

C.—*Orthobenzoicsulphinide*.

By WILLIAM J. POPE.

ORTHOBENZOICSULPHINIDE (commercial saccharin) is put on the market as a white micro-crystalline powder containing a considerable proportion of parasulphaminebenzoic acid. Having occasion to attempt the purification of some of the commercial article some months ago, I dissolved it in acetone, in which it is fairly soluble, and after filtration allowed the solution to evaporate spontaneously; massive, colourless rhombohedra were deposited, and when examined were found to consist of pure saccharin. A very pure and well crystallised sample of saccharin may be thus obtained from the impure commercial substance by one crystallisation from acetone; it was found to be identical with the purified material prepared by Ling's process (English Pat. of 1893, 21417) of boiling the commercial article with sodium acetate. Samples prepared by Mr. Ling, and also by myself, by this process, when crystallised from acetone, yielded crystals which were indistinguishable in properties from those obtained by once crystallising the commercial substance from acetone.

Orthobenzoicsulphinide is deposited from its cold acetone solution in colourless, transparent, monosymmetric crystals which have a vitreous lustre, and may readily be obtained 2 cm. or more in length.\*

\* It does not seem to be generally known that acetone often forms a very good solvent for refractory organic substances which are required in large crystals; thus ammonium picrate, which can only be obtained in small crystals from most solvents, separates from acetone in massive transparent crystals, two or more cm. in length, which are now being examined, as their optical properties are of considerable interest.

The crystals usually affect a rhombohedral habit, being bounded by the forms  $a\{100\}$  and  $q\{011\}$ ; the pinacoid  $a\{100\}$  is usually the predominant form, but the dome  $q\{011\}$  is often as largely developed. Traces of the dome  $r\{\bar{1}01\}$  are generally observable, and sometimes the faces of this form are fairly large; the pinacoid  $c\{001\}$  is less frequently observed, whilst the prism form  $p\{210\}$  is very rarely observed, and when present is ill-defined and gives very poor results on measurement; the forms  $r\{\bar{1}01\}$  and  $c\{001\}$  are generally small, and, as would be expected, usually give better measurements than the more dominant forms  $a\{100\}$  and  $q\{011\}$ .

Crystals showing all the above forms are sometimes obtained, and then have the appearance shown in Fig. 1; butterfly-like twin-crystals (Fig. 2), in which the face of composition is  $r\{\bar{1}01\}$ , are sometimes deposited from the solution and triplets due to repeated twinning on faces of the same form are by no means rare.

Crystalline System. Monosymmetric.

$$a : b : c = 2.7867 : 1 : 1.7187.$$

$$\beta = 76^\circ 8' 30''.$$

Forms observed:—

$a$ .....	$\{100\}$
$c$ .....	$\{001\}$
$q$ .....	$\{011\}$
$r$ .....	$\{\bar{1}01\}$
$p$ .....	$\{210\}$

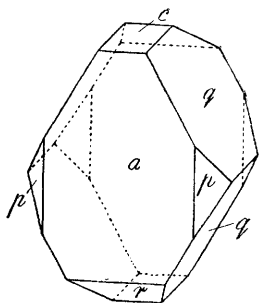


FIG. 1.

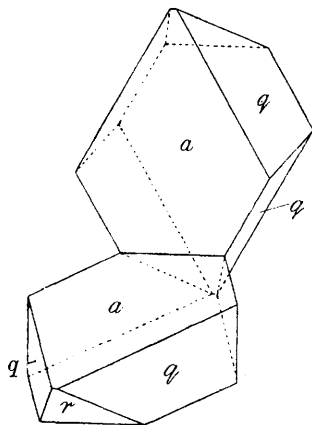


FIG. 2.

The following angular measurements were obtained:—

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$ac = 100 : 001$	46	$75^{\circ} 46' - 76^{\circ} 39'$	$76^{\circ} 8'$	$76^{\circ} 8' 30''$
$ar = \bar{1}00 : \bar{1}01$	54	$68 \quad 5 - 69 \quad 31$	$68 \quad 46$	—
$cr = 001 : \bar{1}01$	51	$34 \quad 45 - 35 \quad 37$	$35 \quad 5 \quad 30''$	—
$ac = 100 : 00\bar{1}$	16	$103 \quad 24 - 104 \quad 9$	$103 \quad 49$	$103 \quad 51 \quad 30$
$aq = 100 : 011$	39	$82 \quad 43 - 83 \quad 15$	$82 \quad 57$	$82 \quad 56$
$aq = \bar{1}00 : 011$	37	$96 \quad 42 - 97 \quad 31$	$97 \quad 3$	$97 \quad 4$
$cq = 001 : 011$	59	$58 \quad 36 - 59 \quad 48$	$59 \quad 4$	—
$qq = 011 : 01\bar{1}$	32	$61 \quad 20 - 62 \quad 29$	$61 \quad 52$	$61 \quad 52$
$ap = 100 : 210$	6	$52 \quad 50 - 54 \quad 1$	$53 \quad 24$	$53 \quad 32$
$pp = 210 : 210$	8	$72 \quad 26 - 73 \quad 35$	$72 \quad 50$	$72 \quad 57$
$pq = 210 : 011$	8	$40 \quad 2 - 40 \quad 58$	$40 \quad 25$	$40 \quad 16$
$qr = 011 : \bar{1}01$	15	$64 \quad 39 - 65 \quad 42$	$65 \quad 7$	$65 \quad 8$
$qr = 011 : 10\bar{1}$	24	$114 \quad 12 - 115 \quad 37$	$114 \quad 49$	$114 \quad 52$

The following measurements were obtained from twin crystals:—

$aa = 100 : 100$	6	$42^{\circ} \quad 3' - 43^{\circ} \quad 31'$	$42^{\circ} \quad 40'$	$42^{\circ} \quad 28'$
$qq = 011 : 011$	8	$49 \quad 12 - 50 \quad 26$	$49 \quad 48$	$49 \quad 44$

On breaking or crushing the crystals, they give out a very vivid, bluish-white light, which, however, is only of momentary duration; this flashing or phosphorescence of the crystals is very brilliant, and is quite noticeable even in a well-illuminated room; it was, in fact, first observed whilst the crystals were being manipulated in the full glare of an incandescent gas lamp. The phosphorescence may be well shown on a small scale by pulverising a crystal between two microscope slides, and on a larger scale by vigorously shaking a bottle containing a few crystals in a darkened room; on grinding a quantity of the material in a glass mortar in the dark an almost continuous, though rather fainter, light is emitted. On closely watching large transparent crystals while crushing them, the illumination appears to consist of a glow which pervades the whole crystal just as it breaks, and then immediately disappears; the emission of light consequently occupies so short a time as to appear instantaneous. The phosphorescence is not always apparent, for a crystal may sometimes be crushed in the dark without becoming appreciably luminous; these cases, however, are rare; on crushing 23 crystals which had been found to be quite normal in optical and geometrical properties in the dark, only one refused to flash, although no other point of difference between it and the other crystals could be established.

The method by which the crystals are broken seems without influence on the flashing; phosphorescence occurs when the crystals are hacked with a knife, rubbed together, crushed between the fingers or between pieces of glass, and also when they are caused to crack by rapid heating, either in the air or in the acetone mother liquor from which they crystallise. There seems to be no particular

plane in the crystal parallel to which breaking occurs without phosphorescence; no matter how carefully a crystal is cleaved along the very perfect cleavage on  $a\{100\}$ , so that parting shall only occur parallel to the cleavage, vivid phosphorescence always occurs, and on carefully cutting the crystals in the two directions perpendicular to the cleavage, so that very little parting occurs along this plane, a brilliant flash almost invariably results.

An exhaustive examination of the properties of the crystals was made in order to allow of some cause being assigned to this peculiar phenomenon; it was at first thought that the crystals might be hemimorphic or hemihedral, and that the phosphorescence might be in some way related to the polar properties inseparable from hemimorphism. Some support seemed to be given to this view by the fact that the crystals are usually very unsymmetrically developed, the forms  $r\{\bar{1}01\}$  and  $c\{001\}$  being frequently represented by only one face each, and a hollow often taking the place of one of the faces of the basal plane; but these anomalies can only be accidental, for such a distribution of planes does not indicate any of the kinds of symmetry possible in the monosymmetric system.

The completely holohedral nature of the crystals is shown pretty conclusively by the following methods. No evidence of pyroelectricity is obtained on heating and testing by Kundt's method; further, on cleaving a crystal parallel to  $a\{100\}$  and dusting with the electrified mixture of red lead and sulphur, no indication is obtained that the two surfaces acquire a difference of electrical potential such as might be expected if this form were perpendicular to a pyro-electrical axis; no pyroelectricity is observed on heating the two cleaved surfaces. These facts seem to indicate that the phosphorescence is in no way connected with pyroelectrical polarity, for the crystals phosphoresce brilliantly when parted along the plane  $a(100)$  although no evidence of pyroelectricity is obtained from the two parted surfaces.

The strongest confirmation of the holohedral symmetry is afforded by the etch-figures obtained by corroding the various forms with solvents. For this purpose, a well developed crystal is immersed in cold acetone for a few seconds, then removed and dried between filter paper; the form  $a\{100\}$ , when examined under a high power, is then seen to be covered with small triangular cavities which are elongated in the direction of the  $c$ -axis; two of the edges of these figures are curved and similar, as shown in the rough sketch appended (Fig. 3), whilst the third is straight. The cavities are bounded at the bottom by three straight edges, two of which are equal in length and equally inclined to the third; the sides of the cavities are drusy and striated. The etch-figures on parallel faces are similar, but point in

opposite directions; they are all symmetrical to the plane (010). The four faces of the form  $q\{011\}$  when etched, become covered with small scalene triangular figures, one side of which is parallel to the axis  $a$ ; the triangles are arranged as shown in the figure and those on the four faces are symmetrical to the plane (010). No characteristic figures could be obtained on the forms  $p\{210\}$  and  $r\{\bar{1}01\}$ , but on the pinacoid  $c\{001\}$ , bow-shaped figures, resembling the letter D elongated vertically, are formed on etching; these are also symmetrical to the plane (010). The holohedral nature of the symmetry is thus conclusively shown by the etch-figures formed on the crystals by acetone, and very similar figures are obtained on corrosion with water.

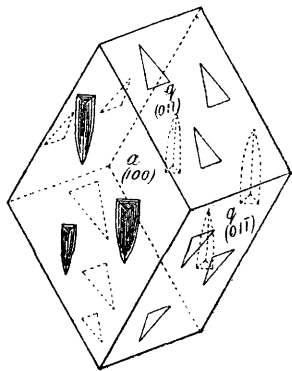


FIG. 3.

An examination of crushed crystals failed to reveal any alteration in crystallographic properties such as would be expected to result from a change in crystalline form, which is, *a priori*, a very probable cause of the peculiar phenomenon exhibited by these crystals.

It has long been known that when mica is cleaved or crystals of cane sugar are crushed, phosphorescence occurs, although the illumination obtained is excessively faint. In the case of sugar, the light can only be seen on crushing the crystals in a well-darkened room after the observer's eyes have become super-sensitised by absence of light for 10 or 15 minutes; the phosphorescence then observed appears of the same colour and character as with the aromatic compound. No case of this kind of phosphorescence has been recorded in which the phenomena at all approach the present in point of brilliancy, and further investigation of orthobenzoicsulphinide would very possibly yield an explanation of this kind of phosphorescence.

Attempts to obtain phosphorescence by the rapid crystallisation of supersaturated solutions, as has been recently done by Bandrowski (*Zeit. phys. Chem.*, 1895, **17**, 234), yielded only negative results, possibly because the solutions do not lend themselves readily to rapid crystallisation. There are, however, no grounds for attributing the phosphorescence of crushed crystals and that of crystallising solutions to the same cause, and the two classes of phenomena are apparently quite distinct.

The plane of symmetry is the optic axial plane, and one optic axis emerges through  $a\{100\}$  in the angle  $\beta$  at  $43^\circ$  in air to the normal; an optic axis emerges almost normally through  $r\{\bar{1}01\}$ , and one

through  $c\{001\}$  at about  $47\frac{1}{2}^\circ$  to the normal in air for sodium light; the obtuse bisectrix emerges through  $a\{100\}$ , and the optic axial angle is  $90-100^\circ$  in air. The extinctions in the faces perpendicular to the plane of symmetry are parallel to the traces of the latter; the extinction in  $q\{011\}$  makes  $48^\circ$  with the edge  $aq$ , and  $30^\circ$  with the edge  $qc$  for yellow light. The double refraction is negative and very strong, and the dispersion is feeble. There is a very perfect cleavage parallel to  $a\{100\}$ , and the cleavage surfaces are faintly striated parallel to the  $b$ -axis; traces of the characteristic etch-figures can also be seen on them.

On heating orthobenzoicsulphinide in a current of air, a sublimate, consisting of long, colourless, glistening needles, is obtained; these are crystallographically identical with the crystals described above, and show the forms  $a\{100\}$  and  $q\{011\}$ .

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