cillation would be independent of plate circuit tuning. The plate circuit was tuned by a 0–1400 $\mu\mu$f. precision condenser in parallel with the dielectric constant cell. The plate circuit voltage, after rectification and amplification, was read on a microammeter. The measuring cell was of the type described by Smyth.[4]

As a check on the method the moments of benzotrifluoride and nitrobenzene were determined in benzene solution: benzotrifluoride 2.56 D (lit. 2.56)[2]; nitrobenzene 3.89 D (lit. 3.90).[4]

Materials.—Benzene and n-heptane were purified following directions given in the literature[2]: benzene, d^{25}_4 0.87319, n^{25}_D 1.4977; n-heptane, d^{25}_4 0.67934, n^{25}_D 1.3850.

The synthesis and purification of the three trifluoromethyl styrene isomers will be described elsewhere by A. B. Conciatori. Physical constants on the purified materials are ortho-isomer: b. p. 61.0° (40 mm.); d^{25}_4 1.1749; n^{25}_D 1.4677; meta-isomer: b. p. 64.5° (40 mm.); d^{25}_4 1.1588; n^{25}_D 1.4632; para-isomer: b. p. 65.8° (40 mm.); d^{25}_4 1.1653; n^{25}_D 1.4648.

(4) Smyth, "Dielectric Constant and Molecular Structure," Chem. Catalog Co., New York, N. Y., 1931, p. 60.

APPLIED SCIENCE RESEARCH LABORATORY
UNIVERSITY OF CINCINNATI
CINCINNATI, OHIO RECEIVED DECEMBER 17, 1949

Small Angle X-Ray Scattering by Cellulose Fibers: Experimental Study of the Orientation Factor in Model Filaments and Rayons

BY A. N. J. HEYN

Preceding papers[1] described the X-ray scattering at small angles by various natural cellulose fibers. Valuable conclusions could be drawn from the scattering patterns regarding orientation and relative distance of the micelles in these fibers.

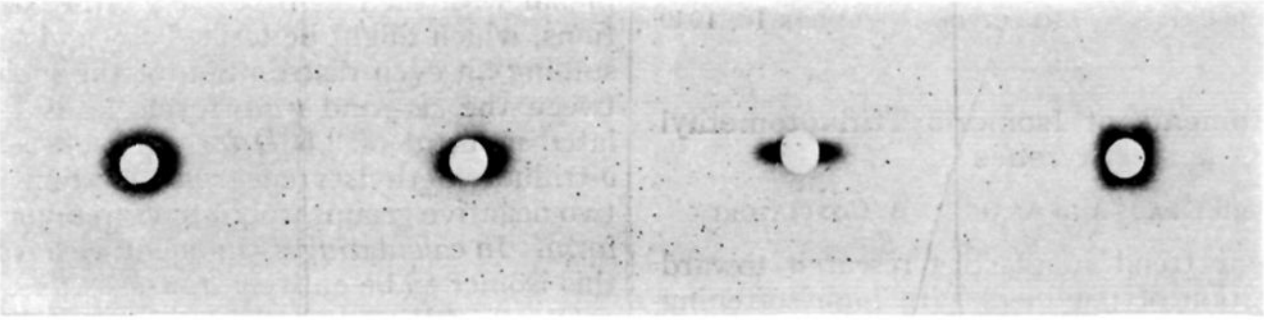
Experimental proof was given[1] that interparticle interference plays a prominent role in this type of scattering, as any experimental change in *distance* of the particles resulted in corresponding changes in the pattern. This scattering is therefore best comparable to that by liquids—the molecules in the liquid being replaced by the micelles.

The present paper represents a continuation of this investigation by presenting further data on the scattering by rayon and cotton recently made possible by the application of a special technique. The most important feature studied in the present investigation is the relationship between experimentally controlled changes in particle *orientation* and the resulting scattered intensity.

A. Experiments with "Model" Filaments.—A special study was made using mono-filaments of regenerated cellulose as they provide a perfect material in which the particle orientation could be controlled. For this work, "model" filaments were prepared from a viscose solution by applying the following forces during coagulation: 1, no force applied, resulting in a random orientation; 2, different degrees of stretch, resulting in longitudinal orientation; 3, twist applied, resulting in a spiral orientation. For each X-ray exposure only one mono-filament was used.

Comparison of the resulting patterns revealed a direct relationship between orientation and scattered intensity. In the case of random orientation, Fig. 1a, the intensity was equally distributed around the primary beam. Stretch, however, changed the intensity to become more and more concentrated on the equator as shown in Fig. 1b and 1c which represent a sample stretched 20 and 50 per cent. Torsion resulted in a cross-like distribution of the scattered intensity (Fig. 1d). This last result substantiated the earlier explanation of a similar cross-like pattern shown by natural fibers having a spiral structure.[2] The above investigations with model filaments are then the first proof by *experimental* methods of the direct relationship between particle orientation and X-ray scattering.

B. Experiments with Commercial Viscose Rayons.—By the use of the new technique very clear and distinct patterns were for the first time obtained of many different commercial viscose rayons, both conventional rayons (Avisco, Narco, Supernarco, Cordura, Bemberg) and materials of high degree of crystallinity (Fortisan, Fiber G). Examination of the patterns revealed a narrow intensity distribution along the equator sharply defined by the highly crystalline rayons contrasted with a more diffuse and wider distribution by the conventional rayons (compare Figs. 2c and 2d with 2a and 2b). The effect of greater Godet stretch (with the resulting orientation) is represented in the patterns (Figs. 2e and 2f) by the higher concentration of intensity on the equatorial line.



a b c d

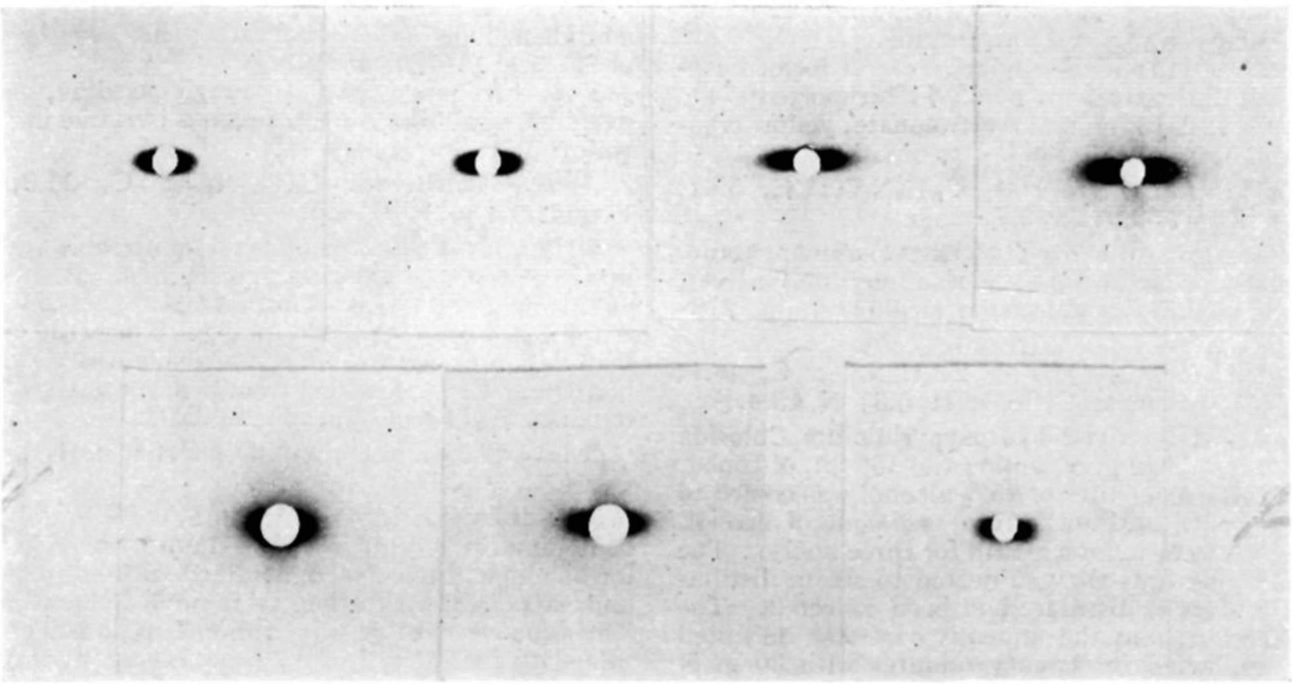
Fig. 1.—Small angle scattering by mono-filaments of regenerated cellulose: (a), no stretch or torsion; (b), low stretch; (c), high stretch; (d), torsion.

C. Experiments with Cotton.—It has been difficult to get a satisfactory pattern of cotton as the scattering intensity diverges so little from the primary beam that the intercepting plate blocked the majority of the pattern. For the first time a satisfactory picture of cotton was obtained by use of the new technique which disclosed a much larger portion of the scattering pattern (Fig. 2g). Thus

(1) A. N. J. Heyn, THIS JOURNAL, **70**, 3138 (1948); **71**, 1873 (1949); *Text. Res. Jour.*, **19**, 163 (1949).

(2) That the cross is not so distinct as that produced by natural fibers but more like a square is in agreement with the fact that torsion of the mono-filament produces a structure which is highly spiraled on the outer surface but only slightly spiraled toward the center.

a b c d



e f g

Fig. 2.—Small angle scattering by commercial rayons. Upper: (a) Avisco, Narco; (b) Supernarco; (c) Fortisan; (d) Fiber G. Lower: (e) Rayon after very low Godet stretch; (f) Rayon after 70% Godet stretch, and (g) cotton.

it was possible to study thoroughly the effects of different influences on the crystalline structure of cotton. For example, mercerization results in a widening of the scattering band along the equator indicating a smaller distance between the crystals which is probably due to the breaking down of crystals into smaller units by the action of the mercerizing solution. Another condition studied was that found in a sample of cotton treated with heptylamine (sample furnished by Dr. Segal of the Southern Regional Research Laboratory), which according to chemical determination had a lower degree of crystallinity.[3] The pattern of the treated sample showed a wider scattering band along the equator than did the untreated sample which may also indicate the breaking down of crystal size.

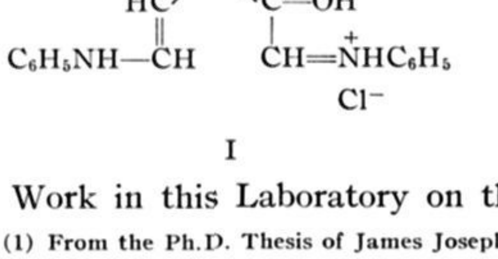
(3) L. Segal, M. L. Nelson, C. M. Conrad, Abstract, 116 Meeting Am. Chem. Soc., p. 12D (1949).

School of Textiles
Clemson Agricultural College
Clemson, S. C. Received December 7, 1949

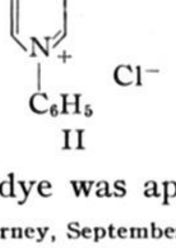
Hydrogenation of Hydroxyglutaconaldehyde Dianil and of 3-Hydroxy-1-phenylpyridinium Salts[1]

By C. F. Koelsch and J. J. Carney

Aniline, aniline hydrochloride and furfural react in alcohol solution to form a red-violet dye[2] which has been shown[3] to have structure I.



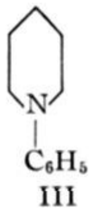
I



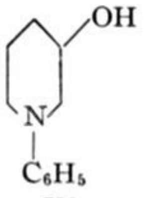
II

Work in this Laboratory on the dye was apparently simultaneous with that cited[3] and covers much the same ground. Although our data are now not needed to establish I, it may be noted that the solution obtained by treating the dye with nitrous acid furnishes iodobenzene in 29% yield[4] with potassium iodide, chlorobenzene (36%) with cuprous chloride, *p*-hydroxyazobenzene (36%) with phenol, and *p*-dimethylaminoazobenzene (80%) with dimethylaniline. Further, it has been found that catalytic hydrogenation of the dye furnishes aniline, *n*-amylaniline and α,ϵ-dicyclohexylaminopentane.

When the dye is heated, it is converted into II.[5] A convenient procedure for obtaining II is described in the present paper. It has been found that the product II can be hydrogenated with platinum to III and IV, whereas hydrogenation of the base corresponding to II yields IV alone. From this compound (IV), by nitrosation and subsequent hydrolysis, there can be obtained 3-hydroxypiperidine.



III



IV

Experimental

Hydrogenation of the Dye.—A suspension of 20 g. of the dye and 0.15 g. of platinum oxide in 150 ml. of absolute alcohol absorbed 4.7–4.8 moles of hydrogen during five to six hours shaking under a pressure of 4 atm. Alcohol and catalyst were then removed, and the residues, combined from two reductions, were taken up in dilute hydrochloric acid. No organic material could be extracted with ether.

(1) From the Ph.D. Thesis of James Joseph Carney, September, 1942.

(2) Stenhouse, *Ann.*, **156**, 199 (1870).

(3) Williams and Wilson, *J. Chem. Soc.*, 506 (1942).

(4) On the basis of two molecules of aniline per molecule of dye.

(5) Zincke and Mulhausen, *Ber.*, **38**, 3824 (1905).