angular distribution of intensity of scattered light is described.

4. Measurements of turbidity, dissymmetry, refractive index increment and depolarization were made on solutions of four cellulose acetate fractions whose molecular weight had been otherwise determined. The molecular weights calculated from the optical measurements agreed within 8% of those measured by other means.

5. The empirical constant, μ, which characterizes the deviation from van't Hoff law behavior was found to be 0.45 ± 0.01 by light scattering measurements as compared with 0.43 ± 0.005 based on osmotic pressure measurements for the cellulose acetate–acetone system.

6. The angular variation of intensity is found to be in agreement with the theoretical prediction.

7. The comparison of the measured dissymmetry with that predicted theoretically for a rod-shaped or random coil molecule indicates that the cellulose acetate molecule in acetone solution is rather extended up to a molecular weight of about 80,000. At higher molecular weights the molecule may coil back on itself to a degree that increases rapidly with molecular weight.

BROOKLYN, N. Y. RECEIVED AUGUST 20, 1945

[CONTRIBUTION NO. 574 FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, UNIVERSITY OF PITTSBURGH]

X-Ray Investigation of Glycerides. III. Diffraction Analyses of Symmetrical Monoöleyl-disaturated Triglycerides[1,2]

BY L. J. FILER, JR.,[3] S. S. SIDHU, B. F. DAUBERT AND H. E. LONGENECKER

Introduction

Previous publications[4,5] from this Laboratory on X-ray diffraction studies of synthetic glycerides have established the importance of X-ray diffraction methods for obtaining reference data on the compounds provided by synthesis for the later identification of those glycerides which may be isolated from natural sources.

The purpose of this publication is to report X-ray diffraction data for the characterization of a series of synthetic 2-oleyl-1,3-disaturated triglycerides, and the simple triglycerides, tristearin and trielaidin, and also to show how these data may be applied to establish the identity of glycerides obtained from natural fats. The long-spacing X-ray diffraction data obtained in this investigation have made possible a postulation of a molecular configuration for the members of this series of synthetic glycerides.

Experimental

Preparation of Glycerides.—The experimental details for the preparation of the symmetrical monoöleyl-disaturated triglycerides have been published previously.[6] The tristearin and trielaidin were prepared by direct esterification of glycerol with the respective acid chlorides in quinoline–chloroform solution.

The oleyldistearin isolated from the seed fat of *Garcinia Indica* (Kokum butter) by low-temperature solvent crystallization was supplied to us through the courtesy of E. S. Lutton.[7]

X-Ray Diffraction Analyses.—The X-ray diffraction patterns of the glycerides were made by the usual powder method previously described.[4,5] The patterns were repeated with the same specimen and with a pin-hole type of camera using a flat cassette and a specimen-to-film distance of 24 cm.

The low-melting glyceride specimens were maintained in the solid state by surrounding the collimator and specimen mount with a chamber packed with Dry Ice. These compounds were crystallized from solvent, dried *in vacuo* at −30°, and maintained at temperatures below their fusing point prior to and during their exposure.

The radiation employed, with but two exceptions, was filtered CuKα of effective wave length 1.5386 Å. Two specimens were examined with filtered CoKα radiation of effective wave length 1.7866 Å.

Discussion

The isolation of mixed triglycerides from natural sources in a high degree of purity has been reported by many investigators. Although the fatty acid composition and the ratio of saturated to unsaturated fatty acid in these isolated mixed triglycerides have been determined by accepted methods of analysis, the positions of the fatty acids in the molecule of triglyceride have not been fixed with certainty. Positiveness as to the fatty acid configuration of the isolated natural occurring glycerides has been lacking primarily because synthetic compounds of definite and known configurations have not been available for comparison to be made. Since a relatively large number of synthetic glycerides have been prepared recently containing both saturated and unsaturated fatty acids, greater promise of certainty is assured in establishing the configuration of those isolated from natural sources.

The isolation of an oleyldistearin from a number of natural fat sources has been reported recently by Meara.[8] Comparison of the thermal behavior of this natural mixed triglyceride with the thermometric data reported by Daubert and

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[1] A grant by the Buhl Foundation in support of this investigation is gratefully acknowledged.

[2] Taken in part from a paper presented at the 108th Meeting of the American Chemical Society, New York City, Sept. 11–15, 1944.

[3] Present address: The University of Rochester School of Medicine and Dentistry, Rochester, New York.

[4] L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert and H. E. Longenecker, THIS JOURNAL, **66**, 1333 (1944).

[5] L. J. Filer, Jr., S. S. Sidhu, C. Chen and B. F. Daubert, *ibid.*, **67**, 2085 (1945).

[6] F. L. Jackson, B. F. Daubert, C. G. King and H. E. Longenecker, *ibid.*, **66**, 289 (1944).

[7] Procter and Gamble Co., Ivorydale, Ohio.

[8] M. L. Meara, *J. Chem. Soc.*, 22 (1945).

TABLE I

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF 2-OLEYL-1,3-DISATURATED TRIGLYCERIDES, SATURATED ACYL RADICAL IN 1,3 POSITIONS

Stearyl, β phase Co radiation		Stearyl, β′ phase		Stearyl,[a] β phase		Stearyl,[a] β′ phase		Palmityl, β phase Co radiation		Palmityl, β′ phase		Myristyl, β′ phase	
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
21.0	VW	14.3	S	16.4	W	23.1	S	20.4	W	20.7	M⁻	15.0	M
12.9	VW	8.63	M	13.0	S	17.2	W	14.1	M	14.0	S	11.8	M⁺
10.6	W	7.93	W	10.9	W	13.8	S	12.7	W	11.6	VW	10.5	W
9.21	W	6.80	VW	9.35	W	10.7	W	10.5	W	10.1	VW	8.92	M
8.12	W	5.24	W	8.00	S	8.66	M	8.14	W	8.43	M	7.46	S
7.44	W	4.72	M	7.12	W	7.80	W⁺	6.89	W	7.86	VW	6.83	VVW
6.57	VVW	4.16	VS	7.03	M	6.84	W	6.04	W	6.99	W⁺	6.11	VVW
6.00	VW	3.84	S	6.39	VW	6.34	VW	5.43	M	6.05	W⁺	5.46	M
5.41	M	3.60	M	5.92	W	5.58	W	5.08	M	5.32	W	4.95	W⁺
5.02	M	3.34	W	5.80	W	4.97	W⁺	4.83	W	4.91	M	4.23	VS
4.80	VW	3.09	VW	5.42	S	4.17	VS	4.56	VS	4.25	VS	4.03	S
4.59	VS	3.04	W	5.20	W	3.85	S	4.41	W	3.94	S	3.80	VS
4.08	W	2.49	M	5.12	W	3.76	VW	4.31	W	3.67	W	3.55	M
4.02	M	2.39	VW	4.60	VS	3.61	W	4.14	W	3.42	W	3.34	VW
3.92	M	2.28	W⁺	4.27	W	3.41	W	3.90	S	3.19	W⁺	3.13	W⁺
3.66	M	2.22	W	4.06	S	3.30	VW	3.73	M	2.94	W	3.04	W⁺
3.60	W	2.18	VW	3.86	S	3.16	W	3.64	M	2.85	VW	2.65	W⁺
3.35	W	2.09	W	3.69	S	3.02	W	3.55	VW	2.75	VW	2.58	W⁺
3.11	W	1.93	W	3.53	VW	2.77	VW	3.33	W	2.64	W	2.47	W⁺
2.98	VW			3.33	W	2.55	W	3.16	W	2.57	VW	2.31	M
2.83	W			3.08	W	2.27	M	3.03	VW	2.38	W⁺	2.24	W
2.72	W			2.97	VW	2.15	VW	2.86	VVW	2.33	W⁺	2.21	VW
2.58	W			2.71	W	2.11	W	2.71	W	2.18	W⁺	2.06	W
2.48	VW			2.58	M	1.94	W	2.59	W⁺	1.97	W	1.91	W
2.38	W			2.37	W			2.47	W				
2.30	W			2.28	W			2.38	VW				
				2.19	W			2.29	VW				
				2.12	W			2.19	VW				
				2.06	W⁺			2.09	W				
				1.98	W								

[a] Glyceride isolated from Kokum butter. Composite data from photographs made with the cylindrical camera and the pin-hole camera, specimen-to-film distance 10 cm.

Clarke[9] for synthetic 2-oleyl-1,3-distearin tentatively established the configuration of the isolated glyceride as 2-oleyl-1,3-distearin. X-Ray diffraction data which undoubtedly would have given additional proof of configuration were not reported by Meara apparently because diffraction data are not available on the synthetic product.

Since an oleyldistearin isolated from the seed fat of *Garcinia Indica* was made available to this Laboratory X-ray diffraction data for both synthetic 2-oleyl-1,3-distearin and the natural product are reported. It may be seen from a comparison of the data in Table I that the two compounds are identical. The comparison of the X-ray diffraction data and thermal behavior of the synthetic glyceride and the natural product in the β and β′ phases definitely establishes the identity of the natural product as 2-oleyl-1,3-distearin.

Lutton[10] recently has published data on the polymorphism of tristearin and related homologs. These data correct a faulty association of X-ray diffraction pattern with melting point in the work of Malkin.[11] In Table II are recorded similar observations made in this Laboratory to confirm the results of Lutton. The presence of long-ordered arrangement in the lowest melting form of trielaidin as well as tristearin indicates that the concept of the gamma or glassy state of simple triglycerides should be eliminated. Complete

TABLE II

X-RAY AND MELTING POINT DATA FOR TRISTEARIN AND TRIELAIDIN

This study			Lutton (ref. 9)			Malkin (ref. 11)		
Form	M. p., °C.	Long spacing, 10^{-8} cm.	Form	M. p., °C.	Long spacing, 10^{-8} cm.	Form	M. p., °C.	Long spacing, 10^{-8} cm.
				Tristearin				
β	72.5	45.2	β	73.1	45.15	β	71.5	45
α	54.0	50.8	α	54	50.6	γ	54.5	None
				Trielaidin				
β	42.0	44.8	..	..	...	β	41.5	44.1
α	16.6	48	..	..	...	γ	15.5	None

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(9) B. F. Daubert and T. H. Clarke, THIS JOURNAL, **66**, 690 (1944).

(10) E. S. Lutton, *ibid.*, **67**, 524 (1945).

(11) Malkin, *et al.*, *J. Chem. Soc.*, 666 (1934); 1628 (1936); 1409 (1937); 103, 577, 1141 (1939).

X-ray diffraction data for the identification of tristearin and trielaidin in the β phase and tristearin in the α phase are given in Table III. It should be noted that the side-spacing data on trielaidin differ somewhat from those reported by Malkin and conform more nearly to typical β results.[12]

TABLE III

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF TRISTEARIN AND TRIELAIDIN

Tristearin, β phase		Tristearin, α phase		Trielaidin, β phase	
d	I/I_0	d	I/I_0	d	I/I_0
20.0	W	17.4	S	15.0	S
15.6	S	13.5	W	11.9	W
12.0	VW	10.6	W	9.01	W$^+$
9.19	W	8.33	W	7.59	VW
7.77	W	6.66	VW	6.51	VW
6.37	VW	5.89	VW	5.25	S
5.80	VW	5.07	VW	4.79	W
5.32	M	4.62	VW	4.57	VS
4.91	VW	4.15	VS	4.15	S
4.60	VS	3.31	W	3.91	S
4.29	W	2.42	M	3.72	S
4.07	VW	2.34	M	3.54	VW
3.89	S			3.40	W
3.69	S			3.22	W
3.45	W			3.09	VW
3.33	VW			2.98	W$^+$
3.14	VW			2.87	VW
2.94	W			2.70	VW
2.85	VW			2.59	M
2.69	VW			2.49	W
2.58	M			2.36	W$^+$
2.37	W$^+$			2.26	W$^+$
2.28	W$^+$			2.21	W$^+$
2.20	W$^+$			2.10	W$^+$
2.13	W			2.03	W
2.07	M			1.96	W$^+$
1.97	M			1.90	W
1.90	W				
1.84	W				
1.78	W				
1.69	W				
1.63	W				
1.61	W				

In 1937, Storkes and Germer,[13] using electron diffraction methods, obtained evidence that the long-ordered arrangement of the glycerides in lard films supported on polished nickel surfaces differed from stearic acid and tristearin films similarly prepared. These investigators attributed rightly the differences to be due to the presence of unsaturated fatty acid chains in the lard.

The difference of 29° between the melting point of tristearin (72°) and the melting point of 2-oleyl-1,3-distearin (43°) would seem to indicate a marked change in structure or alignment of the long hydrocarbon chains of the respective glycerides. This change in melting point may be the result of a transition from a closely-packed glyceride structure of the "tuning-fork" type proposed by Malkin[11] ((a) Fig. 1) for simple triglycerides to a more loosely-packed structure whose possible configuration is represented in (b) of Fig. 1. The London dispersion forces[14] and dipolar interaction in the tuning-fork structure of Malkin[11] are probably more pronounced than similar forces in the glyceride structure which has been postulated from the data in this publication. The strength of these intermolecular forces influences the melting point of the compound (*i. e.*, the greater the dispersion forces and dipolar interaction the higher the melting point).

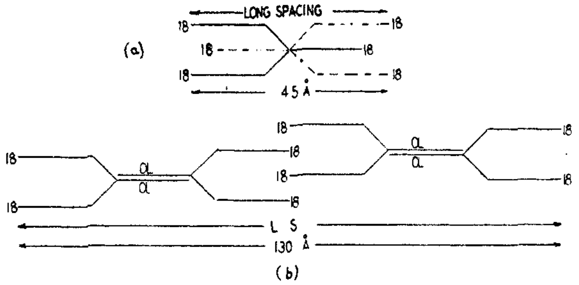

Fig. 1.—(a) Tuning-fork structure proposed by Malkin[11] for simple triglycerides (tristearin) and (b) postulated molecular arrangement for 2-oleyl-1,3-disaturated triglycerides (2-oleyl-1,3-distearin).

The X-ray diffraction patterns for tristearin and 2-oleyl-1,3-distearin obtained with the pinhole camera and flat cassette at a specimen-to-film distance of 24 cm. show considerable differences of long-ordered molecular arrangement. These differences permit the postulation of a molecular structure ((b) Fig. 1) in which the arrangement of a number of molecules is such as to make a crystal unit with about three times the long-spacing value of tristearin. It will be observed from the figure that the closely-packed molecular configuration ((a) Fig. 1) has been unfolded to an extended long-ordered arrangement wherein the unsaturated chains are aligned with respect to one another.

In Table IV the observed orders of the long spacings for the symmetrical monoöleyl-disaturated triglycerides are given. The presence of a third order necessitated the postulation of a double "double-molecule" (*Cf.* (b) Fig. 1). To interpret long-spacing values as a function of the number of effective carbon atoms found in a hypothetical molecular arrangement or as a function of the molecular weight of the glycerides, it is necessary to compare them in the same crystal modification. The crystal modification of a particular glyceride specimen may be established by short-spacing data[4,5] and it was upon this basis that the long-spacing values reported in Table V were associated with the proper melting form.

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(12) Ferguson and Lutton, *Chem. Rev.*, **28**, 371 (1941).

(13) K. H. Storkes and L. J. Germer, *J. Chem. Phys.*, **5**, 131 (1937).

(14) F. London, *Pub. Am. Assoc. Advancement Sci.*, No. **21**, 141 (1943).

TABLE IV

OBSERVED ORDERS OF LONG SPACINGS AT SPECIMEN-TO-FILM DISTANCES OF 24 CM. FOR 2-OLEYL-1,3-DISATURATED TRIGLYCERIDES

Saturated acyl radical	Phase	Line	Intensity	Calcd. interplanar spacing, 10^{-8} cm.	Order	Long spacing, 10^{-8} cm.
Stearyl	β	1	VS	65.4	2	131
		2	M	44.1	3	132
		3	VS	32.2	4	129
		4	W	21.5	6	129
		5	W	16.3	8	130
		6	W+	12.9	10	129
		7	W	8.1	16	130
Stearyl	β'	1	S	46.5	3	140
		2	S	35.0	4	140
Palmityl	β	1	S	61.7	2	123
		2	VS	41.1	3	123
		3	S	30.4	4	121
		4	W	13.7	9	123
		5	W	12.2	10	122
		6	W	10.1	12	121
Palmityl	β'	1	VS	42.9	3	129
Myristyl	β'	1	VS	59.4	2	119
		2	S	39.5	3	119
		3	S	30.2	4	121
		4	W	19.9	6	120
		5	W	15.1	8	121
		6	W	12.2	10	122
Lauryl	β'	1	VS	36.6	3	110
		2	W	28.3	4	113
		3	M	18.5	6	111
		4	W	14.0	8	112
Capryl	β	1	VS	32.6	3	98

The compound 2-oleyl-1,3-dimyristin, m. p. 26.5°, solvent crystallized and previously reported as Form I,[9] on X-ray examination yielded diffraction data characteristic of the β' phase. Although triacid triglycerides have been readily crystallized from solvent in the β' phase it was also possible to crystallize them from solvent in the higher melting β phase.[5] 2-Oleyl-1,3-dimyristin failed to crystallize from solvent in a higher melting form regardless of crystallizing conditions.

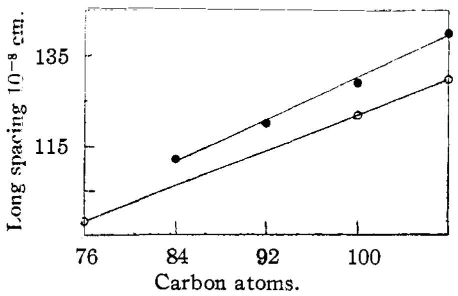

Fig. 2.—The long-spacing values for 2-oleyl-1,3-disaturated glycerides as a function of the number of carbon atoms in the postulated molecular configuration: ○, β phase; ●, β' phase.

TABLE V

LONG SPACINGS AND TRANSITION POINTS OF 2-OLEYL-1,3-DISATURATED GLYCERIDES

Saturated acyl radical	Effective number of carbon atoms	Long spacing, 10^{-8} cm. β phase	Long spacing, 10^{-8} cm. β' phase	Transition points, °C. β Phase	Transition points, °C. β' Phase
Stearyl	108	130	140	43.0[b]	37.6
				41.6	
Palmityl	100	122	129	35.2	30.4
Myristyl	92	...	120	..	26.3
Lauryl	84	...	112	..	16.5
Capryl	76	98	...	6.2	..
Stearyl[a]		130	140	44.5[b]	38.5[b]

[a] Glyceride isolated from Kokum butter. [b] Capillary melting point.

Hence the β' phase of 2-oleyl-1,3-dimyristin appears to be the most stable form of this compound. Although prior experience with crystallization procedures for triacid triglycerides indicated that rapid crystal growth yielded the β' form, slow and rapid crystal growth from solvent of 2-oleyl-1,3-dimyristin resulted in the isolation of the β' form.

In Fig. 2, the long-spacing values for the symmetrical monoöleyldisaturated triglycerides are plotted as a function of the number of carbon atoms in the postulated glyceride configuration. The two phases are found to yield two distinctly independent lines. Extrapolation of the curves to zero effective carbon atoms indicates 22 Å. available for space occupied by the glyceryl residues and their nearest distance of approach in the solid state. A plot of the molecular weights of these triglycerides as a function of their long-spacing values yield similar curves.

The relationship between long-spacing value and melting point of the polymorphic forms is shown graphically in Fig. 3.

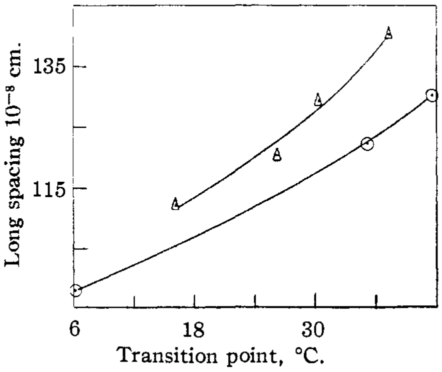

Fig. 3.—Transition points as a function of the long-spacing values for 2-oleyl-1,3-disaturated glycerides: ○, β phase; △, β' phase.

Summary

Identification data are reported for a series of 2-oleyl-1,3-disaturated triglycerides and the simple triglycerides, tristearin and trielaidin.

The long-ordered arrangement of 2-oleyl-1,3-distearin has been found to be different from the long-ordered arrangement of tristearin. From the X-ray diffraction data of 2-oleyl-1,3-distearin and related homologs, it was possible to propose an arrangement of glyceride molecules such that the lowered melting points of these compounds could be explained.

The crystallization of 2-oleyl-1,3-dimyristin from solvent was found to yield the β' phase. This phase is apparently associated with the highest melting form of this compound.

The fatty acid configuration of an oleyldistearin isolated from the seed fat of *Garcinia Indica* (Kokum butter) was definitely established by comparison of its X-ray diffraction data with the data obtained upon a synthetic 2-oleyl-1,3-distearin.

PITTSBURGH 13, PENNA. RECEIVED SPETEMBER 10, 1945

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moment of Hydrogen Fluoride and the Ionic Character of Bonds

BY N. BRUCE HANNAY[1] AND CHARLES P. SMYTH

In the discussion of the ionic character of the chemical bond, the dipole moments of the hydrogen halide molecules have played an important part.[1a,2,3,4] Of these, the moment of the hydrogen fluoride molecule was not determined experimentally because of the extreme reactivity of the substance. An early calculation by Kirkwood[5] gave a moment lower than that of hydrogen chloride, which led to an estimate of 0.8×10^{-18} e. s. u. for its value, while a more recent calculation by Dyatkina[6] gave a value of 3.09.

Since the predominantly ionic character attributed to the hydrogen–fluorine bond in contrast to the predominantly covalent character of the other hydrogen–halogen bonds involves a large difference in polarity and a correspondingly large uncertainty in quantitative conclusions based on the estimated polarity or moment of the hydrogen fluoride molecule, an experimental determination of the moment of the molecule has, for a long time, been highly desirable. It has now been possible to overcome the experimental difficulties caused by the extreme reactivity of hydrogen fluoride and measure the dielectric constant of the vapor.

Apparatus and Method of Measurement

For the measurement of the dielectric constant of hydrogen fluoride vapor over a range of temperature and pressure, a measuring condenser and vacuum system were constructed of materials which, during a run, gave no measurable reaction with hydrogen fluoride at temperatures up to 100°. The cell was attached to the electrical measuring circuit previously used[7] in measuring the dielectric constants of gases and calibrated in the usual way, measurement of the dielectric constants of air and carbon dioxide being used as checks on the calibration. It is hoped that a detailed description of the cell and vacuum system may be given in a future paper. The measurements at each temperature were carried out over a range of pressure, capacity readings being taken at four or five different pressures, and the dielectric constant at 760 mm. was calculated from the slope of the capacity–pressure curve as in earlier work.[7] The absence of any consistent drift in the readings during a period of time comparable to that required for the measurement showed the absence of error due to corrosion effects in the cell and the constancy of the moment values with temperature showed the absence of any error due to molecular association, which, even at atmospheric pressure, is negligible at the higher temperatures used. The accuracy of the measurements was somewhat less than that with the usual cell and vacuum system, but, in the moment values calculated from the results of 11 runs, the maximum deviation from the mean was only 2.1% and the average deviation only 0.9%.

Experimental Results

In Table I are listed the values of the molar polarization, P, of hydrogen fluoride calculated from the dielectric constant measurement at each

TABLE I

POLARIZATION AND DIPOLE MOMENT VALUES OF HYDROGEN FLUORIDE

T, °K.	P, cc.	$\mu \times 10^{18}$
305.1	76.1	1.92
324.1	70.1	1.91
332.3	67.8	1.90
	68.6	1.91
338.6	68.1	1.92
	65.5	1.88
351.8	66.3	1.93
	68.1	1.95
366.9	63.3	1.92
374.1	59.3	1.88
	59.3	1.88
	Mean value	1.91

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[1] Present address: Bell Telephone Laboratories, New York.

[1a] Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, Chap. II.

[2] Malone, *J. Chem. Phys.*, **1**, 197 (1933).

[3] Smyth, *J. Phys. Chem.*, **41**, 209 (1937); THIS JOURNAL, **60**, 183 (1938); **63**, 57 (1941).

[4] Wall, *ibid.*, **61**, 1051 (1939); **62**, 800 (1940).

[5] Kirkwood, *Physik. Z.*, **33**, 259 (1932).

[6] Dyatkina, *Acta Physicochim. U. R. S. S.*, **13**, 639 (1940).

[7] Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941); Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1942).