were evidently the β-form.

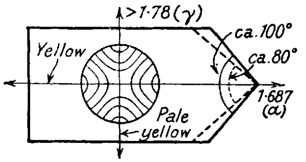


Fig. 1.—*m-Nitroaniline.*

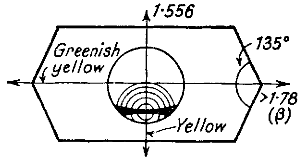


Fig. 2.—*p-Nitroaniline.*

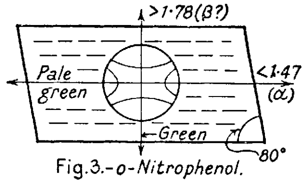


Fig. 3.—*o-Nitrophenol.*

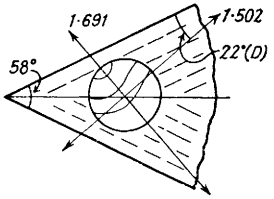


Fig. 4.—*m-Nitrophenol.*

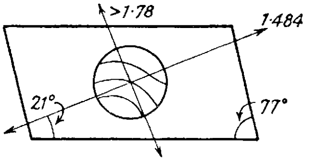
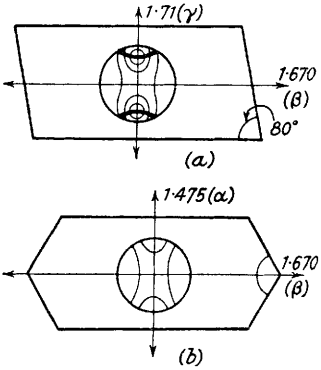


Fig. 5.—*p-Nitrophenol.*



(a)

(b)

Fig. 6.—*p-Nitrotoluene.*

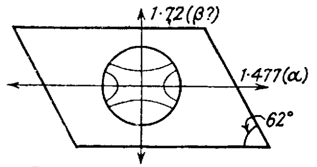


Fig. 7.—*o-Nitrobenzylalcohol.*

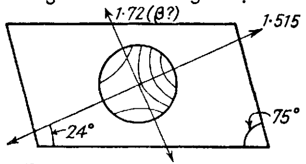


Fig. 8.—*p-Nitrobenzylalcohol.*

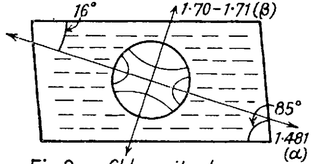


Fig. 9.—*o-Chloronitrobenzene.*

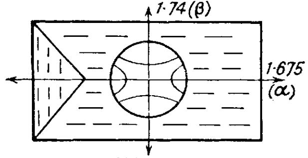


Fig. 10.—*m-Chloronitrobenzene.*

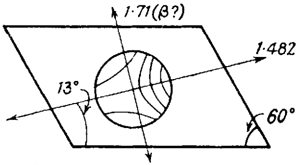


Fig. 11.—*p-Chloronitrobenzene.*

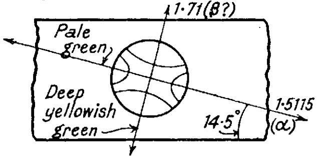


Fig. 12.—*o-Bromonitrobenzene.*

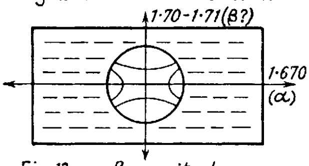


Fig. 13.—*m-Bromonitrobenzene.*

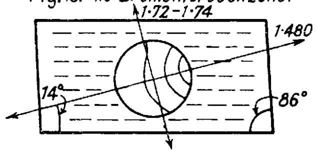


Fig. 14.—*p-Bromonitrobenzene.*

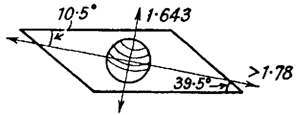


Fig. 15.—*o-Nitrobenzoic acid.*

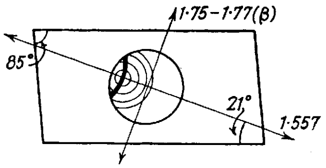
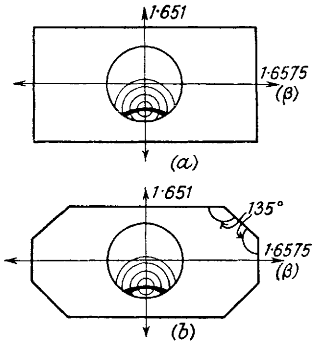


Fig. 16.—*m-Nitrobenzoic acid.*



(a)

(b)

Fig. 17.—*p-Nitrobenzoic acid.*

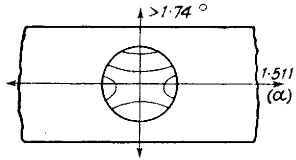


Fig. 18.—*o-Nitrobenzaldehyde.*

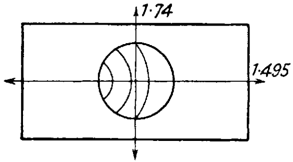


Fig. 19.—*m-Nitrobenzaldehyde.*

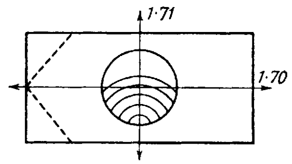


Fig. 20.—*p-Nitrobenzaldehyde.*

Specimens crystallised from alcohol, toluene, and water (by cooling hot solutions) were identical; m. p. 113·5°. They consisted of elongated plates (Fig. 5). From observations on these and the corresponding crystals on the " melted " slide (above), $2V$ is 60—75°, and the optic sign +. Attempts to crystallise the α-form from toluene above 63° were only successful to the extent of affording a few plates with inclined terminations (acute angle 40°) and extinction angle 30°.

p-*Nitrotoluene* [rhombic bipyramidal with perfect cleavage along *b* (010), axial plane *a* (100), optic sign —, and 2H 57° 41′ (D)], crystallised from alcohol and benzene (by cooling hot solutions), had m.p. 54°. In each case two sections were presented (Figs. 6*a* and *b*) which showed clearly the rhombic symmetry of the crystals. The optic sign is negative, and $\rho > v$. The crystals were colourless.

o-*Nitrobenzyl alcohol*, crystallised from alcohol and benzene (by evaporation on a watch-glass), had m. p. 74°. The crystals consisted of pale brownish blades with inclined terminations (Fig. 7), and showed abnormal purple, blue, and gold polarisation colours. The figure is probably an obtuse bisectrix, and the optic sign is — (?).

p-*Nitrobenzyl alcohol* crystallised from alcohol and benzene (on evaporation on a watch-glass) as pale yellow elongated plates with inclined terminations (Fig. 8), m. p. 93°. The extinction position was strongly dispersed, the colours shown in passing through this position being yellow ←→ bluish-green (imperfect extinction) ←→ yellow. The figure was probably an obtuse bisectrix inclined along the optic axial plane; optic sign — (?).

o-*Chloronitrobenzene* [monoclinic, with an extinction angle of 16° on *m* (110), an acute bisectrix figure on the section normal to *c*, and cleavage along *a* (100), and (a little less distinct) along *b* (010)] crystallised from alcohol and benzene (on evaporation on a watch-glass), as colourless elongated plates and blades with inclined terminations (Fig. 9), m. p. 33°. The centred interference figure and oblique extinction indicate that the section is parallel to *b* (010). If the direction of elongation is *c*, the cleavage is along *a* (100) as given by Groth. On the other hand, the extinction angle is the same as that given by him for *m* (110), and so on this point there is disagreement. The figure on our section was probably an obtuse bisectrix, which is in harmony with Groth's statement that an acute bisectrix figure is obtained on the section normal to *c*. Optic sign — (?).

m-*Chloronitrobenzene* [rhombic pyramidal with very perfect cleavage along *b* (010), imperfect along *a* (100); optic sign —; axial plane *a* (100); acute bisectrix *c*; 2E = 91° 23′ (D)], crystallised from alcohol, carbon tetrachloride, and benzene (by evaporation in a watch-glass or small beaker), had m. p. 44·5°. The crystals were hemimorphic prisms presenting inclined upper faces, and showing cleavage parallel to the plane of the section (Fig. 10), which is therefore probably the *b* (010) of Groth. The figure is probably an obtuse bisectrix and the optic sign —. If the direction of elongation is *c*, this is in harmony with Groth's data.

p-*Chloronitrobenzene* [monoclinic prismatic; m. p. 83·5°], crystallised from alcohol and benzene (by evaporation in the stirring apparatus), formed colourless needles and elongated plates with inclined terminations (Fig. 11), m. p. 83·5°. The figure was probably an obtuse bisectrix inclined along the optic axial plane; optic sign — (?).

o-*Bromonitrobenzene* [irregular monoclinic prisms without end faces; m. p. 41°] crystallised from alcohol and benzene (on evaporation on a watch-glass) as deep yellowish-green needles with irregular terminations and some rectangular tablets (Fig. 12), m. p. 43°. The figure was probably an obtuse bisectrix and the optic sign — (?).

m-*Bromonitrobenzene* [rhombic pyramidal, with optic sign —, axial plane *a* (100), acute bisectrix *c*, and 2E 113° 3′; m. p. 56·4°] crystallised from alcohol and benzene (on cooling hot solutions) in colourless elongated rectangular plates, some with prismatic end faces, showing abnormal purple, blue, and pink polarisation colours (Fig. 13), m. p. 56°. The figure was probably an obtuse bisectrix and the optic sign — (?).

p-*Bromonitrobenzene* [triclinic; m. p. 126—127°] crystallised from alcohol and benzene (on evaporation) as creamish elongated plates and needles with inclined end faces (Fig. 14), m. p. 127°. The crystals showed a greatly inclined single optic axial figure; optic sign + (?). The birefringence of this substance is evidently very high.

o-*Nitrobenzoic acid* [triclinic; m. p. 147°] crystallised from alcohol and benzene (on evaporation on a watch-glass) in elongated plates with very inclined end faces, m. p. 144°, crystals from alcohol being thicker and having more secondary faces than those from benzene, which, however, were better developed (Fig. 15). They gave a much inclined single optic axial figure with the axial plane across the crystal length, and the optic sign (determined on more centred figures given by crystals on a "melted" slide, and by one individual from alcohol) was +.

m-*Nitrobenzoic acid* [three modifications, all monoclinic prismatic, the stable form (m. p. 142°) having *b* (010) as the axial plane and the acute bisectrix at 56° to *c*; the axial plane of one of the other forms was also *b* (010)], crystallised from water and acetone (by cooling hot solutions), presented identical sections (Fig. 16), and melted at 137—139°. The crystals consisted of creamish blades with inclined terminations, those from acetone being the larger and showing, in some cases, secondary end faces. Twinning along the length direction was observed. Abnormal polarisation colours of purple and bluish-green were shown. The figure was a slightly inclined single optic axial, and the optic sign + ; $2V$ is about 60°.

p-*Nitrobenzoic acid* [rectangular tablets, with perfect cleavage along *c* (001), the axial plane *b* (010), and an interference figure with very strong dispersion seen through *c* (001) ; m. p. 238°], crystallised from alcohol and benzene (by cooling hot solutions), melted at 238°. Crystals from alcohol (Fig. 17*a*) differed in habit from those from benzene (Fig. 17*b*), but both presented the same section. Abnormal blue and gold polarisation colours were shown. A slightly inclined single optic axial figure was given. $2V = ca.$ 60°, the optic sign is +, and (for the axis visible) $\rho > v$.

o-*Nitrobenzaldehyde* crystallised from alcohol and benzene (on cooling hot solutions) as greenish blades with indefinite terminations (Fig. 18), m. p. 114°. The figure was probably an obtuse bisectrix, inclined in the direction normal to the axial plane, optic sign — (?).

m-*Nitrobenzaldehyde* was not obtained in well-developed forms on crystallisation from alcohol, benzene, ether, water, or carbon tetrachloride (by various methods), but as very small needles and rectangular tablets mixed with a very fine powder. All specimens melted at 58° and were colourless. The rectangular tablets presented the section shown in Fig. 19. They gave a much inclined single optic axial figure, with the axial plane along the length direction of the crystal. Some crystals giving centred optic axial figures were found, and from these the optic sign is +.

p-*Nitrobenzaldehyde*, crystallised from benzene and chloroform (by evaporation), melted at 106°. Crystals from chloroform consisted of colourless needles and rectangular tablets, and those from benzene of needles and hemimorphic tablets, one end being pointed and the other rectangular. Both specimens commonly presented the same section (Fig. 20). The polarisation colours are abnormal yellows, blues, and purples, and observations on " melted " slides (below) showed that the substance exhibits crossed axial plane dispersion.

On freshly prepared " melted " slides, sections corresponding to Fig. 20 and also acute bisectrix sections were presented. The interference figures given by the latter in white light showed strongly coloured " isogyres " (red on their inner, and blue on their outer sides) in the 45° position, these sweeping in to form a black cross in the extinction position. Insertion of light filters showed that the axial plane for red light is at right angles to that for green and blue. The optic sign for red and green is + (that for blue could not be determined with certainty). The reason why the " isogyres " are seen in white light is probably that the dispersion is much smaller in the red and yellow portions of the spectrum than in the green and blue.

On standing, the " melted " slides develop crystals showing acute bisectrix figures in which the axial plane for red and green is the same. This is probably due to polymorphic change. It is hoped to study this compound more closely.

The Identification of Unknown Compounds.—The results were tested by identifying six unknown specimens selected by third party from among the compounds. It was known how many substances were in each specimen.

Three single substances were identified, *viz.*, *m*- and *p*-nitrobenzoic acids and *p*-nitrobenzyl alcohol, as a result of a few minutes' work : *m*-nitrobenzoic acid by the characteristic appearance of the crystals on a " melted " slide and by refractive index determinations; *p*-nitrobenzoic acid by its abnormal blue and gold polarisation colours, a result which was confirmed by its recrystallising from benzene as elongated octagonal plates; *p*-nitrobenzyl alcohol by means of the extinction angle of 24° on the " melted " slide, and by refractive-index determinations on a specimen recrystallised from alcohol.

The following mixtures, in the form of fine powders, were identified : (1) *o*- and *p*-nitrobenzyl alcohols and *m*-nitrobenzaldehyde; (2) *o*- and *p*-chloronitrobenzene; (3) *o*-nitrobenzaldehyde and *p*-bromonitrobenzene. Since no useful information could be obtained from them in their original state, a partial separation of the constituents was effected by fractional crystallisation.

Mixture 1.—A " melted slide " showed the presence of yellow needles giving two types of extinction, *viz.*, straight and an oblique extinction about 25°. Very bright polarisation colours of purple, red, and green were observed pointing to the presence of a nitro-alcohol. The mixture was shaken with water; the solution was poured off, and deposited yellow needles on crystallisation; these gave straight extinction, sign of elongation —, and optic sign —, which indicated *o*-nitrobenzyl alcohol. Solution of the residue in hot water resulted in another crop of yellowish needles with an extinction angle of 24°, optic sign +, which are characteristics of *p*-nitrobenzyl alcohol.

White rectangular tablets together with a very fine powder were obtained from solution in boiling water. The tablets showed optic sign +, and the refractive indices were found to correspond with those of *m*-nitrobenzaldehyde.

The partial separation and identification of *o*- and *p*-nitrobenzyl alcohols was complete in less than 3 hours, and a total of 5 hours sufficed to include confirmatory refractive-index determinations, and detection of the *m*-nitrobenzaldehyde.

Mixture 2.—A " melted " slide showed the presence of white elongated needles all of which gave oblique extinction, the angle varying from 13° to 16°. Two types of interference figure were shown in sodium light, *viz.*, (*a*) an acute bisectrix figure with optic sign +, by needles with an extinction angle of 16°; (*b*) an inclined single optic axial figure with optic sign +, by needles with smaller angles of extinction.

The mixture was dissolved in alcohol at the ordinary temperature. On crystallisation, elongated white needles with inclined terminations were deposited, together with some larger plates. Measurements of the edge angles gave two groups of acute angles, 60° and 85°. The small-angled plates gave an extinction angle of 13° and were very soluble in the usual refractive-index liquids. The other needles and plates were slightly soluble and gave an extinction angle of 16°; they showed acute bisectrix figures in sodium light with optic sign +. These properties are characteristic of *o*-chloronitrobenzene. The other needles and plates showed properties characteristic of *p*-chloronitrobenzene. The results were confirmed by refractive-index determinations.

Mixture 3.—A " melted " slide showed the presence of two types of elongated needles—some creamy white and others a greenish-white. The former gave an extinction angle of 14—15° and very inclined single optic axial figures in white light with optic sign +; the latter gave straight extinction, and an uncentred obtuse bisectrix figure in sodium light with optic sign −.

The powder was dissolved in absolute alcohol at the ordinary temperature, and on crystallisation gave a crop of crystals containing more of the first variety. The acute angle was 85—86°. The needles gave an extinction angle of 14°, sign of elongation −, and very inclined single optic axial figures in white light with optic sign +; the figure merged off towards the other optic axis and was characteristic of *p*-bromonitrobenzene.

Crystallisation from hot alcoholic solution yielded greenish-white needles which were indefinitely terminated. They gave straight extinction and an uncentred obtuse bisectrix figure in sodium light with optic sign −, these being characteristics of *o*-nitrobenzaldehyde.

The results were confirmed by refractive-index determinations.

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UNIVERSITY COLLEGE OF SWANSEA.

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