maintained below 35° by circulating water through a copper trough holding the apparatus.

To carry out the recovery of the protein, 1 g. of protein picrate (CS-5-7)[5] dissolved in 100 ml. of 50% dioxane, was placed in the third cell from the cathode and 100 ml. of 50% dioxane was placed in each of the other cells. Direct current at 1500–2500 volts was applied at the platinum electrodes in terminal cells for four hours, and the voltage was then increased to 4000 volts for sixty-eight hours. The initial current of 1.1 milliamperes gradually increased to 6.0 and then dropped to 2.9 where it remained constant. At the end of this operation the cathode cell contained a gummy precipitate and nearly colorless solution. The other cells contained picric acid as indicated by the yellow color which was progressively more intense toward the anode cell. The supernatant liquid in the cathode cell was decanted and the precipitate was dissolved in 30 ml. of water. This solution, decolorized by boiling with activated charcoal, was centrifuged and filtered through a Seitz sterilizing pad. The clear colorless filtrate was poured into 100 ml. of cold ethanol and precipitated by adjusting the *p*H to 6.3 with dilute acetic acid. A yield of 180 mg. of a white powder was recovered by centrifuging followed by drying in a vacuum over phosphorus pentoxide. The recovered solid contained 19.8% (ash-water free basis) nitrogen and gave protein color tests like CS-13A. The solid diluted to $1:10^6$ induced strongly positive cutaneous reactions on cottonseed sensitive patients.

Allergen Investigations
Bureau of Agricultural Chemistry and Engineering
U. S. Department of Agriculture
Washington, D. C.

Received January 24, 1941

---

(5) Spies, Bernton and Stevens, This Journal, **62**, 2793 (1940).

COMMUNICATIONS TO THE EDITOR

ULTRAVIOLET ABSORPTION OF THE DIPHENIC ACIDS

Sir:

Recent studies have emphasized the fact that absorption in the ultraviolet is a measure of resonance or conjugation and that structure is indicated only incidentally as it contributes to this phenomenon. Recently in this Laboratory the absorption curves have been obtained for ortho-ortho′-, meta-meta′- and para-para′-diphenic acids. It is interesting to report the radically different behavior of these three compounds in respect to their ultraviolet absorption.

The *o-o*′-diphenic acid shows an absorption which differs but little from that of benzoic acid. Evidently the carboxyl groups in the *o*-position interfere to such an extent that the coplanar position is impossible and resonance between the rings completely disappears.

On the other hand, the *p-p*′-diphenic acid (in this case the methyl ester) shows a very great absorption with the maximum near 2800 Å. Here we have exact coplanarity with complete resonance throughout.

By far the most interesting of these compounds, however, is the *m-m*′-diphenic acid. While the absorption is much greater than that of the *o-o*′-compound, it is much less than that of the *p-p*′-acid and the maximum is shifted toward shorter wave lengths so that it lies beyond the range of the medium quartz spectrograph. It is clear that it is not possible for a structure to exist which involves double bonds between the rings and between the ring and the carbon of the carboxyl group at the same time and this is the important structure for total resonance. Hence competition between these structures results in a decreased amount of conjugation.

It is interesting to note that a similar situation arises in the case of diphenylmethane. *p*-Cresol shows a marked increase in absorption and a shift of the maximum toward longer wave lengths. On the other hand, *p*-hydroxydiphenylmethane shows little difference from the diphenylmethane. This is not difficult to understand when we recognize that the principal resonance structure which contributes to the absorption in diphenylmethane is one in which the *p*-carbon acquires a negative charge. This structure does not involve conjugation with the hydroxyl group.

The details of this research will be published later but meanwhile we wish to acknowledge our indebtedness to Dr. N. Kornblum and Messrs. L. Brooks and J. C. Robinson for the preparation of the several acids.

Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois

E. C. Dunlop
Barbara Williamson
W. H. Rodebush
A. M. Buswell

Received March 6, 1941

UNIT CELL MEASUREMENTS OF Pb_3O_4, Pb_2O_3 AND Tl_2SO_4

Sir:

X-Ray measurements and space groups recently determined in these laboratories for Pb_3O_4, Pb_2O_3 and Tl_2SO_4 are listed below. The Pb_3O_4 and Pb_2O_3 represent new structure types.

1. Pb_3O_4. Tetragonal: a_0 = 8.86 Å.; c_0 = 6.66; density, 9.1; 4.2 $\simeq$ 4 Pb_3O_4 per unit cell; extinctions, *h*0*l* interferences present only when *h* is even; probable space group, $P\bar{4}b2$ (D_{2d}^7). These crystals were previously described in a paper from this Laboratory[1] as monoclinic. It is now desired to correct this conclusion which was the result of the high distortion of the crystals, produced under the conditions of their formation (high temperature and pressure). Goniometer X-ray patterns, similar to those shown for Pb_2O_3 in Fig. 1, establish the tetragonal nature of the material.

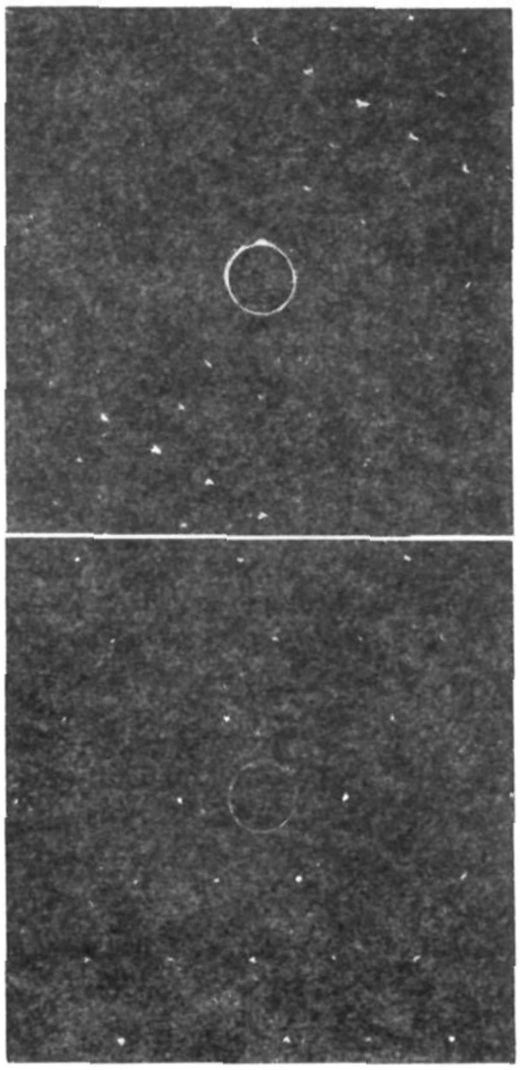

Fig. 1.—Goniometer patterns for Pb_2O_3, $\rho d = K\lambda$. a. *hk*0 interferences (K = 3.46, λ = 1.54 Å.). b. *h*3 interferences (K = 3.00, λ = 1.54 Å.).

2. Pb_2O_3. *Monoclinic:* a_0 = 7.03 Å.; b_0 = 5.62; c_0 = 3.93; β = 82°; density, 9.925; 2.00 $\simeq$ 2 Pb_2O_3 per unit cell; apparent extinctions, 0*k*0 present only when *k* is even; probable space groups, $P2_1/m$ (C_{2h}^2) or $P2_1$ (C_2^2). Patterns of various apparently untwinned crystals of this material, originally described as triclinic,[1] require a monoclinic crystal symmetry (see Fig. 1).

3. Thallous sulfate, Tl_2SO_4. Orthorhombic: a_0 = 10.68 Å.; b_0 = 6.02; c_0 = 7.81; density, 6.77; 4.08 $\simeq$ 4 Tl_2SO_4 per unit cell; extinctions, 0*kl* present only when ($k + l$) is even; *hk*0 present only when *h* is even; space group, *Pnma* (V_h^{16}). Patterns are similar to those of the isomorphous K_2SO_4.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
S. T. GROSS

RECEIVED MARCH 5, 1941

---

[1] G. L. Clark, N. C. Schieltz and T. T. Quirke, THIS JOURNAL, 59, 2305 (1937)

SEPARATION OF STARCH INTO ITS TWO CONSTITUENTS

Sir:

Although numerous attempts have been made to separate the two constituents of starch (α-amylose, amylopectin, erythroamylose and β-amylose, amylose, amyloamylose) in pure form (ultrafiltration, electrodialysis, etc.), there seems to exist no method that would allow the isolation of the two amyloses in sufficiently large quantities and high purity. In searching for such a method it occurred to us that perhaps the preferential adsorption of either constituent on the surface of some suitable material would lead to complete separation. Preliminary experiments carried out on activated carbon, fuller's earth and Brockmann alumina showed that selective adsorption did occur, in that the β-amylose became firmly bound to these materials, whereas the α-amylose remained in solution. Our best results, however, were obtained by the use of cellulose as adsorbent. It is well known that the ancient peoples employed starch for sizing papyrus and paper. Further, it is a matter of common experience that starched linen, even after it has been washed several times in water, retains its ability to give blue coloration with iodine. The preferential adsorption of β-amylose by cotton in considerable amount (1.7%) was recently reported by Samec [*Ber.*, **73A,** 88 (1940)]. We have found that the cotton-β-amylose adsorbate, which is formed instantaneously when a cold 1% corn starch paste is brought in contact with cotton, can be washed free of α-amylose with cold water. The adsorbate is then easily broken up by hot water to yield a clear solution of pure β-amylose. From the solution that has been passed several times through the regenerated cotton α-amylose can be obtained by concentration of the solution and precipitation with alcohol. On the other hand, the isolation of β-amylose from its aqueous solution in dry form is not possible. It can be precipitated with alcohol, but almost all of the substance so obtained becomes insoluble in water when dried in a desiccator. Also, the originally clear solution of β-amylose rapidly develops turbidity and the β-amylose precipitates out in granules (retrograded β-amylose or starch-cellulose), which are insoluble in cold water but soluble in cold, strong alkali solution. By addition of pyridine to the original aqueous solution of β-amylose the retrogradation can be prevented. On distillation of this solution with occasional addition of pyridine finally a clear pyridine solution of β-amylose can be obtained, from which β-amylose can be precipitated with alcohol. Evaporation of this pyridine solution results in the formation of an insoluble film of β-amylose. Preliminary experiments showed that both our α- and β-amyloses possess identical specific rotation $[\alpha]^{20}_{D}$ 145° in a 20% sodium hydroxide solution, and both of them use almost exactly one mole of periodic acid for oxidation. So far the only chemical difference we have found between the two amyloses exists in the complete absence of phosphorus in β-amylose and the presence of this element (0.020%) in α-amylose. Furthermore, the original solution of β-amylose gives a deep blue color with iodine, whereas α-amylose shows a purple color. An extensive investigation of these two materials has been initiated in this Laboratory.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY EUGENE PACSU
PRINCETON, NEW JERSEY JAMES W. MULLEN, 2ND
RECEIVED FEBRUARY 10, 1941

NEW BOOKS

Scattering of Light and the Raman Effect. By S. BHAGAVANTAM, M.Sc., Ramchandra Deo Professor of Physics, Andhra University. The Registrar, Andhra University, Waltair, India, 1940. x + 333 pp. 2 plates and 41 figs. 18 × 25.5 cm. Price 22s. or Rs. 15 net.

As remarked by the author in his preface, this book deals mainly with the physical aspects of the scattering of light and the Raman effect. The chapter headings are as follows:

Preface, Foreword by Sir C. V. Raman
I. Some Natural Optical Phenomena
II. Light Scattering as a Residual Effect
III. Laws of Scattering of Light
IV. Experimental Results in Gases and Comparison with Theory
V. Theory of Light Scattering by Dense Media
VI. Experimental Results in Liquids and Comparison with Theory
VII. Binary Liquid Mixtures and Liquid Boundaries
VIII. Optical Anistropy and Molecular Structure
IX. Optical Anistropy and Different Types of Birefringence
X. The Principal Experimental Results in Raman Effect
XI. Theory of Raman Scattering
XII. Symmetry, Selection Rules and Molecular Oscillations
XIII. Raman Effect and Molecular Structure
XIV. Raman Effect in Relations to Crystal Structure
XV. Experimental Technique
XVI. Raman Effect in Relation to Inorganic Chemistry
XVII. Raman Effect in Relation to Physical Chemistry
XVIII. Raman Effect in Relation to Organic Chemistry

Appendices:
I. Radiation from Moving Charges
II. Convergence Correction
III. Fluctuations
IV. Evaluation of the Various Matrix Elements of Polarizability Tensor
V. Tensor Components and their Transformation from One Coordinate System to Another
VI. Groups and Group Characters
VII. Group Theory and Normal Oscillations of Molecules

Over one-third of the book deals with Raleigh scattering. The experimental material and theory of Raleigh scattering form a natural background for the full understanding of the Raman effect. These are fully presented in an interesting manner with a mathematical formulation that can be followed easily. The chapter on birefringence will be