trinitro-1,3-benzenediamine, m. p. 275–277°; lit. value 275°.[7]

Purification and Identification of the Pyridinium Salt of Chloropicric Acid.—The benzene-insoluble residue obtained in the preparation and purification of chloropicryl chloride was recrystallized from acetone and dissolved in a 1.5% sodium hydroxide solution. The deep red solution which resulted was distilled to dryness at reduced pressure. The distillate contained pyridine which was identified by the preparation of its styphnic acid salt. The residue in the flask was dissolved in 20 ml. of water and acidified with dilute sulfuric acid to give crystals which upon recrystallization from carbon tetrachloride melted at 113–113.5°; lit. value[8] 114°.

Anal. Calcd. for $C_6H_2O_7N_3Cl$: Cl, 13.45. Found: Cl, 13.30.

The identity with chloropicric acid was further ascertained by converting it with gaseous ammonia to 3-amino-2,4,6-trinitrophenol, m. p. 222–223° (cor.), lit. value[9] 219° (uncor.). The acidic portion of the original salt was therefore chloropicric acid, and the basic portion was pyridine. As a final check, the pyridinium salt of the material identified as chloropicric acid was prepared and it was found to melt at 159–161° and to give no melting point depression when mixed with the original material.

Preparation of Dipyridinium Styphnate.—To 50 g. (0.20 mole) of dry styphnic acid was added 200 g. (2.53 moles) of pyridine. The thick slurry which formed was stirred until the reaction was complete. The excess pyridine was filtered off and the yellow product was washed with ether. After drying, 77 g. (93.8%) of salt was obtained, m. p. 173–176°; neut. equiv. calcd. for $C_{16}H_{13}O_8N_5$ 201.6; found, 198.2. When the salt was heated at 60° for eight days, it was converted quantitatively into the monopyridinium styphnate.[10]

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[7] Korner and Contardi, *Atti. acad. Lincei*, **17**, I, 473 (1908).

[8] Hodgson and Moore, *J. Chem. Soc.*, **127**, 1603 (1925).

[9] Blanksma, *Rec. trav. chim.*, **21**, 259 (1902).

[10] Financial support of this research was supplied by the United States Office of Naval Research.

DEPARTMENT OF CHEMISTRY
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Electric Moments of Isomeric Trifluoromethyl Styrenes

BY GERARD KRAUS AND ANTHONY B. CONCIATORI

The recent trend in plastics research toward the preparation of polymers with high softening points and great resistance to chemical changes at high temperatures has created considerable interest in monomers with large dipole moments.[1] In the course of a study of certain fluorine derivatives of styrene we have determined the electric moments of ortho-, meta- and para-trifluoromethylstyrene in benzene and *n*-heptane solution with the results listed in Table I.

TABLE I

Trifluoromethylstyrene isomer	Moment (Debye units) Solvent benzene	Solvent heptane	Calculated
Ortho	2.40	2.45	2.38
Meta	2.48	2.52	2.50
Para	2.44	..	2.42

In computing the moments the small atomic polarization was neglected. The values obtained from measurement in heptane solution are seen to be somewhat larger than those obtained with benzene as the solvent, the difference being of the same order of magnitude as found by Freiser and co-workers with other aromatic fluorine compounds.[2] Unfortunately the quantity of *p*-trifluoromethylstyrene available to us was too small to permit a reliable determination of its moment in *n*-heptane solution to be made.

The calculated values were obtained by vector addition using the data

Group moment of $—CF_3$	2.56[2]
Group moment of $—HC{=}CH_2$	0.37[3]

The direction of the vinyl group moment was obtained from the dipole moments of para substituted styrenes by means of the well known expression

$$\cos\theta = \frac{\mu^2 - m_1^2 - m_2^2}{2m_1m_2} \qquad (1)$$

From the data of Otto and Wenzke[3] on *p*-chlorostyrene, *p*-bromostyrene, *p*-methylstyrene and *p*-ethylstyrene θ was computed as 123°, 132°, 110° and 105°, respectively. In view of the small magnitude of the styrene moment the calculation is rather sensitive to small errors and the agreement must be regarded as satisfactory. In calculating the moments in Table I we have set θ equal to 117.5°, the average of the above values. The dipole moment of the para isomer is readily obtained from equation (1). Since free rotation about the bond between the vinyl group and the ring appears improbable on account of resonance, it seems most likely that the vinyl group is coplanar with the ring occupying either of two positions, which might be termed *cis-* and *trans-*. Assuming an even distribution of the molecules between the *cis-* and *trans*-forms leads to a calculated moment of 2.50*D* for the meta isomer. In *o*-trifluoromethylstyrene the proximity of the two negative groups would tend to favor the *trans*-form. In calculating its moment we have assumed this isomer to be entirely *trans.*

Otto and Wenzke[3] admit the possibility of their value of 0.37*D* for the dipole moment of styrene being too high, the true value being perhaps in the neighborhood of 0.2*D*. If this were the case the angle θ in equation (1) would have to equal very nearly 180° and the calculated moments for the trifluoromethyl styrenes would be: ortho, 2.62*D;* meta, 2.52*D;* para, 2.36*D*. Our results appear to favor the higher value for the electric moment of styrene.

Experimental

Apparatus.—The dielectric constant determinations were carried out by a resonance method with a probable error in ϵ of 0.08%. The electrical apparatus consisted of a voltage regulated power supply, an electron coupled oscillator, detector, and a direct current amplifier. The plate circuit of the oscillator was tuned to the second harmonic of the grid circuit so that the frequency of os-

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[1] Mark, *Chem. Eng. News*, **27**, 138 (1949).

[2] Freiser, Hobbs and Gross, THIS JOURNAL, **71**, 111 (1949).

[3] Otto and Wenzke, *ibid.*, **57**, 294 (1935).

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.

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

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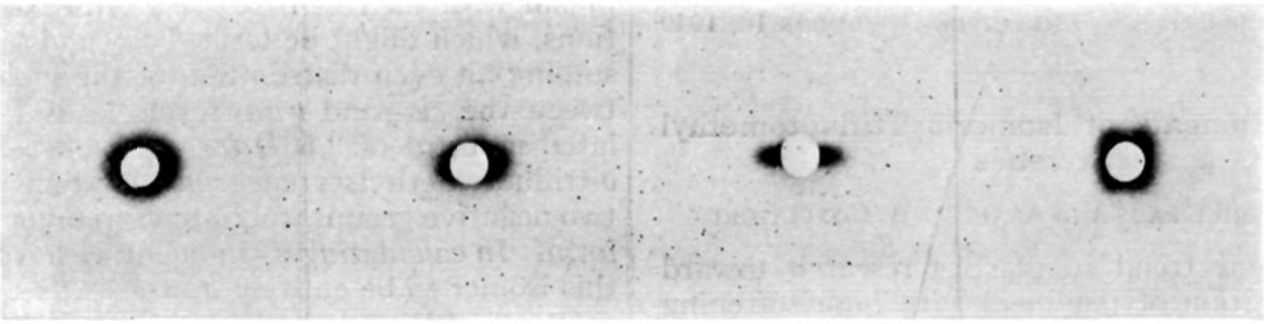
Small Angle X-Ray Scattering by Cellulose Fibers: Experimental Study of the Orientation Factor in Model Filaments and Rayons

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.



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.

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.

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

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[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.