leaved with layers of methylammonium ions. The methylammonium ions are arranged along the four-fold axes so that half are directed with NH_3^+ up and and half with NH_3^+ down; each Cl^- is surrounded by a bisphenoid of NH_3^+ groups.

The predicted value of the C–N distance[2] is 1.47 Å. if we ignore the formal charge correction,[3] or 1.44 Å. if we take it into account. If we consider the ionic radius[12] for Cl^- (1.81 Å.), the van der Waals radius[12] for the methyl group (2.0 Å.) and the ionic radius for the NH_4^+ ion (1.4 Å.) corrected for the effect of change of coördination number[13] we calculate the non-bonded distances $C\ldots Cl^- = 3.8$ Å. and $N\ldots Cl^- = 3.2$ Å. Thus the observed values are in satisfactory agreement with those predicted on the basis of previous structural determinations in other compounds. The formal charge of the NH_3^+ group does not seem to shorten the C–N bond appreciably below the normal covalent value of 1.47 Å.

A partial summary of carbon–nitrogen single-bond distances obtained in the most recent X-ray and electron diffraction studies of various compounds is shown in Table V.

Acknowledgment.—We are indebted to Professor Verner Schomaker for helpful discussions and to Mary S. Lipscomb for assistance with the calculations.

Summary

The crystal structure of methylammonium chloride has been redetermined. The unit cell was found to be tetragonal with the dimensions $a_0 = 6.04$ Å. and $c_0 = 5.05$ Å.; this cell contains two molecules of CH_3NH_3Cl. The space group is $D_{4h}^7 - P4/nmm$; the Cl^- ions are placed at 000 and $\frac{1}{2}\frac{1}{2}0$, the nitrogen atoms at $0\frac{1}{2}z_1$ and $\frac{1}{2}0\bar{z}_1$, and the carbon atoms at $0\frac{1}{2}z_2$ and $\frac{1}{2}0\bar{z}_2$. The z parameters of the carbon and nitrogen atoms were determined by the methods of Fourier projection and least-squares with the results $z_1 = 0.198 \pm 0.001$ and $z_2 = 0.488 \pm 0.001$. The carbon–nitrogen distance is 1.465 ± 0.010Å.

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[12] Reference 3, pp. 352 and 189.

[13] The $NH_4^+\ldots Cl^-$ distance found in "low" ammonium chloride (3.35 Å.) by R. J. Havighurst, E. Mack, Jr., and F. C. Blake, THIS JOURNAL, **46**, 2368 (1924) yields an ionic radius of 1.54 Å. for NH_4^+ when the ionic radius for Cl^- is subtracted. This value may be corrected for change of coördination number from eight to four (reference 3, p. 368) to give the NH_4^+ ionic radius of 1.41 Å.

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X-Ray Investigation of Glycerides. IV. Diffraction Analysis of 1-Monoarachidin (1-Monoeicosanoate)

BY S. S. SIDHU AND B. F. DAUBERT

The only reference in the literature to the preparation of a 1-monoarachidin was that recorded by Berthelot[1] in 1856. The constants on this compound were incomplete and of doubtful value. In the course of our program on the study of the physical properties of glycerides, it became desirable to synthesize this compound in a high degree of purity. Therefore, the purpose of this communication is to report the method of preparation and the physical data obtained on a highly purified 1-monoarachidin.

Experimental

Preparation of Intermediates.—The arachidic acid was prepared from a mixture of hydrogenated fish oil fatty acids[2] by fractional distillation of the methyl esters and subsequent repeated fractional crystallization of the arachidic acid from ethyl ether. The arachidic acid so obtained had the following constants: m. p. 75.1° (cor.); sap. eq., 312.2 (theory 312.5); iodine value (Wijs), 0.0.

The acetone–glycerol was prepared by the method of Malkin and Shurbagy.[3]

Preparation of 1-Monoarachidin.—The monoglyceride was prepared by a modification of the method of Malkin and Shurbagy[3] and is as follows: Dry hydrogen chloride was passed into a mixture, cooled to 15°, of arachidic acid (30 g.) and sufficient acetone–glycerol (*ca.* 75 g.) to make a paste. Completion of the reaction required approximately six hours, during which time the mixture liquefied. The liquid product was dissolved in an equal volume of ethyl ether and filtered. The filtrate was cooled to 5° in an ice-bath and the product hydrolyzed with cold hydrochloric acid (36%). After one-half hour, 500 ml. of ice water was added to the mixture. The precipitated monoglyceride was washed repeatedly with cold water to remove the mineral acid. The monoglyceride was then suction filtered and dried *in vacuo*. After several crystallizations of the product from ethyl ether, it was dried *in vacuo* over phosphorus pentoxide; m. p. 83.5–84.0°; mol. wt.[4] 385.5 (calcd. 386.6). *Anal.*[5] Calcd. for $C_{13}H_{46}O_4$: C, 71.45; H, 11.99. Found: C, 71.74, 71.62; H, 12.07, 12.09.

By the capillary tube method and thermometric techniques previously described[6,7] crystalline modifications of the monoglyceride melted at 77.0, 81.5 and 83.5°, respectively.

X-Ray Diffraction Analysis.—The X-ray diffraction patterns of the 1-monoarachidin were made with filtered CuKα radiation, $\lambda = 1.5386$ Å. A finely powdered specimen of the solvent-crystallized material was packed into a nylon tube and the tube was mounted first in a cylindrical

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[1] M. Berthelot, *Ann. chim. phys.*, [3] **47**, 355 (1856).

[2] The fish oil fatty acids were hydrogenated by Dr. Alton E. Bailey at the Southern Regional Research Laboratory, New Orleans, La.

[3] Malkin and Shurbagy, *J. Chem. Soc.*, 1628 (1936).

[4] Hanson and Bowman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 440 (1939).

[5] The microchemical analyses were performed by Mr. George Stragand.

[6] Daubert and Clark, THIS JOURNAL, **66**, 690 (1944).

[7] Daubert and Clark, *Oil and Soap*, **22**, 113 (1945).

camera of 17.19 cm. effective diameter and rotated during the exposure. It was next mounted in a pin-hole type of camera and the patterns made with specimen-to-film distance of 10 cm. and 24.35 cm.[8,9,10]

The observed short-spacing diffraction data are given in Table I, and the observed long-spacing data, together with the calculated long-spacing values, are given in Table II. The observed values given in both tables are the composite data obtained from the patterns made with both types of cameras.

Discussion

It will be observed that the side-spacing data in Table I correspond to the diffraction data typical for the *beta* form of 1-monoglycerides.

TABLE I

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF THE β-FORM OF 1-MONOARACHIDIN

$d \times 10^{-8}$ cm.	I/I_0	$d \times 10^{-8}$ cm.	I/I_0
18.2	M+	3.34	W
15.7	VW	3.11	W+
13.6	M	2.99	VW
9.03	M	2.90	VW
7.96	VW	2.78	W
6.98	W	2.54	VW
6.00	W	2.45	M+
5.55	VW	2.29	VW
5.08	W	2.24	W
4.60	VS	2.15	W
4.42	VS	2.08	M
4.17	W	1.95	VW
3.92	VS	1.91	VW
3.83	VS	1.80	M
3.55	VW	1.75	VW
3.42	W	1.68	W
3.40	VW	1.64	W

TABLE II

LONG-SPACING VALUES AND MELTING POINTS OF 1-MONOGLYCERIDES

	Number of carbons in fatty acid chain	Long Spacing Obs.	Long Spacing Calcd.	M. p., °C.
[a]	10	32.6	32.7	53.0
	12	36.9	37.0	63.0
	14	41.6	41.4	70.5
	16	45.7	45.7	77.0
	18	49.9	50.1	81.5
	20	54.4	54.4	84.0

[a] Repeated from an earlier paper for comparison (ref. 8).

The long-spacing value in Table II represents the average weighted value obtained from a very strong first order line of 54.0 Å., a weak second order of 27.3 Å., a strong third order of 18.2 Å., a medium fourth order of 13.6 Å., and a medium sixth order of 9.03 Å.

The average increment in long-spacing value for the C_{10-20} series of saturated 1-monoglycerides is 4.36 Å. The calculated long-spacing value for the 1-monoarachidin was based upon an empirical relation between long-spacing values and the effective number of carbon atoms in a double monoglyceride molecule, as derived in a previous paper.[8]

Acknowledgment.—The assistance of Gretta L. Scott in obtaining the X-ray diffraction patterns is gratefully acknowledged. Acknowledgment is also made of the generous financial assistance of the Buhl Foundation which made this investigation possible.

Summary

X-Ray diffraction and melting point data for the solvent-crystallized *beta* form of 1-monoarachidin are reported.

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[8] Filer, Sidhu, Daubert and Longenecker, THIS JOURNAL, **66**, 1333 (1944).

[9] Filer, Sidhu, Chen and Daubert, *ibid.*, **67**, 2085 (1945).

[10] Filer, Sidhu, Daubert and Longenecker, *ibid.*, **68**, 167 (1946).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Kinetics of the Decomposition of Benzoyl Peroxide in Various Solvents

BY W. E. CASS

Previous studies of the rate of decomposition of benzoyl peroxide have indicated approximately first order kinetics for the reactions in toluene,[1] nitrobenzene,[1] benzene,[2,3,4] styrene–benzene,[5] vinyl acetate–benzene,[3] and allyl acetate.[6] However, in certain cases,[5,6] the first order constants were found to increase with higher initial peroxide concentrations. Furthermore, the rates of decomposition of benzoyl peroxide in vinyl acetate–benzene[3] and in styrene–toluene[7] and of 3,4,5-tribromobenzoyl peroxide in styrene–benzene[8] were increased several times over those in the non-polymerizing solvents alone. The possibility of recombination of benzoyloxy radicals has been suggested[9,10] in explanation of the latter observation.

In the present work the rates of decomposition of benzoyl peroxide in a number of solvents were measured in the absence of air at 30 ± 0.2°. It was found that not only the rates but also the

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[1] Bartlett and Altschul, THIS JOURNAL, **67**, 812 (1945).

[2] McClure, Robertson and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942).

[3] Medvedev and Kamenskaya, *Acta. Physicochim. U. R. S. S.*, **13**, 565 (1940).

[4] Brown, THIS JOURNAL, **62**, 2657 (1940). In this case the order determined for the reaction was approximately 1.3.

[5] Cohen, *ibid.*, **67**, 17 (1945).

[6] Bartlett and Altschul, *ibid.*, **67**, 816 (1945).

[7] Breitenbach and Taglieber, *Ber.*, **76**, 272 (1943).

[8] Price and Tate, THIS JOURNAL, **65**, 517 (1943).

[9] Price, *Ann. N. Y. Acad. Sci.*, **44**, 365 (1943).

[10] Matheson, *J. Chem. Phys.*, **13**, 584 (1945).