equal since they are optical antipodes. IVa may have a very different residence time but has equivalent fluorines. At low temperatures in CS$_2$ solution, IIb and IIc show evidence of slow rotation about the C–C bond.[3] Thus at $-80°$, IIb appears to "freeze" to about a 1.4:1 mixture (analysis by line heights) of IVa (identifiable by its single resonance) and the *d,l*-pair IVb,c (identifiable by its quartet of resonance lines). With IIc, the rotational isomer IVa appears only to be present to the extent of about 10% at $-80°$.

Similar observations have been made for proton spectra of a few[4] compounds similar to I and II with $-CH_2-$ in place of $-CF_2-$. Compounds related to I like methyl 2,3-dibromo-2-methylpropanoate show "abnormal" spin–spin splittings for the $-CH_2-$ absorptions while those related to II like 1,2-dibromo-2-methylpropane give normal patterns; *cf*. Fig. 1. With substances like these, rotation about the C–C single bonds are unquestionably rapid.

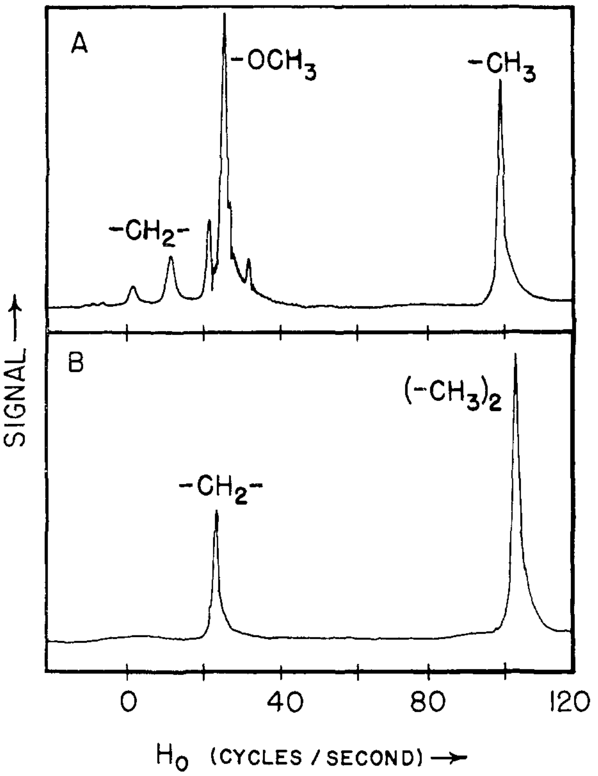

Fig. 1.—Pure liquid n.m.r. spectra of A, methyl 2,3-dibromo-2-methylpropanoate (J for coupling between *gem*-hydrogens at 3-position ~10–11 c.p.s.); B, 1,2-dibromo-2-methylpropane, taken with Varian Associates High Resolution Nuclear Magnetic Resonance Spectrometer, 12-in. magnet equipped with Super Stabilizer and at room temperature and 40 mc. Zero of reference scale was water absorption.

The importance of these observations is several fold. First, they establish beyond doubt that the residence times and populations for the various possible rotational configurations of compounds like I are not equal; second, with the aid of the reasoning used previously,[2] it becomes possible in principle to estimate, and perhaps determine, the population of the several configurations even though these are being rapidly interconverted. Third, populations of configurations may be measured directly for favorable cases by "freezing in" at low temperatures. Finally, a new and extraordinarily simple means is provided for possible detection of a carbon attached to a group without a plane of symmetry by observation of nuclear magnetic resonance spin–spin couplings without recourse to resolution into optical antipodes.[5]

(5) The method does not strictly provide a means for locating asymmetric atoms. Thus, 2-methyl-2-nitropropanediol shows nonequivalent methylene hydrogens although it is not capable of resolution into optical antipodes. However, each of the methylenes is attached to a group which has no plane of symmetry.

(6) Arthur Amos Noyes Fellow, 1956–1957.

CONTRIBUTION NO. 2211
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RECEIVED JUNE 10, 1957

NEW LINES IN THE X-RAY DIFFRACTION PATTERN OF ORTHORHOMBIC SULFUR. "AMORPHOUS" (μ)-SULFUR

Sir:

In connection with another problem[1] we had occasion to purify some sulfur by a recommended[2-4] method.[5] On comparing the X-ray diffraction pattern with the ASTM card file[6] for orthorhombic sulfur, we were surprised to find several extra lines in our diffraction pattern.[7] Since different radiation sources were used[8] one might expect differences in relative intensity values but not in the number and positions of diffraction peaks. We found later that the sulfur we purified was not completely soluble in carbon disulfide and thus considered the possibility that the new lines we observed might be due to the presence of this insoluble sulfur.[9] Thus we determined the diffraction pattern

(1) A. G. Pinkus and J. S. Kim, *Can. J. Chem.*, accepted for publication, 1957.

(2) "Gmelin's Handbuch der anorganischen Chemie," System-Nummer 9, Schwefel, Teil A, Lieferung 3, 8 Auflage, Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse, 1953, pp. 511, 512.

(3) "IUPAC Münster Colloquium on Silicon-Sulphur-Phosphates," Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse, 1955, p. 82.

(4) W. N. Tuller, ed., "The Sulphur Data Book," McGraw-Hill Book Co., New York, N. Y., 1954, p. 12.

(5) R. F. Bacon and R. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

(6) ASTM X-Ray Powder Data File, Special Technical Publication No. 48-F, 1957.

(7) Our data have been deposited with Dr. G. W. Brindley, Editor, "ASTM X-Ray Powder Data File," College of Mineral Industries, Pennsylvania State University, University Park, Pa., and list the d values and intensities of reflection.

(8) The ASTM samples were run with MoKα radiation and film whereas we used Cu Kα radiation and a recording North American Philips X-ray diffractometer.

(9) The insoluble sulfur as determined by repeated extraction with carbon disulfide until there was no further loss in weight (within 0.2 mg.) was 3.25%. This is close to the equilibrium value of 3.75% at 121° listed in J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, Green and Co., New York, N. Y., 1930, p. 47. Following a suggestion in a letter from Dr. Fanelli that the amount of insoluble sulfur could be reduced by heating at 125° overnight followed by slow cooling, the amount of insoluble sulfur was reduced to 2.49% after one such treatment using a ten-hour cooling period (heating mantle control). After the work in this paper was completed, a paper appeared (N. H. Hartshorne and M. Thackray, *J. Chem. Soc.*, 2122 (1957)) in which the amount of insoluble sulfur was reduced by "annealing at 100° for two days" (see also the Mellor reference on this point).

of sample of insoluble sulfur prepared according to the method in ref. 9. This diffraction pattern[7] was remarkably similar to that of orthorhombic sulfur. It is clear that this insoluble sulfur must have a crystalline structure. Since the line widths were comparable in the two cases, we conclude that the crystal size must be similar (since the half-width of the peak is proportional to particle size). This insoluble sulfur is commonly referred to as amorphous sulfur[10] or μ-sulfur and is thought to consist of long-chain polymers having molecular weights ranging from 18,000 to 73,000.[11] The only differences we have been able to observe between the diffraction patterns of the insoluble sulfur and orthorhombic sulfur are (1) differences in the relative intensities of several of the lines[7] and (2) the insoluble sulfur and the orthorhombic sulfur show a few lines not present in each others pattern; for example, lines at 2.99 Å. (insoluble) and 2.62 Å. (orthorhombic). The significance of these small differences is not clear at present. It is of course possible for polymeric materials to be in a crystalline form; however, one might expect a greater difference in the diffraction patterns of polymeric μ-sulfur and orthorhombic sulfur.

It is interesting that Das in a recent summary of his work[12] (some of it unpublished) has found an orthorhombic X-ray powder diagram for milk of sulfur (which has commonly been described as an amorphous modification) and also the same for colloidal sulfur prepared by the reaction of sulfur dioxide and hydrogen sulfide. In view of our findings and those of Das, it would seem advisable to discontinue the use of the term "amorphous" sulfur for these crystalline forms. The insoluble sulfur in the present paper could more aptly be referred to simply as "insoluble sulfur" or *u*-sulfur.

The X-ray diffraction patterns were obtained on a North American Philips X-ray diffractometer using a rotating sample holder of the type previously described.[13] This sample holder minimizes the possibility of orientation effects in powdered samples and thus makes it possible to obtain a more complete and accurate diffraction pattern.

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(10) Ref. 1, pp. 522, 574, 576; ref. 2, pp. 81, 83; ref. 3, pp. 4, 5, 7, 8; ref. 6, pp. 30, 32, 46; "Facts About Sulfur," Texas Gulf Sulphur Co., New York, N. Y., 1953, p. 19.

(11) H. Specker, *Z. anorg. allgem. Chem.*, **261**, 116 (1950).

(12) S. R. Das in ref. 3, p. 103.

(13) J. L. McAtee, Jr., *Am. Mineralogist*, **41**, 942 (1956).

(14) Baroid Division.

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CHEMISTRY OF THE NEOMYCINS. I. A PARTIAL STRUCTURE FOR NEOBIOSAMINES B AND C[1]

Sir:

Though the isomeric antibiotics neomycins B and C have been investigated extensively and widely employed clinically (as a mixture of the two isomers),[2] the structures of these compounds thus far have resisted complete elucidation. We wish to report here evidence that the neobiosamine[3] portion of both neomycins B and C consists of a diaminohexosido-pentose. In an accompanying Communication it is shown that the same pentose, D-ribose, is found in both isomers.[4]

Methanolysis of neomycin C gave neamine[2b] and methyl neobiosaminide C,[3] the latter, crude product, was carefully chromatographed and isolated as a mixture of its anomeric α- and β-glycosides [*Anal.* Calcd. for $C_{11}H_{21}N_2O_7(OCH_3)$: C, 44.44; H, 7.46; N, 8.64. Found: C, 44.60; H, 7.72; N, 8.55] and characterized as its derivative, methyl N,N′-dibenzoylneobiosaminide C, m.p. 250–252° [*Anal.* Calcd. for $C_{11}H_{19}N_2O_7(OCH_3)(COC_6H_5)_2$: C, 58.63; H, 6.00; N, 5.27. Found: C, 58.52; H, 5.77; N, 5.01]. These analytical values are in excellent agreement with the formulation of neobiosamine C as $C_{11}H_{22}N_2O_8$, a disaccharide composed of diaminohexose and pentose moieties, but do not support the formula $C_{11}H_{22}N_2O_7$, which would be a disaccharide containing desoxydiaminohexose and pentose moieties, as previously proposed.[3]

The α- and β-anomers were separated ($[\alpha]^{25}\mathrm{D}$ 113° and $[\alpha]^{25}\mathrm{D}$ 61°, respectively) and each was hydrolyzed in dilute hydrochloric acid to neobiosamine C (identical mutarotation value, $[\alpha]^{25}\mathrm{D}$ 104°), which gave a single strong papergram spot [R_f 0.227 (TBAW)],[5] both reducing and ninhydrin-positive. The formation of a single compound from hydrolysis of methyl neobiosaminide C argues strongly for the formulation of neobiosamine C as a diaminohexosido-pentose, cleaved with difficulty, rather than as a pentosido-diaminohexose, which would be readily cleaved during hydrolysis to a pentose and a diaminohexose (or methyl diaminohexoside) and thus would give two papergram spots.

Similar arguments obtain for neobiosamine B. Both α- and β-anomers ($[\alpha]^{25}\mathrm{D}$ 13° and $[\alpha]^{25}\mathrm{D}$ $-17°$, respectively) of methyl neobiosaminide B [*Anal.* Calcd. for $C_{11}H_{21}N_2O_7(OCH_3)\cdot H_2O$: C, 42.10; H, 7.66; N, 8.19. Found: C, 41.82; H, 7.42; N, 7.95] are hydrolyzed to constant rotation ($[\alpha]^{25}\mathrm{D} + 33°$) and a single strong papergram spot [R_f 0.251 (TBAW)]; thus neobiosamine B also may be formulated as $C_{11}H_{22}N_2O_8$, a diaminohexosido-pentose.

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(1) Presented in part at the XVIth International Congress of Pure and Applied Chemistry, Paris, July 18 to 24, 1957.

(2) For recent reviews, *cf.* (a) J. H. Ford, M. E. Bergy, A. A. Brooks, E. R. Garrett, J. Alberti, J. R. Dyer and H. E. Carter, THIS JOURNAL, **77**, 5311 (1955); (b) J. R. Dyer, Ph.D. Dissertation, University of Illinois, June, 1954; (c) S. A. Waksman, "Neomycin," Rutgers University Press, New Brunswick, N. J., 1953.

(3) J. D. Dutcher, N. Hosansky, M. N. Donin and O. Wintersteiner, THIS JOURNAL, **73**, 1384 (1951).

(4) K. L. Rinehart, Jr., P. W. K. Woo and A. D. Argoudelis, *ibid.*, **79**, 4568 (1957).

(5) TBAW is *tert*-butyl alcohol : acetic acid : water, 2 : 2 : 1.