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Measurement of Optical Activity of Isotropic Compounds in Suspension

Jan Bartus and **Otto Vogl**

Polytechnic University, Six MetroTech Center, Brooklyn, NY 11201, U.S.A.

Summary. A reliable method for the measurement of the optical activity of optically active isotropic solid substances in suspension was developed using two miscible liquids as media for suspending the fine solid powders. The optical rotation was measured after precise matching of the refractive index of the suspending media with that of the solid particles. Sodium chlorate and sodium bromate were used as optically active solids for the development of this method. The measurements were in complete agreement with the measurements of the optical rotation of the corresponding large crystals.

Keywords. Isotropic solids; Optical activity; Sodium bromate; Sodium chlorate; Suspension measurements.

Messung der optischen Aktivität isotroper Verbindungen in Suspensionen

Zusammenfassung. Es wurde eine verläßliche Methode zur Messung der optischen Aktivität isotroper Verbindungen in Suspensionen unter Verwendung zweier mischbarer Flüssigkeiten als Medium zur Suspension feiner Pulver entwickelt. Die optische Rotation wurde nach einer präzisen Anpassung des Brechungsindex des Suspensionsmediums an den der Festpartikel gemessen. Zur Entwicklung der Methode wurden Natriumchlorat und Natriumbromat als Festkörper eingesetzt. Die Messungen waren in perfekter Übereinstimmung mit Rotationswerten aus entsprechenden großen Kristallen.

Introduction

Optical activity of most organic compounds is usually measured in solution. If dissymmetric substances form large crystals their optical rotation in the crystal can be accurately measured. The measurements usually have been carried out only in the direction of the optical axes (growth axes) of the crystals.

Some attempts had been made to measure the optical rotation of inorganic crystals in suspension in liquid media, but with unsatisfactory results. Landolt [1] published some measurements of the optical activity of sodium chlorate powder in a mixture of carbon disulfide and ethyl alcohol. Inhomogeneity (probably due to insufficiently accurate matching of the refractive index) of the solid powder and the suspending media influenced the results which did not agree with the measurements of the optical rotation in the crystal; only about one third of the actual value was measured. Kahn [2] attempted a similar technique for the measurement of the optical activity of crystalline cystine in silicon polyether/dodecane mulls, but he did not compare the results of his measurements with those obtained by other methods. Bonsignori [3] measured the optical activity of some stereoregular polyolefins and found relatively good agreement between the values of the optical rotation measured in suspension, in solution and in thin films. These measurements are isolated examples and cannot be considered as a general technique for suspension measurements of the optical rotation for all optically active solid compounds.

Substances which exhibit optical activity can be divided into two groups: (i) those which are optically active only in the crystalline state, and (ii) those which have optical activity both in the solid state and in solution [4]. Sodium chlorate and sodium bromate are optically active only in the crystalline state. The crystals of these compounds in polarized light are optically isotropic but dissymmetric (their optical rotation is identicial in all three crystal axes). The crystals of sodium chlorate and bromate are optically active because the sodium and halate ions are arranged in dextro- and leavo-dissymmetries and presumably helicities in the crystal lattice. Individual crystals may have the same or opposite senses of optical rotation [5]. In crystallization experiments the crystals have equal statistical possibilities to form leavo- or dextrorotatory crystals, based on statistical nucleation.

We have been interested for some time in understanding the relationship between the chirality and the optical activity of crystalline materials, especially in the solid state and found some inspiration in previously published papers [6–8]. Recent work on the molecular recognition at crystal interfaces [9] and on some new aspects of sodium chlorate crystallization [10] only emphasize the importance of this problem.

The objective of this work was to develop a simple, reliable method for the measurement of the optical rotation of solid substances in powder form in liquid suspending media. Some of our preliminary results have been published previously [11–13]. Sodium chlorate and sodium bromate were identified as the best examples for developing this reliable method of measurement.

Experimental Part

Sodium chlorate (Allied Chemical Company) was recrystallized from aqueous solution. Large rectangular chiral crystals (about 10 x 10 x 4 mm) (Fig. 1) were grown from saturated solution at room temperature during a period of 2 days. Separation of the dextro- (*D*) and leavorotatory (*L*) crystals was done manually. Fine powders were prepared by grinding the large crystals in an agate mortar and sieving the powder through a set of sieves.

Sodium bromate (Matheson Company) was recrystallized from a saturated aqueous solution (Fig. 2). Three types of crystals were obtained: (i) single square pyramids, (ii) bipyramidal structures, and (iii) irregularly shaped crystals. Separation into *D* and *L* crystals was possible only by measuring the optical activity of individual crystals as rectangular samples prepared by polishing pyramidal crystals on wet filter paper.

Carbon disulfide, diiodomethane, 1-naphthaldehyde, and acetone were obtained from the Aldrich Chemical Company and used without purification.

Optical Activity of Single Crystals

The optical rotation of the sodium chlorate crystals was measured in all three crystal axis directions on a Perkin-Elmer 241 Polarimeter. A beam diameter of 2 or 6 mm was used. The rotation per mm was calculated from the measured rotation and the thickness of the crystals as determined with a

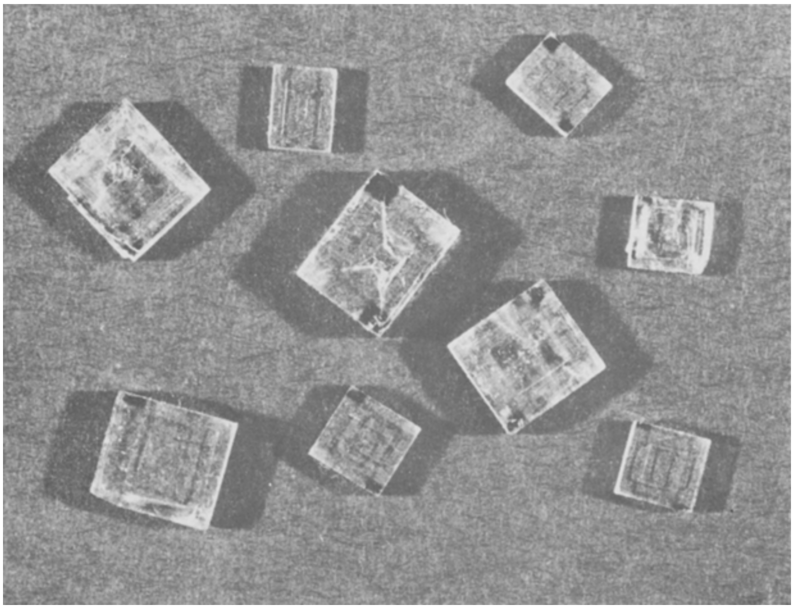


Fig. 1. Sodium chlorate crystals

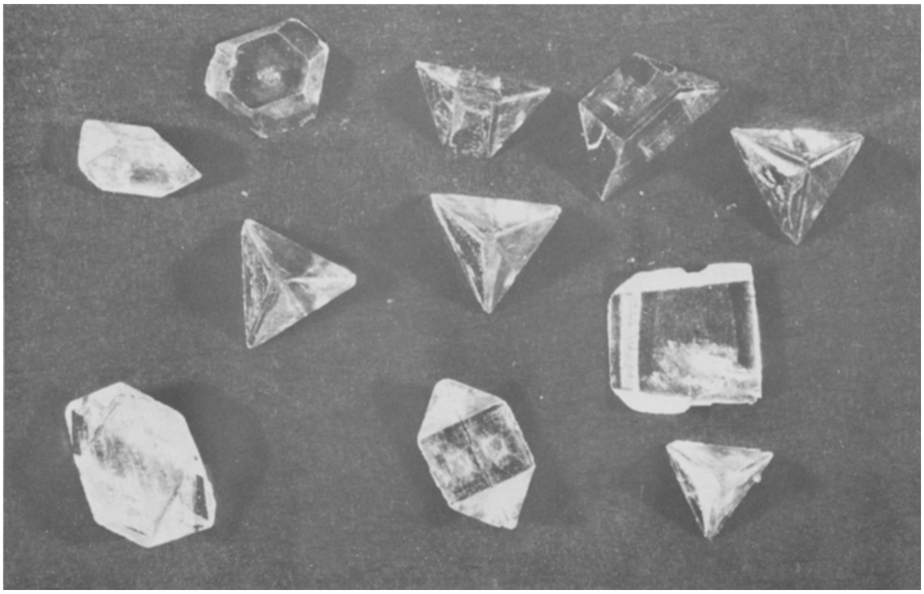


Fig. 2. Sodium bromate crystals

micrometer. The specific rotation was calculated using the density of the compounds as reported in the Ref. [8].

Optical Activity of Powder Samples in Liquid Media

The optical rotation of the solid powder samples was measured on suspensions in a mixture of two miscible liquids, one with a lower and the other with a higher refractive index than the powder to be measured. The liquid mixtures were prepared in a volumetric flask. The refractive index of the liquids was measured on an Abbe Refractometer (Erma, Japan).

The accurate measurements of the optical rotation of suspensions were carried out in 4 ml rectangular glass cells with a path length of 10 mm, closed with a Teflon stopper. A sodium lamp (589 nm), generally with a beam diameter of 6 mm and an integration time of 1 s, was used as a light source. The suspensions were stirred with a Teflon stirring bar driven by a rotating magnet attached to the bottom of the cell. The speed of stirring was regulated with an autotransformer and monitored by a Digital Stroboscope (Pioneer, Model DS-303).

Results and Discussion

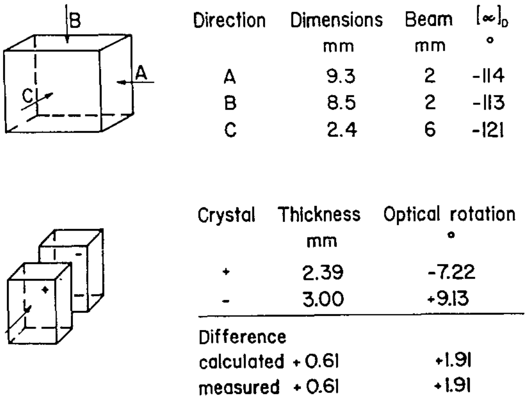
We have succeeded in measuring the optical rotation of isotropic inorganic powders in suspension. Only samples where the rotatory power was independent of the direction of measurement and represented the average contribution of all particles could be measured at this time and at this stage of development of our technique. In order to obtain reliable results, the liquid used as suspending medium had to be closely matched in refractive index with the solid particles and at the same time should not dissolve the particles. Sodium chlorate (Fig. 1) and sodium bromate (Fig. 2) crystals were found to be ideally suited for the development of this general method of measurement of optical rotation.

Initially the optical rotation of sodium chlorate crystals was measured (Table 1). In the direction of the *c* axis of the crystal at a light beam width of 6 mm, the photocell current was at least 40 microamperes and at this amount of energy through-put the data were the most accurate. The values of the optical rotation were the same in all three crystallographic directions (Fig. 3). The average value of the rotation per mm for the crytals in the direction of the *c* axis was 3.05° and the specific rotation was 122.2° ± 2°.

The optical rotation of the sodium bromate single crystals was measured after they were polished to rectangular plates. The results are summarized in Table 2.

Table 1. Measurement of optical activity of sodium chlorate single crystals

Crystal	Direction (crystal axis)	Path length in mm	Optical rotation in degrees	Photocell current in μA	Beam diameter in mm	Rotation per mm in degrees	Specific rotation in degrees
1	*a*	9.29	−26.45	20	2	−2.85	−114.0
	b	8.47	−23.83	25	2	−2.81	−113.1
	c	2.39	−7.21	77	6	−3.02	−121.3
2	*a*	11.90	+37.06	27	2	+3.11	+124.7
	b	11.01	+28.58	30	2	+2.56	+102.6
	c	3.73	+11.36	74	6	+3.05	+122.3
3	*c*	3.23	+10.00	77	6	+3.10	+124.4
4	*c*	3.65	+11.03	75	6	+3.02	+121.4
5	*c*	3.35	+10.19	75	6	+3.04	+12 .2
6	*c*	3.00	+9.12	76	6	+3.04	+122.2



Direction	Dimensions mm	Beam mm	$[\alpha]_D$ °
A	9.3	2	-114
B	8.5	2	-113
C	2.4	6	-121

Crystal	Thickness mm	Optical rotation °
+	2.39	-7.22
-	3.00	+9.13
Difference		
calculated	+0.61	+1.91
measured	+0.61	+1.91

Fig. 3. Measurements of optical activity of a sodium chlorate crystal in different direction

Table 2. Measurement of the optical activity of sodium bromate single crystals; beam diameter 6 mm

Crystal	Path length in mm	Optical activity in degrees	Photocell current in μA	Rotation per mm in degrees	Specific rotation in degrees
1	1.23	−2.42	47	−1.96	−59.4
2	0.70	+3.80	42	+2.23	+67.6

The average value of the optical rotation per mm was 2.09° and the specific rotation was 63.5° ± 2°, which is in good agreement with the literature values [8] of 2.12° and 64.2°, respectively.

For the measurement of the optical rotation of sodium chlorate (Fig. 4) and sodium bromate powders (Fig. 5) in suspension, the samples were prepared by grinding the crystals to particle sizes less than 150 microns. The actual measurements were carried out in glass cells with a path length of 0.5 mm or 1.0 mm. The suspensions were found to be sufficiently transparent to obtain accurate measurements. The samples were not very homogeneous and it was difficult or nearly impossible to fulfill the requirements of equal density and refractive index of the solid and the liquid suspending medium without stirring.

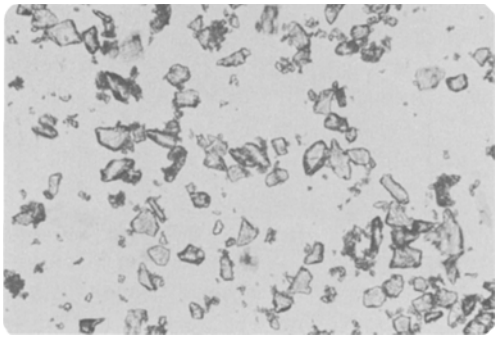


Fig. 4. Microphotograph of sodium chlorate powder, particle size 60 μm, magnification 100×

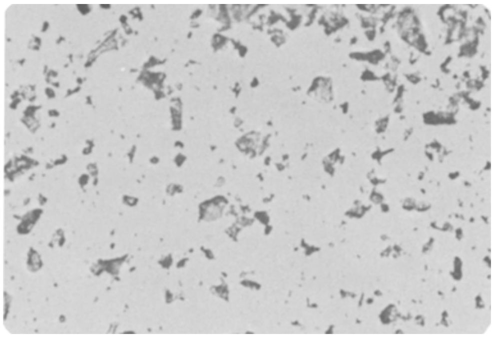


Fig. 5. Microphotograph of sodium bromate powder, particle size 100 µm, magnification 100×

As a consequence, the suspension which contained the solid powder and the liquid suspending media of isorefractive index had to be stirred. A small magnetic stirrer was placed at the bottom of the measuring cell which had a path length of 10 mm; the stirrer was driven externally by a rotating magnet placed below the cell. The stirring rate was kept constant and controlled by a stroboscope; a stirring rate of 600 rpm was found to be optimum. The suspension was now "homogeneous" and the particles were distributed evenly throughout the entire liquid suspending medium and the suspension appeared transparent (Fig. 6).

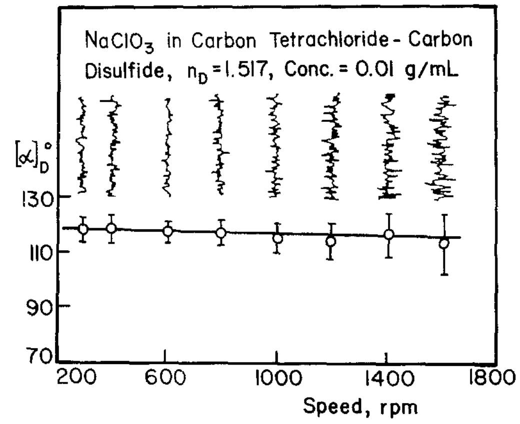


Fig. 6. Specific rotation of sodium chlorate in carbon tetrachloride/carbon disulfide as a function of speed of stirring

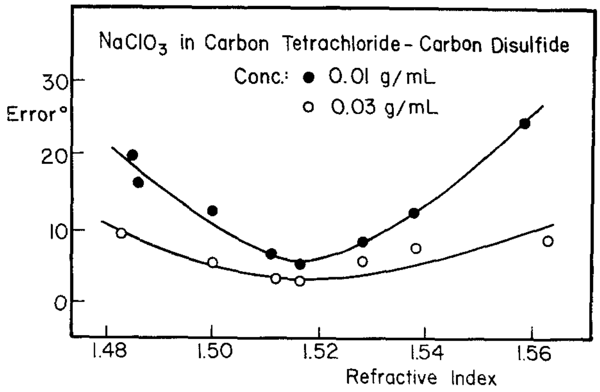


Fig. 7. Error of measurement of optical activity of sodium chlorate in carbon tetrachloride/carbon disulfide as a function of refractive index

The deviation from the ideal stirring rate could be most conveniently recorded using an attachment which was connected to a recorder. The uniformity of the suspension was best maintained when the particle size of the solid powder was less than 50 microns. Fig. 7 shows our study of the accuracy of the measurements displayed on a recorder; it again demonstrates the relative ease of selection of the optimum refractive index for the measurements.

The best matching of the refractive index of the solid powder with the suspending media was found when the transparency of the suspension was at its maximum, in our case at about 600 rpm (Fig. 6). The transparency of the suspension is proportional to the energy through-put which is expressed as the photocell current. The optical rotation of the suspension was measured at "constant concentration" of the suspended solid powder in the liquid suspending media as a function of the refractive index.

Fig. 8 shows the comparison of the relative specific rotation of the suspension as a function of the relative refractive index of the suspending medium for sodium chlorate and sodium bromate. In both cases similar patterns were observed. It is also clear that excellent measurements of the rotation could only be made when the deviation of the refractive index from the maximum did not exceed one percent even though at higher deviations, the measurements may still be meaningful.

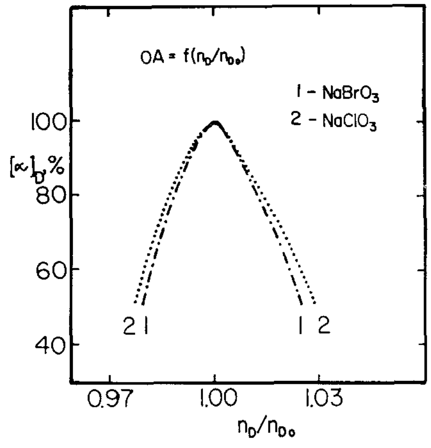


Fig. 8. Comparison of the matching of the refractive indices of the solid powders with the liquid media for sodium chlorate and sodium bromate

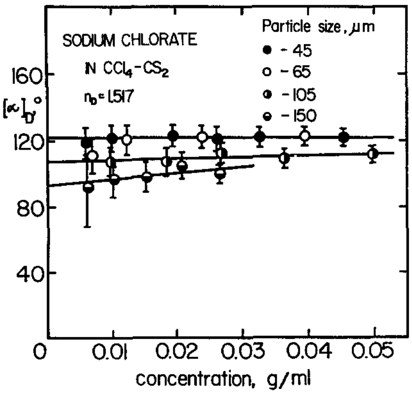


Fig. 9. Specific rotation of sodium chlorate in a mixture of carbon tetrachloride/carbon disulfide ($n_D = 1.517$) as suspending medium as a function of "concentration" and particle size

For more precise measurements, the specific rotation of the solid in the liquid suspending media was measured as a function of its "concentration". Fig. 9 shows the optical rotations of sodium chlorate samples of different particle sizes. This figure shows specifically the effect of the size of sodium chlorate particles larger than 65 μm on the value of the specific rotation as a function of the overall "concentration" of sodium chlorate in suspension. The values for suspensions of smaller particles were found to be the same as those obtained from measurements on single crystals of sodium chlorate. The larger particles, even at higher speeds of stirring (1200 rpm), were not sufficiently homogeneously distributed in the liquid suspending medium.

Fig. 10 shows the optical rotation of sodium bromate suspensions as a function of solid particle "concentration" in a mixture of two different liquid media, carbon tetrachloride/1-napthaldehyde and carbon tetrachloride/diiodomethane. Both mixtures had a refractive index $n_D = 1.616$. Fig. 10 shows clearly that the specific rotations of sodium bromate powder in both of these isorefractive mixtures are the same and in full agreement with measurements of the optical rotation of sodium bromate crystals [8].

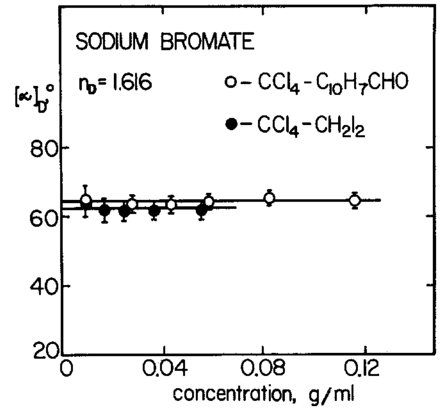
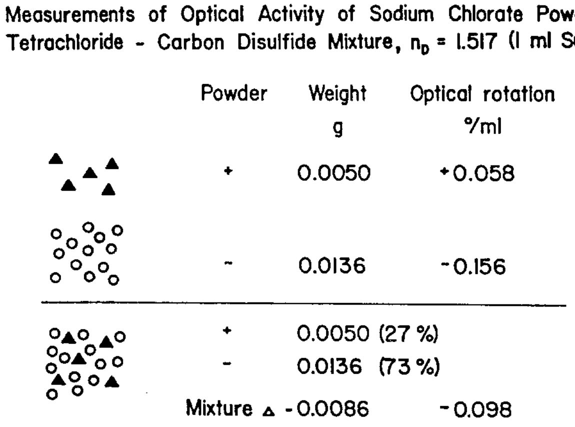


Fig. 10. Optical activity of sodium bromate in a mixture of isorefractive liquids ($n_D = 1.616$) as a function of "concentration"



Measurements of Optical Activity of Sodium Chlorate Powder in a Carbon Tetrachloride - Carbon Disulfide Mixture, n_D = 1.517 (1 ml Suspension)

	Powder	Weight g	Optical rotation °/ml
▲ ▲ ▲ ▲ ▲	+	0.0050	+0.058
○ ○ ○ ○ ○ ○ ○ ○ ○ ○ ○	-	0.0136	-0.156
○▲○ ▲○ ○○▲ ○○ ▲○○▲ ○ ○	+ -	0.0050 (27 %) 0.0136 (73 %)	
	Mixture △	-0.0086	-0.098

Fig. 11. Measurements of the optical activity of sodium chlorate powder with positive and negative rotation

Fig. 11 shows the values of the measurements of the optical activity of a mixture of sodium chlorate powders obtained from dextro- and leavorotatory crystals. The mixture of the (+) and (−) sodium chlorate powders showed values of their optical rotation measured (−0.098°) similar to those calculated (−0.086°).

Attempts were also made to measure other inorganic and organic crystals but without success. Sodium periodate (Fig. 12) together with quartz (Fig. 13) belong to the category of uniaxial crystals. The optical activity of sodium periodate crystal was measured and reported in the direction of the main optical axis [4].

We were not able to obtain reliable powder suspension measurements for sodium periodate. Quartz (specific rotation: 845°, or 21.7°/mm [4]) gave good optical activity measurements in the direction of its crystal growth axis (we measured 21.7°/mm), but even when properly ground and measured in suspension, gave unsatisfactory results.

We have also attempted to measure the optical rotation of benzil. Crystals of benzil are known to be optically active but the optical rotation was described as being strongly wavelength dependent. The values of our benzil crystals (Fig. 14) showed an specific rotation of 28°/mm (Ref. value [14] is 25.3°/mm). We could not

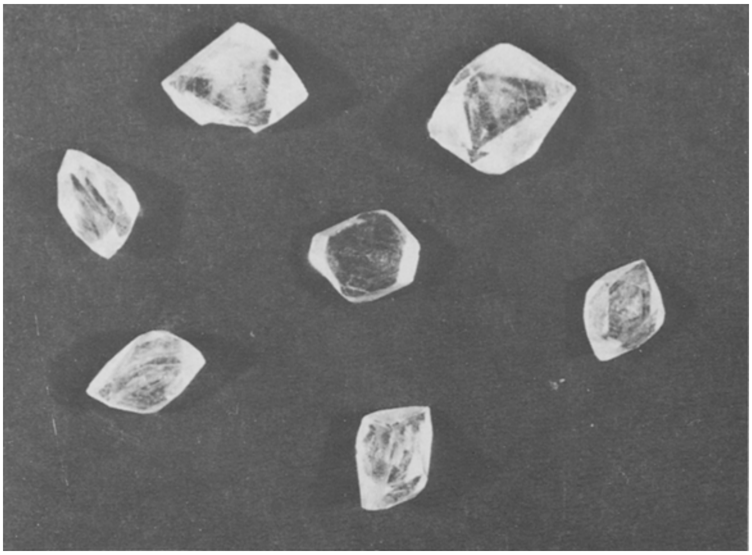


Fig. 12. Sodium periodate crystals

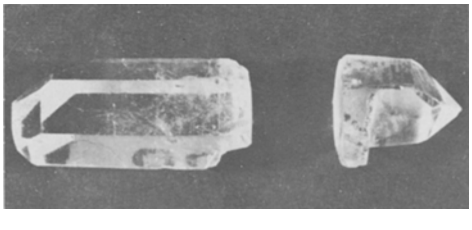


Fig. 13. Quartz crystal

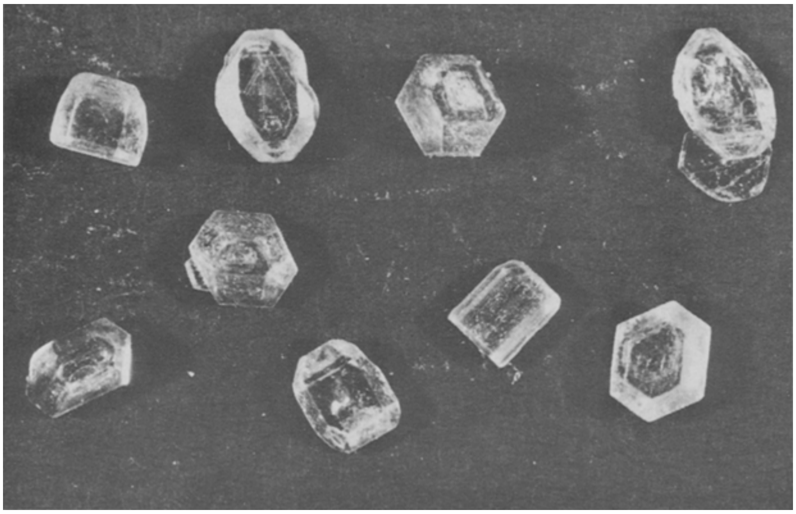


Fig. 14. Benzil crystals

measure the optical rotation of benzil powder in suspension because benzil was soluble in the organic liquids that we tried for matching the refractive index of benzil.

In conclusion we have demonstrated that the optical activity of isotropic crystalline solids can be measured precisely if the particle size of the crystal is small enough and the refractive index of the suspending liquid and the evenly suspended solid phase is carefully matched. The method also allows measurements of the optical activity of polymers which are insoluble and are not highly crystalline.

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