TABLE I

TRIARYLAMINOSILANES

Silicon compound	Nitrogen compound	Product	M. p., °C.	Yield, %	Silicon, % Calcd.	Silicon, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$(C_6H_5)_3SiH$	$(CH_3)_2NLi$	$(C_6H_5)_3SiN(CH_3)_2$	80–81	74.5	9.24	9.2	4.67	4.6
$(C_6H_5)_3SiH$	$(C_2H_5)_2NLi$	$(C_6H_5)_3SiN(C_2H_5)_2$	84–85	74.2	8.46	8.6	4.23	4.3
$(C_6H_5)_3SiH$	$(n\text{-}C_4H_9)_2NLi$	$(C_6H_5)_3SiN(C_4H_9\text{-}n)_2$	60–62	63	7.23	7.6	3.61	3.6
$(C_6H_5)_3SiCl$	$(n\text{-}C_4H_9)_2NLi$	$(C_6H_5)_3SiN(C_4H_9\text{-}n)_2$	62	10	7.23	7.2	3.61	3.9
$[p\text{-}(CH_3)_2NC_6H_4]_3SiOH$	$(n\text{-}C_4H_9)_2NH$	$[p\text{-}(CH_3)_2NC_6H_4]_3SiN(C_4H_9\text{-}n)_2$	62–64	92	5.42	5.3		

amine in 25 ml. of anhydrous ether. The suspension was refluxed for one-half hour, after which time Color Test II-A[6] was negative and Color Test IV[2] was positive. Then 8.8 g. (0.034 mole) of triphenylsilane in 50 ml. of dry ether was added to the suspension of lithium di-*n*-butylamide, and the mixture was refluxed for one-half hour. The suspension was filtered and the solvent was removed by distillation. The residue from the distillation was refluxed with benzene for one hour, filtered, and the solvent was distilled. A similar treatment of this residue with petroleum ether (b. p. 60–70°) yielded a gummy solid which, after crystallization from absolute ethanol, weighed 7.6 g. (63%) and melted at 60–62°. A mixed melting point with the triphenyl-(di-*n*-butylamino)-silane obtained from triphenylchlorosilane was not depressed. Triphenyldimethyl- and triphenyldiethylaminosilane were prepared from triphenylsilane by suitable modification of this procedure.

Tris-(*p*-dimethylaminophenyl)-di-*n*-butylaminosilane.—One gram (0.0025 mole) of tris-(*p*-dimethylaminophenyl)-silanol[7] (m. p. 183°) was refluxed with 50 ml. of di-*n*-butylamine for thirty minutes. About two-thirds of the di-*n*-butylamine was then distilled off very slowly so as to remove water continuously as it formed during the reaction. The remaining solution, on cooling, deposited a sticky solid which, when recrystallized from di-*n*-butylamine and washed with petroleum ether (b. p. 30–60°), melted at 62–64° and weighed 1.2 g. (92%). This material was shown to be tris-(*p*-dimethylaminophenyl)-di-*n*-butylaminosilane by the following procedure. The material was agitated in 50 ml. of water at 70° for thirty minutes, filtered, and the precipitate (0.88 g.) was shown to be tris-(*p*-dimethylaminophenyl)-silanol by a mixed melting point determination. The filtrate was extracted with ether, and the extract was dried and distilled. The liquid remaining was identified as di-*n*-butylamine by a mixed melting point between its picrate and that of an authentic specimen.

Conversion of Triphenylsilanol to Hexaphenyldisiloxane. (a) **By Di-*n*-butylamine.**—Fifteen grams of triphenylsilanol (m. p. 151–153°) was refluxed with 25 ml. of di-*n*-butylamine for one and one-half hours. After removal of the insoluble solid and repeated concentration of the mother liquor, 13.7 g. (94.5%) of crude hexaphenyldisiloxane was obtained. The yield after recrystallization was 12.8 g. (88%), m. p. 222–224°. In a subsequent run, 10 g. of triphenylsilanol was converted to 5.2 g. (54%) of hexaphenyldisiloxane after being refluxed for three hours in 25 ml. of di-*n*-butylamine. The excess amine was washed out with acid, and the product was obtained by fractional crystallization.

(b) **By Diethylamine.**—Triphenylsilanol (0.0181 mole) was heated in a Carius tube with 0.0487 mole of diethylamine for three and three-quarter hours at 180–195°. The crystalline product, after being washed free of amine with petroleum ether (b. p. 60–70°), weighed 4.35 g. (91%). A mixed melting point with an authentic specimen showed no depression.

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(6) Gilman and Swiss, THIS JOURNAL, **62**, 1847 (1940).

(7) The preparation of this compound will be reported in a forthcoming publication.

A Quantitative Evaluation of Small-Angle X-Ray Scattering by Various Cellulose Fibers for the Determination of Crystallite Size with Special Reference to the Problem of Inter-particle Interference

BY A. N. J. HEYN

Previous articles by the author[1] discussed the scattering of X-rays at small angles by various cellulose fibers and the relation of this scattering to the orientation of the particles on a qualitative basis.

The quantitative evaluation of scattering to determine the size and distance of the particles was complicated because inter-particle interference was found to play an important role in this scattering. Therefore, application of simple approximation formulas for the calculation of the particle size as given by Guinier did not appear permissible under such conditions of "*densely packed systems*," as has been stressed already by Kratky and collaborators.[2] This is so because these formulas are based on the assumption that the particles scatter independently.

Interpretation of the increased intensity of scattering and the different distribution of intensity caused by the swelling of fibers (compare diagrams a and b of Fig. 1 of dry and wet flax) in previous experiments[1] offered a means of solving this problem; whereas with fibers in the dry state particle interference plays an important part, it was presumed that this no longer proved to be the case with fibers that have been swollen in various ways so as to increase the distance between the particles. The experiments discussed in this article show that when applying this new swelling technique it is indeed possible to use the above approximation formulas for the calculation of particle size. The results so obtained with different natural cellulose fibers and rayons are reported here.

Experimental

The formula by which Guinier, as based on Debye's general scattering formula, approximated the theoretical formula is given as formula (a). This approximation holds only for small angles, but if this condition is fulfilled—as in the present case—it affords one of the simplest methods for calculating of the particle size from the distribution of intensity.

$$I = NI_e n e^{-(4\pi^2/3\lambda^2)R^2\epsilon^2} \qquad \text{(a)}$$

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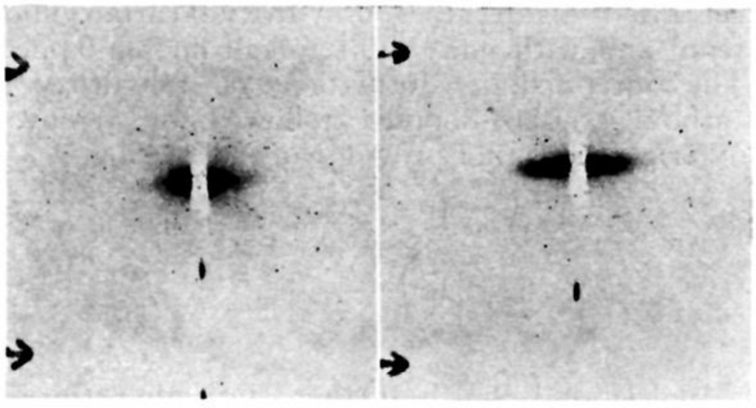
(1) A. N. J. Heyn, THIS JOURNAL, **70**, 3138 (1948); **71**, 1873 (1949); **72**, 2284 (1950); *Text. Res. J.*, **19**, 163–172 (1949).

(2) O. Kratky, *Naturwissenschaften*, **26**, 94 (1938); **30**, 542 (1942); O. Kratky, A. Sekora and R. Treer, *Z. Elektrochem.*, **48**, 587 (1942); O. Kratky and Wurster, *ibid.*, **50**, 249 (1944).



(a) (b)

Fig. 1.—Low angle scattering diagram of flax, (a) in the normal dry state: inter-particle interference influences the scattered intensity; (b) same sample (at same exposure time) in swollen state: probably no particle interference at all.

where I is the scattered intensity and I_e the intensity diffracted by one electron, N the number of electrons of all particles, n the number of electrons of each separate particle, R the radius of gyration of the particles, and ϵ the scattering angle. If the particles have the shape of elongated cylinders, as is probable in our case, it might be necessary to slightly modify the formula (a) into

$$I/I_e \sim e^{-(2\pi^2/\lambda^2)R^2\epsilon^2} \qquad \text{(b)}$$

and the radius of gyration of the particle has to be taken with reference to the longitudinal axis of the cylinder (as suggested by Guinier) so that the radius will be $1/\sqrt{1/2}$ times the radius of gyration.

For the purpose of our experiments, the scattered intensity along the equator was determined by measuring the *density of a photograph with a microphotometer which* results in curves like the one represented in Fig. 2. The logarithm of the intensity is plotted against the square of the scattering angle ϵ in Fig. 3 for dry and wet flax and in

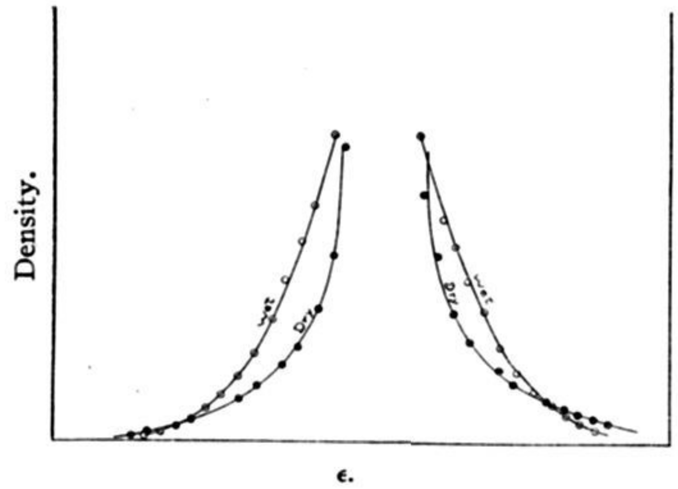


Fig. 2.—Distribution of intensity on both sides of primary beam in flax: outer curve swollen state; inner curve dry state.

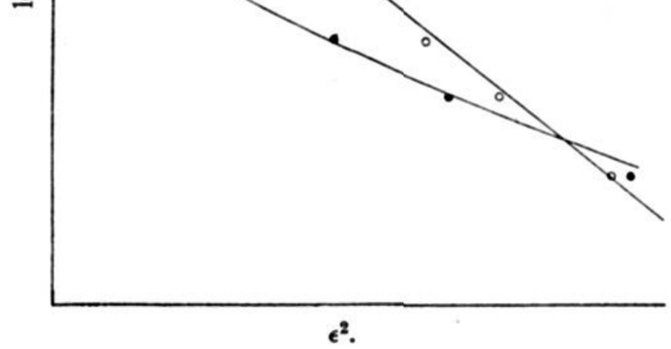


Fig. 3.—Log intensity *vs.* ϵ^2 for flax in the swollen (above) and dry (below) states comparing the swollen and original fiber.

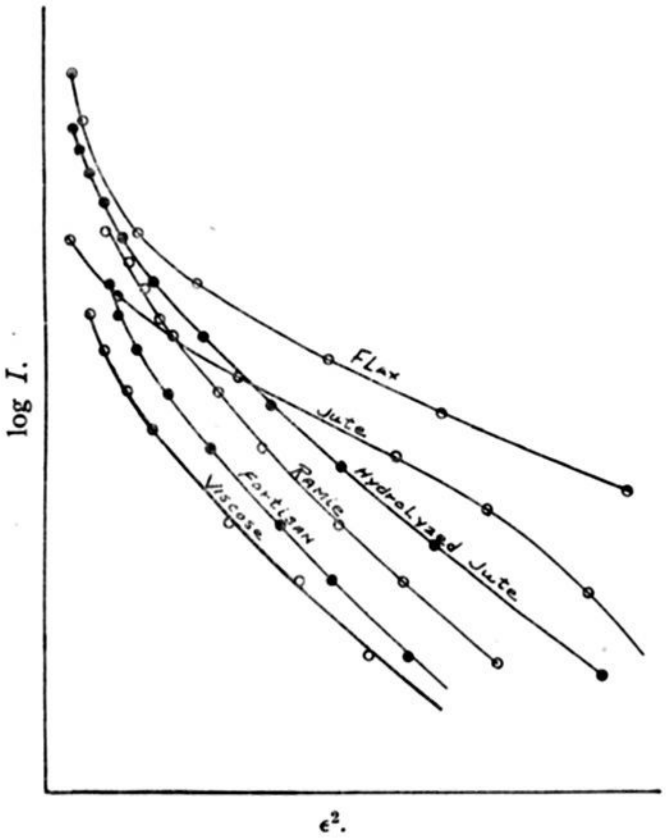


Fig. 4.—Log intensity *vs.* ϵ^2 for various cellulose fibers (flax jute,) hydrolyzed jute, ramie, fortisan viscose rayon, in the dry state.

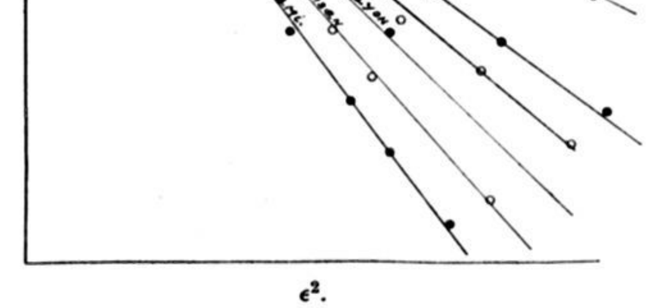


Fig. 5.—Log intensity *vs.* ϵ^2 for same fibers in the swollen state.

Fig. 4 for different fibers in the dry state and in Fig. 5 for the same fibers in the swollen state.

When the curves are straight lines, this would highly support (although not fully prove) the conclusion of independent scattering by the particles[3]; but this is seldom the case, as Warren and Biscoe[4] for example pointed out in their experiments on carbon black.

The curves of Fig. 4 show that in the case of dry fibers no straight lines are ever obtained. The curves obtained with swollen fibers (Fig. 5), on the other hand, differ from those of dry fibers by being perfectly straight as would be the case when the above assumptions are fulfilled.

The conclusion, therefore, is obvious that due to the swelling process, the particles are so far moved apart that inter-particle interference no longer plays a part, and the calculation of the particle size from the slope of the curves appears permissible. Another important conclusion from the straight shape of the curve is that the size of the particles will not vary to a large extent around an average value.

In Table I the slopes of the curves obtained with different fibers following this new swelling technique are given; these values are proportional to the sizes of the particles in the different fibers, indicating their ratios.

TABLE I

Fiber	Slope	Radius of gyration, Å.		Diameter, Å.	
		a	*b*	*a*	*b*
Jute	218	9.50	7.75	26.87	21.92
Hydrolyzed jute	296	11.07	9.03	31.32	25.54
Flax	313	11.39	9.29	32.21	26.27
Rayon (viscose)	396	12.81	10.45	36.23	29.55
Rayon (fiber G)	396	12.81	10.45	36.23	29.55
Rayon (fortisan)	450	13.65	11.14	38.62	31.50
Ramie	540	14.95	12.20	42.31	34.51

Values for radii of gyration are given in two columns in Table I, one using formula (a) and the other formula (b). The values of the particle diameter given also in Table I were calculated from the two sets of radii of gyration but under the assumption that the particles in both cases have the shape of an elongated cylinder.

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(3) If the various assumptions are fulfilled on which Guinier's theory is based, including independent scattering, the theory requires these curves to be straight lines.

(4) J. Biscoe and B. E. Warren, *J. Applied Phys.*, **13**, 364–371 (1942).

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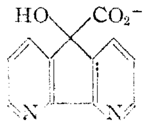
The Loss of Carbon Monoxide from 1,2-Diketones

BY P. H. GORE AND G. K. HUGHES

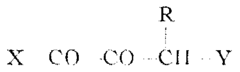
In a recent communication, G. E. Inglett and G. F. Smith[1] have recorded the formation in almost quantitative yield of 4,5-diazafluoren-9-one by alkaline treatment of 1,10-phenanthroline-5,6-quinone.

They regarded this removal of the elements of carbon monoxide as a "very surprising development," yet the reaction is perfectly analogous to the benzilic acid-type rearrangement[2] of phenanthrene-5,6-quinone, which with fairly concentrated alkali gives 9-hydroxy-9-carboxyfluorene[3] and with more dilute alkali fluoren-9-one.[4] The intermediate formation of 9-hydroxy-9-carboxy-4,5-diazofluorene followed by removal of formate ions thus provides an explanation.



Inglett and Smith further state that this is "the first reaction in which carbon monoxide has been observed to be lost from a 1,2-diketone grouping." However, several 1,2-diketones have long been known to lose carbon monoxide by the action of heat: diethyl 3,4-diketoadipate (ketipinic ester), 2,4,5,7-tetraketoöctane, 1,6-diphenyl-1,3,4,6-tetraketohexane and 1,4-diphenyl-1,4-dicyano-2,3-diketobutane.[5]

It appears from this, and from work carried out in this Laboratory, that for loss of carbon monoxide to occur at temperatures below about 160° (for 2-keto esters) or 250° (for 1,2-diketones), the following grouping should be present, both in 2-keto esters and in 1,2-diketones



$$X-CO-CO-\overset{R}{\overset{|}{CH}}-Y$$

where

X = CHCOR' or OR'
R = H, alkyl or aryl
Y = electron-attracting group

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(1) G. E. Inglett and G. F. Smith, THIS JOURNAL, **72**, 842 (1950).

(2) J. Liebig, *Ann.*, **25**, 27 (1838); N. Zinin, *ibid.*, **31**, 329 (1839); M. Bösler, *Ber.*, **14**, 323 (1881); L. Gattermann, *Ann.*, **347**, 364 (1906); etc.

(3) A. Baeyer, *Ber.*, **10**, 125 (1877); P. Friedländer, *ibid.*, **10**, 534 (1877).

(4) R. Anschütz and F. R. Japp, *ibid.*, **11**, 211 (1878).

(5) W. Wislicenus, *ibid.*, **28**, 811 (1895).

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RECEIVED JUNE 9, 1950

4,4'-Difluorobenzhydrol

BY F. A. GUNTHER AND R. C. BLINN

The authors recently reported[1] the synthesis of 4,4'-difluorobenzhydrol, a compound previously unrecorded in the literature, along with its simple properties and some of its reactions. In February, 1950, Picard and Kearns reported[2] the synthesis of the same compound by a different series of reactions. Whereas our benzhydrol melted at 47.3–47.5°, theirs melted at 92–93°. Rigid comparisons of the two compounds indicate different structures.

In our hands reduction of 4,4'-difluorobenzophenone with zinc and alkali gave the desired benzhydrol (II), whereas attempted reductions by aluminum isopropoxide yielded an unidentified substance (V) in the hands of Picard and Kearns The reaction schemes are as follows:

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(1) F. A. Gunther and R. C. Blinn THIS JOURNAL, **72**, 4282 (1950).

(2) Picard and Kearns, *Can. J. Research*, **28B**, 56 (1950).