

LXI.—*Substances exhibiting Circular Polarisation both in the Amorphous and Crystalline States.*

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As two of the compounds described by Dr. Kipping in the preceding paper are of unusual crystallographic interest, they merit description apart, in order that the attention of chemists may be drawn to the importance of fully studying the morphology and physical properties of new products.

Substances which possess the power of converting plane polarised light into circularly polarised light may be conveniently classified under three heads. (1) Those which exhibit circular polarisation only in the amorphous state (that is, when dissolved, melted, or converted into gas), (2) those showing circular polarisation only in the crystalline state, and (3) those which rotate the plane of polarisation, both when amorphous and when crystalline.

To Class 1 belong the numerous substances containing asymmetric carbon atoms; these owe their rotatory power solely to the asymmetry of the chemical molecule, but lose it when the chemical molecules become arranged in a homogeneous symmetrical manner by crystallisation, the asymmetry of the chemical molecule being frequently traceable in the hemihedral or tetrahedral structure of the crystals.

Class 2 consists at present of some score or so of substances only; its members may be conveniently subdivided into (a) those which owe their circular polarisation merely to their assumption of that more or less complex twinned crystalline structure termed pseudo-symmetrical, and (b) those of which the circular polarisation is an inherent property of the crystalline structure which they possess.

The known members of Class 3 are but very few in number, and are again of two kinds, namely, (a) those which owe their circular

polarisation in the solid state to pseudo-symmetry, and (*b*) those of which circular polarisation in the solid state is a specific property of the crystalline individuals, and is not due to complex lamellar structure. Of several instances of Class 3a the best known example is strychnine sulphate; a new case, namely, that of *trans*- π -camphotricarboxylic acid, is described below. Only two or three members of Class 3b are known with any certainty; matico-camphor (H. Traube, *Zeit. f. Kryst.*, 1894, **22**, 47) and the rubidium salts of the dextro- and lævo-tartaric acids (Wyrouboff, *Journ. de Physique*, 1895, [3], **3**, 451) are optically active both in the amorphous and crystalline conditions, and the circular polarisation of the crystals seems not to be due to pseudo-symmetry; another example of this little known, though very important, class is now described, namely, that of *cis*- π -camphanic acid. Matico-camphor and *cis*- π -camphanic acid are lævorotatory both in the amorphous and crystalline states, their specific rotations being thus of the same sense in the two physically different conditions; rubidium dextro-tartrate, however, is lævorotatory when crystalline, but dextrorotatory when amorphous or structureless, so that with this substance the sense of the rotation is different in the two states.

The question of the correspondence in sense between the specific rotations of the crystalline and amorphous materials is one of great importance in connection with the much vexed question of the disappearance of circular polarisation which attends the crystallisation of an optically active substance belonging to Class 1, and also in relation to the possibility that in substances belonging to Class 3b the circular polarisation, both in the amorphous and crystalline states, may be due to the same cause. If the latter possibility be actually realised, it obviously becomes necessary to explain away the opposite sense of the rotatory powers of rubidium tartrate in the two states. The explanation of this apparent anomaly lately given by Liebisch (*Physikal. Kryst.*, 1896, 428), namely, that the disagreement in sign is due to the dissociation occurring in aqueous solution would seem to have some claim to recognition did we not possess an accurate knowledge of the electrical conductivities of aqueous solutions of rubidium tartrate between wide limits of concentration. Eberhard Rimbach (*Zeit. physikal. Chem.*, 1895, **16**, 671) has shown, from the polarimetric and electrical conductivity determinations made with such solutions, that non-dissociated rubidium tartrate has the specific rotation $[\alpha]_D = +25.63^\circ$, whilst the rotatory power of the wholly dissociated salt is $[\alpha]_D = +19.51^\circ$. Were the apparent anomaly capable of explanation on the basis of the electrolytic dissociation hypothesis, it is obvious that crystalline rubidium dextro-tartrate should have an even greater positive specific rotation than its aqueous

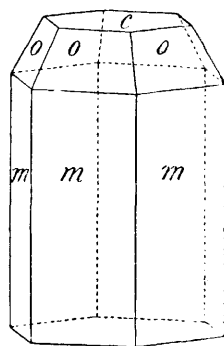
solution, instead of which the rubidium tartrate crystals have the negative specific rotation of $[\alpha]_D = -10.7^\circ$ (G. Wyruboff, *loc. cit.*; compare also H. Traube, *Sitz. Berl. Akad.*, 1895, 10, 195).

Nearly all the known examples of Classes 2*b* and 3*b* have been exhaustively examined by Wyruboff, whose careful investigations have led to the relegation of many of the supposed members of these divisions to Classes 2*a* and 3*a*. It is, however, difficult to accept the whole of Wyruboff's conclusions; he seems to consider that Classes 2*b* and 3*b* do not exist, and that all circular polarisation in the crystalline state originates in complicated lamination. It will be shown below that an exhaustive examination of the crystals of *cis*- π -camphanic acid failed to reveal any evidence of twin structure, so that this substance must be considered, for the present at least, as a legitimate representative of Class 3*b*.

cis- π -Camphanic acid has been recently prepared by Dr. Kipping (this vol., p. 943), who, recognising its crystallographic interest, was so good as to take considerable pains to obtain it in large and well-developed crystals, which he then handed to me for examination. The crystals, deposited by the spontaneous evaporation of the solution in a mixture of alcohol and chloroform, consist of hexagonal prisms showing the basal plane $c\{0001\}$, the pyramid $o\{10\bar{1}1\}$, and a second pyramid form, $m\{hokl\}$; they can be obtained of 3—5 mm. in length and 2 mm. in thickness (Fig. 1). The forms $c\{0001\}$ and $m\{hokl\}$ are usually predominant; the basal plane gives only moderately good reflections, but the images obtained from $m\{hokl\}$ are usually very good. The faces of the pyramid $o\{10\bar{1}1\}$ are generally small but brilliant (Fig. 1).

The crystals are hemimorphic, the forms $o\{10\bar{1}1\}$ and $m\{hokl\}$ being only present at one end. On heating the crystals, passing them rapidly through the flame of a spirit lamp to de-electrify the surface, and then dusting them during cooling with the electrified mixture of powdered red lead and sulphur projected from the Kundt bellows, the end showing the form $o\{10\bar{1}1\}$ attracts the positively electrified red lead, whilst the negatively electrified sulphur becomes attached to the other end; the former is, therefore, the negatively electrified end, whilst the latter is the positively electrified one. The optic axial direction is consequently a pyroelectrical axis, and the antilogous pole emerges through the end showing the pyramid $o\{10\bar{1}1\}$, the analogous pole emerging at the truncated end of the crystal. The fact that the optic axial direction is a pyroelectrical

FIG. 1.



axis having been thus determined, numerous experiments were made to ascertain whether the horizontal axes of hexagonal symmetry are also pyroelectrical axes, as in the case of quartz; but no selective attraction of the constituents of the powder to particular parts of the basal plane $c\{0001\}$ or to $m\{hokl\}$ was observed. It must be noted, however, that the evidence thus obtained is of a purely negative character, for, the horizontal and vertical axes of symmetry being crystallographically different, it might well happen that, although the pyroelectrical properties of the vertical axis are sufficiently well marked to allow of ready determination, any polarity in the horizontal axes of symmetry might find so slight an expression in the pyroelectrical behaviour as to escape detection by the applicable methods.

On examining the crystals orthoscopically in the direction of the principal axis, they are observed not to extinguish, but to remain bright, on rotation between crossed nicols. The conoscopic examination of crystals less than a millimetre or so in length shows the optic axis, the double refraction being weak and positive in sign; on examining crystals of several millimetres in length under a $\frac{1}{4}$ -in. objective, they are found to be circularly polarising, the black cross disappearing almost entirely in the centre of the field when the beam traverses a considerable length of crystal. By rotating the analyzer alone it can just be ascertained that the substance is *lævorotatory*. The same conclusion is arrived at with certainty by employing a device which apparently has not been previously described; this consists in using several pairs of right- and left-handed circularly polarising plates of quartz of different thicknesses cut perpendicularly to their optic axes, and examining the crystal plate conoscopically under the lowest power that will show the interference figure distinctly, using one or other quartz plate in place of a microscope slide. Proceeding in this way, one pair of the quartz plates of the same thickness can be ultimately selected, such, that when the crystal under investigation is placed on one of the quartz plates, a confused interference figure alone is observed, whilst, on placing the crystal on the quartz plate of opposite rotation, the characteristic Airy's spirals can be plainly seen. The latter quartz plate must be of opposite rotation to the crystal under examination. This method constitutes a far surer one for determining the sign of the circular polarisation of a thin crystal plate than the ordinary method of rotating one nicol against the other; the author hopes soon to be able to apply the same principle to the approximate measurement of the specific rotation of uniaxial crystalline substances which is, at present, a practical impossibility with small crystals.

All hexagonal or trigonal crystals which exhibit circular polarisation belong to one of the four crystalline sub-systems named below,

the numbers being those adopted in Groth's classification (*Physikal. Krist.*, 1895, 330).

16. Pyramidal trigonal class.
18. Trapezohedral trigonal class.
23. Pyramidal hexagonal class.
24. Trapezohedral hexagonal class.

The principal or vertical axes of crystals belonging to Classes 16 and 23 only are pyroelectrical axes, consequently *cis*- π -camphanic acid must crystallise in one of these two systems. Further, in the pyramidal trigonal class the horizontal symmetry axes are also pyroelectrical axes. No polarity in these axes could be detected by the pyroelectrical test, and, further, since the six faces of the half-forms $o\{10\bar{1}1\}$ and of $m\{hokl\}$ are perfectly similar in crystallographic character, it must be concluded that the crystals belong to the pyramidal hexagonal class.

This conclusion was confirmed by an examination of the corrosion figures produced on the crystal faces on washing them with alcohol or acetic acid. Regular hexagonal figures were produced on the half-forms $\{0001\}$ and $\{000\bar{1}\}$, and corrosion lines perpendicular to the principal axis were eaten into the faces of $m\{hokl\}$, thus confirming the lack of sense previously ascribed to the secondary axes and the similarity between the faces of the two pyramid forms indicated by their symmetrical development. The determination of the crystalline sub-system is thus quite satisfactory.

A glance at the appended table of measured angles will show that the angle $000\bar{1} : m$ varies only between $90^\circ 10'$ and $90^\circ 22'$, and has the value $90^\circ 16'$ as the mean of 15 readings; it can, therefore, be depended on as accurate within a very few minutes. If the form $m\{hokl\}$ had the indices $\{10\bar{1}0\}$, the angle $000\bar{1} : m$ would be defined as 90° by the symmetry; it is evident, therefore, that the form m is a very steep pyramid form, which, like $o\{10\bar{1}1\}$, is only developed around the analogous pole of the crystal, in accordance with the hemimorphism. The indices calculated for m from the angle cm are $\{440 : 0 : \overline{440} : 1\}$, but it is naturally impossible to assign accurate values to the indices of such a form.

Crystalline system. Pyramidal Hexagonal.

$$a : c = 1 : 1.7691.$$

Forms observed :

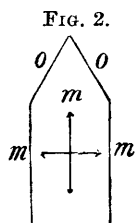
$$+ c\{0001\}, - c\{000\bar{1}\}, + o\{10\bar{1}1\}, \text{ and } + m\{440 : 0 : \overline{440} : 1\}.$$

The following angular measurements were obtained :

	Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$co =$	$000\bar{1} : 10\bar{1}1$	16	$63^{\circ} 41' - 64^{\circ} 15'$	63 55	—
$om =$	$\left\{ \begin{array}{l} 10\bar{1}1 : 10\bar{1}0 \\ 10\bar{1}1 : ho\bar{k}l \end{array} \right\}$	14	25 28 — 26 7	25 48	$\left\{ \begin{array}{l} 26^{\circ} 5' \\ 25 49 \end{array} \right\}$
$oo =$	$10\bar{1}1 : \bar{1}0\bar{1}1$	8	127 41 — 128 10	127 55	127 50
$oo =$	$10\bar{1}1 : 01\bar{1}1$	5	53 9 — 53 24	53 16	53 22
$om =$	$10\bar{1}1 : 01\bar{1}0$	4	63 1 — 63 26	63 16	63 19
$cm =$	$\left\{ \begin{array}{l} 000\bar{1} : 10\bar{1}0 \\ 000\bar{1} : ho\bar{k}l \end{array} \right\}$	15	90 10 — 90 22	90 16	$\left\{ \begin{array}{l} 90 0 \\ 90 16 \end{array} \right\}$

The minute crystals deposited on rapidly cooling a hot aqueous solution of the acid, consist of extremely thin, broad, hexagonal plates, which show perfect single refraction in the direction of the principal axis; in these very thin plates, the circular polarisation naturally cannot be detected. In none of the crystals, whether thick or thin, can any trace of twin structure be detected, the extinction being never patchy, but always in accordance with the hexagonal nature of the crystals. The possibility that the circular polarisation might be due to lamellar structure, as in the case of Reusch's mica piles, or of strychnine sulphate, is thus practically excluded.

On precipitating the acid from its sodium carbonate solution by hydrochloric acid, it is deposited in microscopic, pentagonal-shaped plates, having the outline shown in the figure (Fig. 2); the extinction



is parallel to the two long parallel sides, and bisects the acute angle, which is one of about $60-65^{\circ}$. These crystals are evidently crystallographically identical with those measured above; the large, flat face is one of the form $m\{ho\bar{k}l\}$ or $\{10\bar{1}0\}$, and the crystals are developed hemimorphically in the ordinary way.

After melting the substance on a microscope slide under a cover slip, it solidifies readily to a very irregular, confused mass, showing aggregate polarisation.

The sense of the circular polarisation of a large number of crystals of *cis*- π -camphanic acid was determined by the method described above, and found to be always the same, the crystals being lævorotatory; this substance, therefore, always crystallises in one of the two enantiomorphous forms possible in the pyramidal hexagonal system, this being the lævorotatory one, the dextrorotatory form being never observed. This case, then, is essentially different from that of a substance like sodium chlorate, which is optically inactive in solution, but, on crystallisation, may be obtained in either the dextrorotatory or lævorotatory crystalline form at will. The first cause of the lævorotation always observed with *cis*- π -camphanic acid is consequently the asymmetric structure of the chemical molecule. Wyruboff, who has done much admirable work on the crystallo-

graphy of optically active substances, concludes, however, "que l'hémiédrie de la forme cristalline et le pouvoir rotatoire (of the solution) sont deux phénomènes d'ordres différents, et n'ont entre eux aucun rapport constant et nécessaire" (*Ann. Chim. Phys.*, 1894, [7], 1, 16); this conclusion is based on the observation that either right- or left-handed crystalline forms may be obtained by varying the conditions with certain optically active substances. That this argument is fallacious may be best shown by an instance. The sphenoidally hemihedral orthorhombic camphorsulphonic bromide, described by Kipping and Pope (*Trans.*, 1895, **67**, 366), may be obtained in large crystals, showing both the forms $\kappa\{111\}$ and $\kappa\{1\bar{1}1\}$; the latter form is ordinarily very small as compared with the former, but, by varying the conditions of crystallisation, both forms may readily be obtained of the same size, and the form $\kappa\{111\}$ may sometimes even be observed to be smaller than the form $\kappa\{1\bar{1}1\}$, so that the crystals appear to have the enantiomorphous form to those of dextrocamphorsulphonic bromide. The behaviour of this substance is thus quite similar to that of the cases cited by Wyruboff; it cannot, however, be supposed that the slight variations possible in the conditions of crystallisation cause a change in the hemihedral crystalline structure, of which the external form is merely the outward expression. The crystalline structure and the hemihedrism of the crystalline form retain the asymmetry imparted by the asymmetry of the chemical molecule, but the external form, which is conditioned by the crystalline structure and the conditions attending crystallisation concurrently, may be altered by varying the latter. On crystallising two optical antipodes under identical conditions, so that the only differentiating factor is the crystalline structure, the two crops of crystals obtained are identical in habit, but, provided the crystalline system be one capable of enantiomorphism, they will consist respectively of right- and left-handed individuals, as in the case of *sobrerol* (Armstrong and Pope, *Trans.*, 1891, **59**, 315).

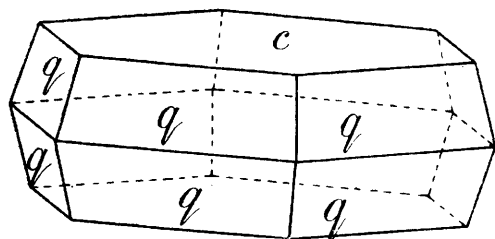
Obviously, disturbing factors, such as a change of the conditions attending crystallisation, can be eliminated if, in any particular case, it be possible to select for characterising the hemihedral forms or structures some polar physical property, such as circular polarisation in the solid state, which is governed by nothing but the hemihedral crystalline structure. The case of *cis*- π -camphanic acid is one of the few in which the circular polarisation can be so employed, and it is seen that the crystals are invariably *lævorotatory*, this being a constant expression of the constant hemihedral crystalline structure which cannot be masked by variations in conditions. In this case, then, it is shown that there is a specific relation between the hemihedrism of the crystals, the existence of which is proved by the

circular polarisation, pyroelectrical properties, and geometrical development of the latter, on the one hand, and the circular polarisation of the solution, on the other; in this example, one of the very few in which an absolute criterion is possible, Wyruboff's conclusion does not hold.

The same would be true if the crystals owed their circular polarisation to pseudosymmetry, for then, unless the crystalline structure were a hemihedral one, no reason could be assigned for the constant sense of winding of the laminae, which alone can give constancy to the circular polarisation.

Dr. Kipping has been successful in obtaining very beautiful hydrated crystals of *trans*-camphotricarboxylic acid (this vol., 951), which he handed to me for crystallographic examination. They consist of colourless, transparent plates of hexagonal outline (Fig. 3),

FIG. 3.



and may readily be obtained of a centimetre in diameter and half a centimetre in thickness; they have a brilliant lustre and weak double refraction. The form $c\{001\}$ is fairly bright and gives fairly good reflections on the goniometer, whilst the

smaller dome form $q\{011\}$ is usually not so well developed and gives poor results on measurement; the form $c\{001\}$ is lightly striated parallel to its six sides. There is a perfect cleavage parallel to $c\{001\}$.

The crystals have all the geometrical characteristics of the holohedral hexagonal system, and so far as the goniometrical results lead, would be regarded as hexagonal. On examining them orthoscopically between crossed nicols through the basal face (001), however, it is found that they do not extinguish regularly during the rotation of the nicols, except just in the centre of the plate. The crystal may, in fact, be divided into six triangular-shaped sectors, as shown in Fig. 4, each of which extinguishes at 60° to its neighbour; there are hence three extinctions at 60° to each other, parallel to the sides of the hexagon. The conoscopic examination shows that each sector is biaxial, the optic axial plane being parallel to the side of the hexagon bounding the sector. The optic axial angle is very small and the double refraction is positive in sign. These interference figures can only be distinguished near the edges of the crystal, and if the centre part of the plate be examined, a certain area is nearly always found which

remains quite bright during rotation between crossed nicols, and is uniaxial with negative double refraction. The black cross which divides the uniaxial interference picture is seen to almost disappear in the centre of the figure, so that the substance is circularly polarising.

The only possible explanation of this anomalous behaviour is that the crystals are really mimetic twins on the form $\{110\}$ of orthorhombic crystals consisting of the forms $c\{001\}$ and $q\{011\}$; the twins simulate hexagonal symmetry. The c -axis is the first mean line, the optic axial plane is (010) and the optic axial angle is very small. Near the edges of the crystal plates this biaxial interference figure can always be seen, but in the centre of the field where the six sectors meet there is a certain amount of overlapping of the six pieces, the optic axial planes of which are arranged at 60° to each other; in this part of the naturally occurring plate circular polarisation is observed.

As is well known, circular polarisation was artificially realised by Rensch by the piling together of biaxial cleavage laminae of mica, each piece being rotated through 60° to the two laminae in contact with it; the conditions artificially established in this case are precisely similar to those which arise naturally during the crystallisation of *trans*-camphotricarboxylic acid, with the only exception that it cannot be positively certified that the piling is performed in a constant sense as in the artificial packets of mica cleavage plates. This new case affords a very beautiful imitation of the circularly polarising mica piles.

Since the crystals are orthorhombic, and no form occurs which makes a finite intercept on the a -axis, it might seem impossible to assign a value to the axial ratio a/b . The twinning on the form $\{110\}$, however, causes the (010) faces of two adjacent wings of the twin to make a normal angle of 60° with each other

FIG. 4.

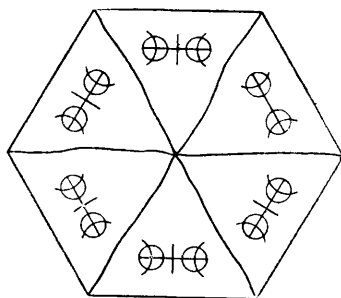
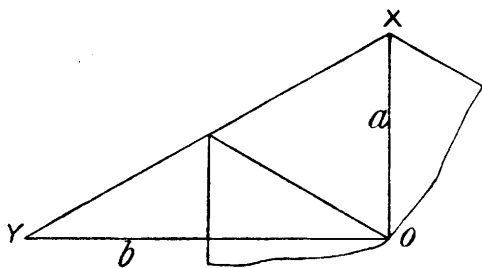


FIG. 5.



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so that the lengths of the axes a and b stand in the ratio of the intercepts OX and OY on those axes in Fig. 5.

Therefore

$$a/b = \tan 30^\circ = 1/\sqrt{3}.$$

Thus, although the twin junctures are not straight lines, but run more or less irregularly across the plate as shown in Fig. 4, the ratio a/b can be determined at least approximately.

The crystals of *trans*-camphotricarboxylic acid, obtained by rapidly cooling a hot, saturated aqueous solution, consist of very minute six-sided plates which extinguish parallel to one side and show positive double refraction; they are too small and thin however to show interference pictures, but do not appear to be twinned. The examination of these crystals thus confirms the orthorhombic character of those described above, and could they be obtained of greater dimensions they would doubtless afford still further confirmation of the above analysis.

Crystalline system. Orthorhombic.

$$a : b : c = 1/\sqrt{3} : 1 : 3.302.$$

Forms present:

$$c\{001\}, q\{011\}.$$

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$cq = 001 : 011$	16	$73^\circ 6' - 73^\circ 15'$	$73^\circ 9'$	—
$qq = 011 : 01\bar{1}$	9	$33^\circ 30' - 33^\circ 59'$	$33^\circ 47'$	$33^\circ 42'$

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