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Physical Sciences

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ANGULAR CONSTANTS OF MICROCRYSTALLINE PROFILES AND SILHOUETTES IN THE CONCLUSIVE IDENTIFICATION OF SUBSTANCES. III. ACETANILIDE, ASPIRIN, MERCUROUS ACETATE, PHENOBARBITAL, POTASSIUM CHLORATE, SULFONAL, TRIONAL, VERONAL. NOTES.

Arthur Curtis Shead, *Norman, Oklahoma*

This third paper in the series is devoted to the microcrystallization and angular measurements of slightly water soluble (0.25-3.5 pct.) compounds that have some pharmaceutical or toxicological importance. Such substances cannot be subjected to the same technique required by the less soluble group as overly large, too coarse or irregularly outlined forms would result. Rapid cooling and violent agitation in small test tubes (⅜" x 3") tend to favor the smaller and more perfect crystals, while pouring off the

mother liquor from the slide followed by careful and repeated blotting by filter paper removes the excess which would later crystallize as a fringe upon the useful forms first appearing. The crystallization takes place from a partially saturated solution as hot as is compatible with the separation of the solute in the solid condition. With the exception of luminal, which was allowed to cool spontaneously with removal of the first more perfect crop for examination, the compounds listed yielded forms suitable for measurement.

Acetanilide yields mostly hexagonal crystals having two apicial angles of 99.5° with four others each of 130.2°. Truncation of the apicial angles yields in place of each, two angles of about 140°. Acetanilide crystals are not stable in air and are photographed while freshly formed.

Aspirin yields mostly hexagons with apicial angles of 119.7° with four others, each of 120.3°. The crystals show perfect cleavage in the direction connecting the apicial angles and afford brilliant interference colors under crossed nicols. Aspirin is stable in the air.

Mercurous acetate crystallizes from hot water or hot dilute acetic acid solutions in parallelograms, hexagons or combinations of the two. The acute angle of the paralellogram is 83.5°; the obtuse angles of the parallelogram and two apicial angles of the hexagon are 97° and the other four angles of the hexagon are 131.5°.

Phenobarbital (luminal) generally crystallizes in longitudinally striated "laths" with jagged ends. At times it crystallizes on slow cooling without agitation, with good forms, especially in the earlier crops. Sublimation at 120°-140° also affords useful forms in some part of the preparation. By either method hexagons, parallelograms and modifications in either of two facies may be found. One facies yields hexagons with two apex angles of 113.4° and four others of 123.3° each which also appear as obtuse angles in a parallelogram having an acute angle of 56.7°, half the apex angle of the hexagon. The other facies consists of a hexagon having two apex angles of 122.1° and four others, each of 119.5°. The corresponding parallelogram was not noted though it is possible. The crystals are not clear because of the strong tendency to a fibrous structure. Colors under crossed nicols are not strong. Compare with the closely related veronal.

Potassium chlorate yields parallelograms with an acute angle of 79.8° and an obtuse angle of 100.3°.

Sulfonal usually separates as *small* rectangles. Some few diagnostic forms may appear especially by spontaneous evaporation of thin films of solution saturated at room temperature. A 95.1° angle appears as the obtuse angle of a parallelogram (acute angle of 85°) and as the two apicial angles of a hexagon having four other angles each of 132.5° c. f. the closely related trional.

Trional crystallizes below its melting point (76°C) mostly as *large* parallelograms with an acute angle of 86.5° and an obtuse angle of 93.5°. An extinction angle of 42-44° lies apparently in the diagonal connecting the acute angles of the parallelogram.

Urea nitrate described in the first paper of this series is here illustrated.

Veronal or barbital crystallizes from hot dilute HCl solution (to transpose any sodium salt) as parallelograms (acute angle 36.4°; obtuse angles of 144.4°) with extinction angles of 18-20°. The interference colors are remarkably brilliant. Rectangular forms of no diagnostic value also appear.

NOTES

Modifications of the simple parallelogram, hexagon and combinations of the two are frequently encountered among crystal forms. The simplest useful unit is the parallelogram. From this, by truncation of the acute

angle, the hexagon may be derived. This form has the obtuse angle of the parallelogram for four of its angles (b) and its two apicial angles

$$(a) = \frac{720^\circ - 4b}{2}.$$

The hexagon may be bisected through its apicial angles to form an iscosceles trapezoid with acute angles equal to half the apex angles of the original hexagon and the same obtuse angles. The parallel sides of the hexagon may approach each other closely to produce an elongated lath-like form with no alteration of angles but of profoundly different appearance. The apex angles of the hexagon may be truncated even to the extent of producing a rectangular form. Triangles may result by obliterating all the hexagon except the apex angle, etc.

Sometimes two different facies of a given substance appear. These result from the more or less equal development of two different aspects (e.g. two different pinacoids) of the crystal.

Notwithstanding the possibilities, the simplest forms are generally the most prominent and little confusion results in practice.

SUMMARY

This paper gives angular and other constants for pharmaceutically and toxicologically important substances, shows how certain closely related substances, chemically indistinguishable, can be readily differentiated by profile angle measurements, and discusses modifications of simple parallelograms and hexagonal crystal forms that may be encountered.

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