[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

Optical Crystallographic Data for Some Salts of Cinchonine

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Introduction

Only a small amount of data on the optical properties of the salts of cinchonine could be found in the literature. Incomplete data are given for some of the halogen salts, for the sulfate, the nitrate and the thiocyanate in the publications of Kley,[1] Bolland[2] and Groth.[3] Wright[4] and Wherry and Yanovsky[5] list the refractive indices of cinchonine itself.

The present communication describes a number of cinchonine salts which were prepared to perfect a method for the microchemical detection of cinchonine and presents the optical crystallographic data for these salts.

Preparation of Salts.—The hydrochloride, iodate, nitrate, perchlorate, sulfate, benzoate and *o*-chlorobenzoate were prepared in the following manner. The cinchonine and the corresponding acid in equivalent quantities were mixed in water and boiled until the reaction was complete. The solution was evaporated until saturated, and the salt was allowed to crystallize out. Some of the salts had a light yellow color, and these salts were recrystallized from water after boiling the solution with animal charcoal.

The method for the preparation of the bromate, hydrobromide, chlorate, hydriodide, thiocyanate, and thiosulfate was slightly modified. Cinchonine and the sodium or potassium salt of the corresponding acid in the equivalent proportions were added to water which contained acetic acid in a slight excess of the amount necessary to liberate the acid from the sodium or potassium salt. The remainder of the procedure was the same as in the first method described above. No salts in which both of the basic nitrogens of cinchonine had reacted were prepared.

Analysis of Salts.—Each salt was analyzed for the cinchonine content by the ether extraction method, after the solution of the salt had been made alkaline with dilute ammonium hydroxide. The water of crystallization was determined in each case. Some of the crystals were placed in a desiccator over water and allowed to stand for several days. A given amount of each salt was quickly weighed and allowed to dehydrate over phosphorus pentoxide. The water of crystallization was calculated from the loss of water.

The compounds prepared and studied together with their analyses are reported in Table I. Of the salts studied, the preparation of the perchlorate, bromate and *o*-chlorobenzoate could not be found in the literature. The nitrate, chlorate and iodate were each found to contain one molecule of water of crystallization, whereas these salts have been previously reported to contain one-half molecule of water.

TABLE I

SALTS OF CINCHONINE (ALL WHITE)

Salts of cinchonine	Formula $Ci = C_{19}H_{22}N_2O$	Crystal habit	Cinchonine, % anhydrous basis Calcd.	Found	Water, % Calcd.	Found	Molecules of H_2O
Benzoate	CiC_6H_5COOH	Needles and rods	70.67	70.92			None
Bromate	$CiHBrO_3 \cdot 2H_2O$	Fine needles	69.53	69.85	7.85	7.80	1.99
Chlorate	$CiHClO_3 \cdot H_2O$	Needles and rods	77.69	77.63	4.54	4.57	1.01
o-Chlorobenzoate	$CiClC_6H_4COOH$	Needles and rods	65.28	65.50			None
Hydrobromide	$CiHBr \cdot H_2O$	Needles and rods	78.43	78.74	4.58	4.50	1.98
Hydrochloride	$CiHCl \cdot 2H_2O$	Needles and rods	88.97	89.06	9.82	9.90	2.02
Hydroiodide	$CiHI \cdot H_2O$	Needles and rods	69.69	69.72	4.09	4.07	1.00
Iodate	$CiHIO_3 \cdot H_2O$	Fine needles	62.57	62.71	3.69	3.75	1.02
Nitrate	$CiHNO_3 \cdot H_2O$	Plates	82.35	82.61	4.80	4.84	1.01
Perchlorate	$CiHClO_4 \cdot H_2O$	Needles and rods	74.54	74.56	4.36	4.28	0.98
Sulfate	$Ci_2H_2SO_4 \cdot 2H_2O$	Plates	85.71	85.66	4.99	5.01	2.01
Thiocyanate	$CiHCNS$	Plates	83.28	83.23			None
Thiosulfate	$Ci_2H_2S_2O_3 \cdot 2H_2O$	Rods	83.75	83.62	4.88	4.71	1.93

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(1) Kley, *Z. anal. Chem.*, **43**, 160 (1904).

(2) Bolland, *Monatsh.*, **31**, 387 (1910).

(3) Groth, "Chemische Krystallographie," 1908–1919.

(4) Wright, THIS JOURNAL, **38**, 1647 (1916).

(5) Wherry and Yanovsky, *ibid.*, **40**, 1063 (1918).

TABLE II

OPTICAL CRYSTALLOGRAPHIC DATA FOR SOME SALTS OF CINCHONINE

Cinchonine salt	Opt. char. (sign)	Sign of elongation	Refractive indices at 25°			2E, degrees	Rhombic dispersion	Extinction angle, degrees	Crystal system
			Alpha	Beta	Gamma				
Benzoate	+	±	1.547	1.596	1.684				Monoclinic
Bromate	−	+		1.636	1.670	53	$\nu > \rho$		Monoclinic
Chlorate	−	+	1.573	1.641	1.664	101	$\nu > \rho$		Monoclinic
o-Chlorobenzoate	+	−	1.519		1.625	Large			Monoclinic
Hydrobromide	−	+		1.649	1.691	Large	Weak		Orthorhombic?
Hydrochloride	−	+	1.545	1.617	1.661	Large	$\nu > \rho$	24	Monoclinic
Hydroiodide	−	+	1.596	1.649	1.684		$\rho > \nu$	19	Monoclinic
Iodate	−	+	1.600	1.660	>1.700	Large			Monoclinic
Nitrate	+	+	1.550	1.568	1.655	59	$\nu > \rho$	45	Monoclinic
Perchlorate	−	+	1.518	1.572	1.620	Large	$\nu > \rho$	12	Monoclinic
Sulfate	−	+	1.587	1.641	1.667		$\nu > \rho$	38	Monoclinic
Thiocyanate	−	−	1.554	1.651	1.700	Large	$\rho > \nu$		Monoclinic
Thiosulfate	−	±	1.578		1.690	82	$\nu > \rho$	35	Monoclinic

Optical Crystallographic Data.—The optical properties of the salts reported in Table I were obtained by the methods used in a similar study[6] for salts of strychnine. The refractive indices were determined in all cases by the immersion method. The temperature at which the indices were taken was 25 ± 1°, and the source of light was ordinary daylight from a window with a northern exposure. The extinction angle was determined by turning the crystal to extinction and measuring the angle between this position and the long edge of the crystal. Not all of the optical data could be obtained for each salt because of the difficulty involved in orienting properly the crystals. The refractive indices, together with the other optical data, are given in Table II.

Summary

1. Three new salts of cinchonine have been prepared and described.

2. The data in the literature concerning ten salts of cinchonine have been determined, and corrections have been made in the water of crystallization of the nitrate, chlorate and iodate.

3. The optical crystallographic data for thirteen salts of cinchonine have been determined.

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(6) Poe and Sellers, THIS JOURNAL, **54**, 249 (1932).

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

A Further Study of Phenyl- and Diphenylarsines[1]

BY F. F. BLICKE AND J. F. ONETO[2]

In this investigation, which represents a continuation of our previous studies of phenyl- and diphenylarsine,[3] we have shown that phenylarsine reacts with phenylchloroethoxyarsine to form arsenobenzene and it might be expected that the arsine and triphenylchloromethane would react in an analogous manner to yield arsenobenzene and triphenylmethyl. However, in the latter instance the reaction products isolated were phenyldichloroarsine and triphenylmethane formed, probably, through decomposition of the initial reaction product, phenyl-bis-triphenylmethylarsine, by the hydrogen chloride formed during the reaction.

Diphenylarsine and chloroacetyl chloride yield diphenylchloroarsine as reported by Steinkopf, Schubart and Schmidt.[4] Diphenylchloroarsine was also obtained from diphenylarsine and chloroacetic acid (D), at an elevated temperature, with the intermediate formation of tetraphenyldiarsyl; since it has been shown, in a separate experiment,

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(1) This paper represents one part of a dissertation to be submitted to the Graduate School by Mr. Oneto in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Parke, Davis and Company Fellow.

(3) Blicke and Powers, THIS JOURNAL, **54**, 3353 (1932); *ibid.*, **55**, 315, 1161 (1933).

(4) Steinkopf, Schubart and Schmidt, *Ber.*, **61**, 679 (1928). Instead of a distillation of the crude reaction product we dissolved it in petroleum ether (30–60°), filtered the solution in air and allowed the solvent to evaporate. A 65% yield of diphenylchloroarsine was obtained; m. p. 40–41°.