

ANGULAR CONSTANTS OF MICROCRYSTALLINE PROFILES AND SILHOUETTES IN CONCLUSIVE IDENTIFICATION OF SUBSTANCES. V. METALLIC HELIANTHINATES, OO TROPAEOLINATES, AND MISCELLANEOUS COMPOUNDS

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This paper (six preceding papers) ^{1, 2, 3, 4, 5, 6} continues the study of flat tabular crystals exhibiting a preferred orientation and constant habit suitable for the accurate determination of silhouette (plane, edge, profile) angles. No effort has been spared to avoid the difficulties that arise in the attainment of the objective, namely, impurities, unrecognized inversion temperatures between polymorphic modifications, side reactions, instrumental deficiencies, etc.

Shead⁶ previously pointed out that the profile or silhouette angle, as a constant, is invaluable to the microchemist in the characterization of substances that decompose or sublime their more familiar melting points or boiling points are attained. Even though the substance does not decompose or sublime before the melting point is attained, it is believed that the data in this series of papers may be of value in that they may afford a simple means by which substances may be quickly and conveniently characterized.

Owing to the wide range of conditions and variety of reagents available to the microchemist, the production of microcrystals suitable for angular measurement is assured in a large number of cases. This is supported by the fact that since the first paper was published, Shead and his co-workers have prepared ninety-eight micro-crystals suitable for angular measurements, covering a wide variety of substances. At first generalization was the important factor, for the usefulness of the profile or silhouette angle, as a constant, had to be established for crystalline substances in general. This paper deals not only with generalization but also with specific instances. For example, helianthin (methyl orange) and tropaeolin 00 (orange IV) were selected as general reagents for metallic ions because they furnish simple monobasic anions in a solution; and these "helianthinates" and "00 tropaeolinates" were found to afford, in many cases, crystalline metallic salts suitable to the specific purpose outlined above. The color and index of refraction render some of these crystals difficultly visible when suspended in the mother liquor; therefore caution must be exercised in order that the crystals may not be overlooked.

PREPARATIONAL METHODS

In the preparation of helianthin and tropaeolin 00 crystals, flat filter paper can not be used to remove the mother liquor from the microscope slides without serious damage to the crystals themselves. This difficulty was overcome by using a ring of blotting paper. This technique, known as the "ring blotting method," consists of using an absorbing agent in a circle surrounding the droplet of suspended crystals on the slide. An ordinary filter paper is folded in the center and then repeatedly folded from this straight edge, one centimeter at a time, until a strip results, the length of which is equal to the diameter of the filter paper. The filter paper is now one centimeter in width and several thicknesses of filter paper thick. The strip is then formed into a circle of such size as the

droplet on the slide requires. The circle of blotting paper effects a pulling force of equal intensity in all directions (planar), thus drawing the liquid from the edge of the drop and pulling it to the walls of the ring, leaving the crystals undisturbed and dry without subjecting them to breakage by direct contact with blotting material.

For the formation of crystals, where slow cooling is necessary, Shead² recommends the following procedure. As micro-amounts of solution have low heat capacity, they are best treated in a small test tube held in the mouth of an Erlenmeyer flask by a cork segmented to permit the escape of steam. The comparatively large body of hot water in exterior contact with the solution under treatment through the walls of the containing tube permits slow cooling when the system is set aside.

In all cases where crystals are prepared from solvents, the following method of transfer to a microscope slide is used. The crystals, after being formed in a test tube, are poured upon the slide, the "mother liquor" poured off at a low pouring angle, and the remaining liquid is blotted away. In the preparational methods below, if no specific directions are given for transferring crystals to the slide, it is to be assumed that this procedure was used.

In the preparation of crystals for substances designated as (C), (H), (I), and (J), optimum crystals can be obtained by employing the same procedure for each case. Add 2—3 cc. of the desired solvent to a micro-test tube and saturate, at its boiling point, with the solid substance to be characterized. Let the solution cool spontaneously (with frequent agitation to start crystallization) and prepare the crystals on a slide as directed above.

(A). *Mercuric iodide*. A method for the crystallization of the form of HgI_2 , stable above $126^\circ C.$ was reported by Shead¹. A less cumbersome method of preparation has been devised, giving identical results with the first. Saturate 3—4 cc. of boiling hot ethyl alcohol, in a micro test tube, with HgI_2 . Place the tube and contents in a vessel containing hot water and allow the system to cool to room temperature. Transfer a few drops of the cool alcohol, with crystals in suspension, to a microscope slide and let the alcohol evaporate, leaving yellow, unstable parallelograms of mercuric iodide on the slide.

(B). *Silver sulphate*. Saturate 2—3 cc. of boiling water, in a micro test tube, with silver sulfate and transfer a few drops of the solution to a microscope slide. Agitate the solution, by shaking the slide, while cooling. When the crystals have grown to a desired size, remove the water from the slide with a ring filter paper.

(C). *Silver acetate*. From hot water.

(D). *β -Naphthol*. Add 2 mg. solid β -naphthol to 8—10 drops of water and dissolve by heating. Cool in a hot water vessel, as described above, without shaking.

(E). *Hexamethylene tetramine mercuric bromide*. Add approximately one mg. $HgBr_2$, to a small test tube containing 4—6 drops of water and 3 drops of 40% HBr . After the $HgBr_2$ has dissolved place on a microscope slide a drop or two of the solution into which a small crystal (1 mg.) of hexamethylene tetramine is dropped. Observe the crystal growth with a microscope and when crystals are of sufficient size, blot the supernatant liquid from the slide with a filter paper. With proper variations of procedure, a test for either hexamethylene tetramine or mercury may be perfected.

(F). *Naphthalene*. Approximately 1 mg. of naphthalene is dissolved in 2 ml. of hot ethyl alcohol and allowed to cool spontaneously to room temperature, with intermittent shaking. Place a few drops of the alcohol, with crystals in suspension, into a cell (the cell consisting of a glass ring, 10 mm. in diameter and 4 mm. in height, a cover glass for the base, and a microscope slide for the ceiling). Invert the cell in a manner such that the alcohol is retained inside the cell and observe the crystals clinging to the cover glass, with a microscope.

(G). *Thiocarbanilid*. Saturate 2—3 cc. of hot ethyl alcohol with solid thiocarbanilid and cool to slightly above room temperature. Pour a few drops of the warm solution on to a microscope slide and immediately blot the supernatant liquid with an ordinary filter paper.

(H). 1, 2-*Dinitrotetralin*. From hot alcohol.

(I). 3, 5-*Dinitrobenzoic acid*. From hot water.

(J). 2, 4-*Dinitrophenylhydrazine*. From hot ethyl alcohol.

(K). *Sulfamic acid*. Add about 2 mg. of sulfamic acid to 2 cc. of water, at room temperature, and allow the water to evaporate spontaneously until optimum crystals result.

(L). *Sodium 00 tropaeolate*. Saturate 2—3 cc. of boiling water, in a micro test tube, with tropaeolin 00, and allow the solution to cool spontaneously to room temperature. Centrifuge, decant, and wash the crystalline residue with cold water. Dissolve the washed precipitate in the least amount of boiling water and allow to cool spontaneously with intermittent agitation.

(M). *Manganese 00 tropaeolate*. Add $MnCl_2$ (0.2 M), at room temperature, to a dilute solution of tropaeolin 00 (saturated at room temperature), until the yellow color of the tropaeolin 00 is almost gone. Suspend the precipitate in distilled water. Centrifuge again and discard the water. Wash the precipitate with cold water and dissolve the residue in the least amount of boiling water. If precipitation does not start at once agitate until it does and cool spontaneously.

(N). *Magnesium 00 tropaeolate*. To a solution of tropaeolin 00 saturated at room temperature add magnesium chloride solution (very dilute) until the orange color is discharged and a silky precipitate appears. Centrifuge and pour off the supernatant liquid from the orange brown residue. Dissolve this residue in the least possible amount of boiling water. Agitate while cooling until a faint precipitate appears. Place the tube and contents in a 125 cc. hot water vessel and set aside to cool spontaneously.

(O). *Calcium 00 tropaeolate*. Add a dilute solution of $CaCl_2$, drop by drop, to a saturated solution of tropaeolin 00 until the orange color is almost discharged and is succeeded by a dirty brown precipitate. Centrifuge and discard the liquid. Dissolve the precipitate in the least amount of boiling water, place the test tube containing the solution in a 125 cc. hot water vessel and let the system cool spontaneously, shaking from time to time to start crystallization, and to prevent clustering or formation of smaller perfect crystals which tend to grow too large. Blot with ring filter paper.

(P). *Strontium 00 tropaeolate*. The strontium salt is prepared like the calcium salt except that the solution in boiling water is filtered free from needle crystals and allowed to cool spontaneously to room temperature, thus forming a supersaturated solution. This is then agitated until

precipitation starts after which it is set aside until it settles. A supersaturated solution at room temperature seems to be a necessary preliminary to the formation of good crystals. Blot with a ring filter paper after the solution and crystals have been placed on a microscope slide.

(Q). *Zinc 00 tropaeolinate*. Add a very dilute solution of zinc chloride (filtered if necessary) to 2—4 cc. of boiling solution of tropaeolin 00 (saturated at room temperature) until precipitate appears. Let cool until room temperature is attained, without agitation. The precipitate is remarkably insoluble so that a much more dilute solution (perhaps 1/10 saturated) of tropaeolin 00 could be employed satisfactorily. Wash the precipitate with cold distilled water, dissolve in the least amount of boiling water and let the solution cool spontaneously.

(R). *Cobalt 00 tropaeolinate*. Add drop by drop a very dilute solution of CoCl_2 to 5—7 cc. of a boiling hot solution of tropaeolin 00 (0.2—0.1 saturated at room temperature, i. e., saturate a tropaeolin 00 solution at room temperature and dilute 5—10 times) until a precipitate appears. The very dilute solution must be set aside to cool slightly as the cobalt tropaeolinate is somewhat soluble at boiling temperature. No agitation is required as it precipitates spontaneously. When cooled almost to room temperature some agitation may be necessary to prevent clustering of the crystals.

(S). *Nickel 00 tropaeolinate*. Add 4—6 drops of NiCl_2 (very slightly greenish, dilute solution) drop by drop to a boiling hot, dilute solution of tropaeolin 00 that is 0.2 saturated at room temperature. If no precipitate forms at once let cool spontaneously to room temperature (agitate violently while cooling) until crystals begin to appear. Then the system may be agitated intermittently until room temperature is reached. Pour solution and crystals on a slide, let crystals settle and blot liquid with a ring filter paper. Crystals are mostly yellow hexagons.

(T). *Ethyl orange*. To 2 cc. of a 0.1 N. solution of ethyl orange (sodium salt) in a micro test tube, add dilute acetic acid until precipitation is complete. Centrifuge, decant and wash the residue with cold water. Finally dissolve the precipitate in the least amount of distilled water (boiling). Cool spontaneously in air without agitation. After crystals and solution is added to a microscope slide blot the supernatant liquid with a ring filter paper.

Metallic salts of helianthin (methyl orange). The same procedure may be used for the preparation of each of the salts of helianthin. Add two ml. of a very dilute solution (0.05 per cent) of the metallic salt to a micro test tube containing 1 cc. of a saturated water solution of helianthin. Centrifuge, decant and wash the precipitate with cold water. Dissolve the precipitate in the least amount of boiling water and cool spontaneously to room temperature without agitation. Place a drop or two of the suspended crystals on a microscope slide and blot the supernatant liquid with a ring filter paper.

The data for the foregoing crystals are collected in Tables 1 and 2. Any other angles (including those of the other form, i. e., the less frequently appearing parallelogram) may be calculated by methods already described. 5, 6

TABLE 1
Miscellaneous Compounds

Substance	Method of Preparation	Usual Shape	Obtuse Angle Degrees
Mercuric iodide	From ethyl alcohol	Parallelogram	115.4
Silver acetate	From hot water	Hexagon	132.4
β -Naphthol	From hot water	Parallelogram	108.4
Silver sulfate	From hot water	Parallelogram	120.8
Hexamethylene tetramine mercuric bromide	Special	Parallelogram	131.3
Thiocarbanilid	From ethyl alcohol	Parallelogram	108.6
2, 4-Dinitrophenyl- hydrazine	From ethyl alcohol	Parallelogram	128.8
1, 2-Dinitrotetralin	From ethyl alcohol	Hexagon	136.5
3, 5-Dinitrobenzoic acid	From hot water	Parallelogram	96.5
Sulfamic acid	From cold water by spontaneous evaporation	Hexagon	139.2
Naphthalene	Special	Parallelogram	108.0
Sodium OO Tropae- olinate	Special	Parallelogram	101.0
Magnesium OO Tro- paeolinate	Special	Hexagon	(Apex 98.3) 130.3 and 131.3
Manganese OO Tro- paeolinate	Special	Parallelogram	98.6
Calcium OO Tropae- olinate	Special	Hexagon	130.4
Strontium OO Tropae- olinate	Special	Parallelogram	100.2
Zinc OO Tropaeolinate	Special	Hexagon	130.9
		Octagon	139.1
Cobalt OO Tropaeolinate	Special	Hexagon	130.9
Nickel OO Tropaeolinate	Special	Hexagon	130.9
Ethyl Orange (free acid)	From hot water	Parallelogram	130.0

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TABLE 2
Heilanthinates

METALLIC SALT	PARALLELOGRAM			HEXAGON OR OCTAGON		
	Obtuse An. and Apex An. of Hexagon	Acute An. and Apex An. of Hexagon	Obtuse An. other form	Acute An. other form	Shoulder Angle	Shoulder Angle
Barium	100.9	79.1	114.5	65.5	129.5	XXX.X
Calcium	99.1	80.9	XXX.X	XX.X	130.4	XXX.X
Strontium	XX.X	XX.X	116.4	63.6	XXX.X	XXX.X
Cobalt	97.9	82.1	XXX.X	XX.X	131.0	139.0
Nickel	97.7	82.3	XXX.X	XX.X	131.2	138.8
Iron	98.4	81.6	XXX.X	XX.X	130.8	XXX.X
Manganese	97.2	82.8	XXX.X	XX.X	131.4	138.6
Magnesium	97.8	82.2	XXX.X	XX.X	131.1	138.9
Cadmium	98.6	81.4	XXX.X	XX.X	130.7	XXX.X
Copper	97.9	82.1	129.9	50.1	129.9	XXX.X
Lead	XX.X	XX.X	114.9	65.1	XXX.X	XXX.X
Zinc	98.2	81.8	XXX.X	XX.X	130.9	139.1

An attempt has been made in this table to list comparable angles in the same column. All angular measurements are in degrees.