

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

**X-Ray Investigation of the Decamethylene Series of Polyesters**

BY C. S. FULLER AND C. J. FROSCH

In two previous papers<sup>1,2</sup> results of X-ray studies on several members of the ethylene series of polyesters have been reported. The present investigation deals with the decamethylene series of polyesters and is a continuation of this work, the general aim of which is to clarify the structures of substances composed of chain molecules of high molecular weight.

The previous work has shown that polyesters of sufficiently high average molecular weight are capable of producing sharp X-ray fiber patterns when oriented specimens<sup>3</sup> are employed. An analysis of the fiber patterns obtained from the ethylene esters and the self ester of  $\omega$ -hydroxydecanoic acid<sup>2</sup> has shown that in general two types of fiber patterns are present. One type found in the case of polyethylene succinate gives a much shorter fiber period than that calculated for this ester on the assumption of a planar zigzag model<sup>1</sup> and agrees best with a helical or coiled form of the long-chain molecules present. The other type of pattern, the one usually observed, gives fiber periods which are only slightly less (0.3 to 0.4 Å.) than the values calculated for a planar zigzag model.

In the ethylene polyesters showing the zigzag type of pattern the ester groups apparently play a part in the alignment of the chain molecules with respect to one another. The previous work on the ethylene polyesters indicated that in the odd esters studied, *i. e.*, those containing an odd number of chain atoms in the repeating unit, the chains were arranged so that the carbonyl groups of adjacent chains fell in planes perpendicular to the fiber axis. In the even esters, however, evidence favored an arrangement whereby these groups fell in planes inclined to the fiber axis. For the three even esters studied the inclination of this plane to the fiber axis was calculated to be approximately 65°.

All the members of the decamethylene series of polyesters examined in the present work show the zigzag type of fiber pattern. These patterns differ from those obtained on the ethylene series in several respects, however, and indicate that the

laws determining the manner in which the chains associate are perhaps not as simple as heretofore expected. As will be shown later, however, most of the present results can be explained, qualitatively at least, by a theory proposed recently by T. Schoon.<sup>4</sup>

**Compounds Examined.**—The preparation of the polyesters and the X-ray technique employed already have been described.<sup>1</sup> In the present experiments decamethylene glycol reacted with the successive members of the aliphatic dicarboxylic acid series up to and including sebacic with the exception of pimelic. Polyesters suitable for X-ray investigation were obtained in all cases except that of malonic acid. The average molecular weight in each case was above 10,000 as determined by viscosity measurements. The purity of the final polyesters in view of the small amount of cyclic ester theoretically produced was considered sufficient without fractionation. Table I lists the compounds studied and their melting points.

TABLE I  
SOFTENING POINTS OF DECAMETHYLENE POLYESTERS

Compound	Softening point, °C.
1 Oxalate	77
2 Succinate	69
3 Glutarate	60
4 Adipate	74
5 Suberate	75
6 Azelate	66
7 Sebacate	73

**X-Ray Results.**—Highly oriented specimens of the various esters were employed in order to secure sharp X-ray fiber patterns. Characteristic copper X-radiation filtered free of beta was employed. The interplanar spacings were calculated on the basis of the known spacings in sodium chloride, which was applied as a powder directly to the specimens. The patterns corresponding to the compounds listed in Table I are shown in Fig. 1, A to G inclusive. Figure 1H illustrates the type of picture obtained when sodium chloride powder is applied to the sample of Fig. 1G. The results of the measurement of these fiber patterns are shown in Tables II and III. Table II

(1) Fuller and Erickson, *THIS JOURNAL*, **59**, 344 (1937).

(2) Fuller and Frosch, *J. Phys. Chem.*, **43**, 323 (1939).

(3) Carothers and Hill, *THIS JOURNAL*, **54**, 1579 (1932).

(4) T. Schoon, *Z. physik. Chem.*, **39B**, 385 (1938).

TABLE II

## INTERPLANAR SPACINGS OF DECAMETHYLENE POLYESTERS

Reflection	Oxalate		Succinate		Glutarate		Adipate		Suberate		Azelate		Sebacate	
	<i>d</i> , Å.	Int.	<i>d</i> , Å.	Int.	<i>d</i> , Å.	Int.	<i>d</i> , Å.	Int.	<i>d</i> , Å.	Int.	<i>d</i> , Å.	Int.	<i>d</i> , Å.	Int.
A <sub>1</sub>			4.75	W.	4.61	W.	4.64	W.	4.67	W.	4.63	W.	4.64	W.
A <sub>2</sub>	4.23	V.S.	4.20	V.S.	4.17	V.S.	4.22	V.S.	4.20	V.S.	4.19	V.S.	4.18	V.S.
A <sub>3</sub>	3.50	V.S.	3.67	V.S.	3.70	V.S.	3.70	V.S.	3.70	V.S.	3.70	V.S.	3.69	V.S.
A <sub>4</sub>	2.92	S.	2.99	M.	2.98	S.	2.99	S.	2.99	S.	2.99	S.	3.00	S.
A <sub>5</sub>	2.64	S.	2.53	M.	2.49	M.	2.51	M.	2.51	S.	2.49	M.S.	2.50	M.S.
A <sub>6</sub>	2.47 <sup>a</sup>	V.W.	2.38	W.	2.35	W.	2.40	V.W.	2.37	W.	2.37	M.W.	2.38	W.
A <sub>7</sub>	2.12	S.	2.21	S.	2.22	S.	2.23	S.	2.22	S.	2.22	S.	2.23	S.
A <sub>8</sub>			2.08	M.	2.08	M.	2.09	M.	2.08	M.	2.07	M.	2.08	M.
1 <sub>1</sub>	13.2	V.S.	13.1	S.			15.2	M.						
11 <sub>1</sub>					19.9	S.	11.0	M.	12.4	V.S.	25.0	S.		
11 <sub>1</sub>	6.62	S.	6.62	W.	13.4	M.			4.65	W.			12.0	S.
111 <sub>1</sub>	4.38 <sup>a</sup>	W.	4.43	V.W.			6.64	M.	5.77	W.			8.50	M.
111 <sub>1</sub>	3.77	W.							3.67	W.				
111 <sub>1</sub>	3.39	W.												
1V <sub>1</sub>	3.66	W.	4.31	V.W.			5.33	M.	3.87 <sup>a</sup>	V.W.	9.80	M.	4.17	V.W.
1V <sub>1</sub>	3.36	W.												
V <sub>1</sub>	3.07	M.			5.25	W.	4.24	W.	4.03	V.W.	6.10	W.	4.98	W.
V1 <sub>0</sub>			3.20 <sup>c</sup>	W.	6.88	W.			4.11	S.	8.49 <sup>c</sup>	M.		
V1 <sub>1</sub>					5.03	W.	3.55	W.	3.19		7.58	M.	4.42	W.
V11 <sub>1</sub>							3.09 <sup>c</sup>	W.						
V11 <sub>1</sub>	2.22	S.			5.58	M.			3.16	V.W.			3.73	V.W.
V11 <sub>1</sub>	2.05 <sup>b</sup>	S.			4.59	M.								
V111 <sub>1</sub>					5.20	M.	2.67 <sup>c</sup>	W.	3.03 <sup>c</sup>	W.				
V111 <sub>1</sub>			2.22	V.S.	3.23	W.							3.29	V.W.
V111 <sub>1</sub>			2.08 <sup>b</sup>	M.										
V111 <sub>1</sub>			1.89	M.										
1X <sub>0</sub>									2.69 <sup>c</sup>	W.				
1X <sub>1</sub>					3.93	M.	2.22	V.S.	2.41	W.			2.94	V.W.
X <sub>1</sub>					2.94	W.			2.21	S.			2.66	V.W.
X <sub>2</sub>									2.13 <sup>b</sup>	M.				
X <sub>3</sub>									1.98	M.				
X1 <sub>0</sub>													2.39 <sup>c</sup>	W.
X1 <sub>1</sub>													2.22	V.S.
X1 <sub>2</sub>													2.13	M.
X1 <sub>3</sub>													2.07	S.
X1 <sub>4</sub>													1.90	M.
X1 <sub>5</sub>													1.71	M.
X1V <sub>0</sub>					2.95 <sup>c</sup>	W.								
XV1 <sub>0</sub>					2.61	W.					3.16 <sup>c</sup>	W.		
XV1 <sub>1</sub>					1.97	W.								
XV11 <sub>0</sub>					2.37 <sup>c</sup>	W.								
XV11 <sub>1</sub>					2.21	V.S.								
XV11 <sub>2</sub>					2.11	M.								
XV111 <sub>1</sub>					1.95	W.								
XX <sub>1</sub>											1.97	W.		
XX1 <sub>1</sub>											2.22	S.		
XX1 <sub>2</sub>											2.13	M.		
XX1 <sub>3</sub>											2.06	M.		
XX1 <sub>4</sub>											1.90	W.		
XX1 <sub>5</sub>											1.85	W.		
XX1 <sub>6</sub>											1.70	S.		
XX11 <sub>1</sub>											1.99	W.		

<sup>a</sup> Doubtful reflection. <sup>b</sup> Probably a multiple reflection. <sup>c</sup> This may be a pseudo meridian reflection due to overlapping of layer-line arcs.

gives the interplanar spacings and Table III gives the observed fiber periods and the fiber periods calculated on the basis of a planar zigzag chain for comparison.

Several reflections not reported in Table II have also been found. At least four inner equatorial spots have been observed in the various decamethylene compounds which were not observed in the ethylene compounds. Some of these, however, may be caused by the Ag or Br

TABLE III  
COMPARISON OF OBSERVED AND CALCULATED FIBER PERIODS OF DECAMETHYLENE POLYESTERS (ÅNGSTRÖM UNITS)

Polyester	Fiber period	
	Obsd.	Calcd.
Oxalate	17.0	17.24
Succinate	19.6	19.76
Glutarate	41.6	42.04
Adipate	22.1	22.27
Suberate	24.6	24.79
Azelate	51.7	52.10
Sebacate	27.1	27.30



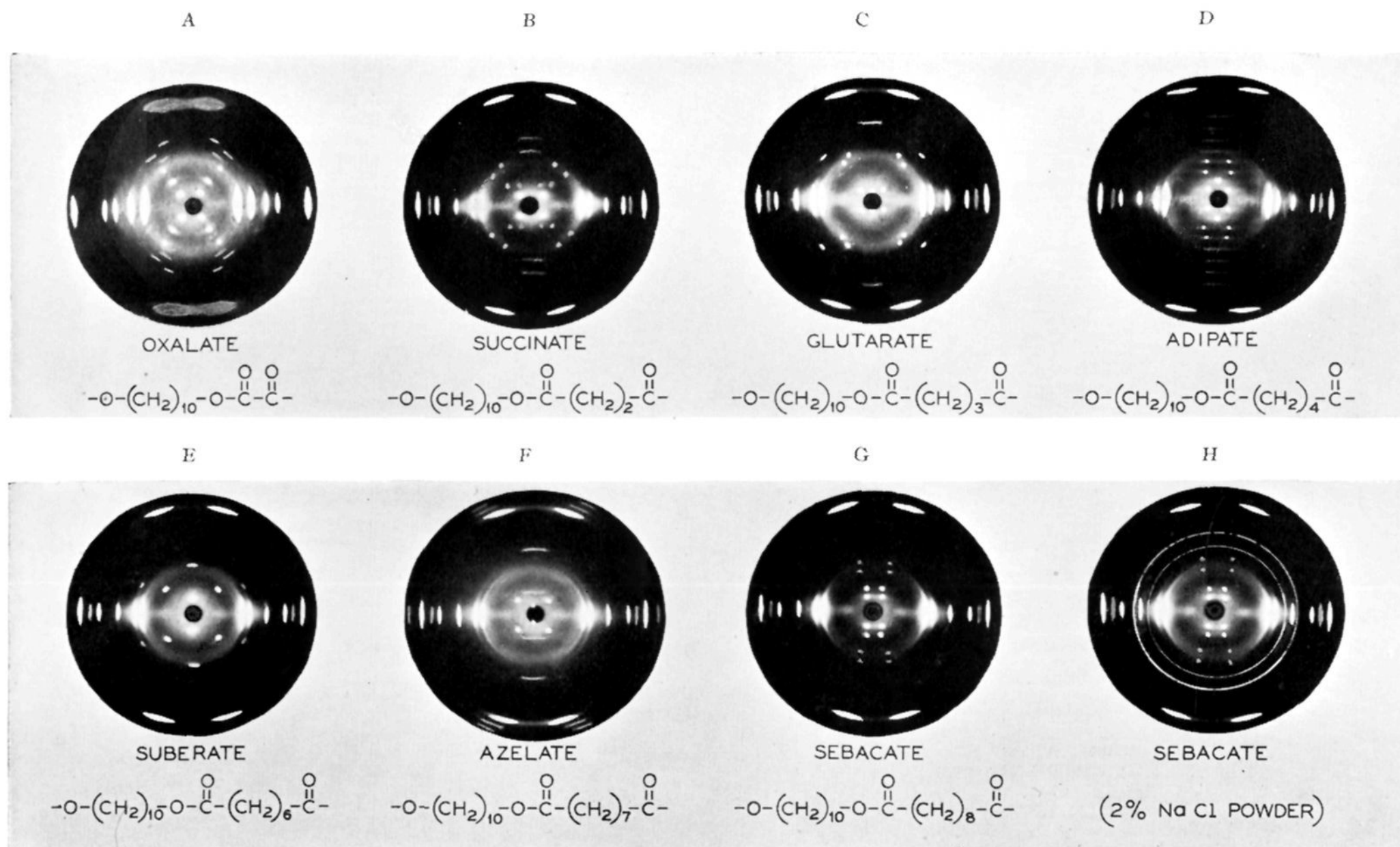


Fig. 1.—X-Ray fiber patterns of decamethylene polyesters. Fiber axis vertical.

absorption edges or by copper beta radiation. Further work is necessary before their presence can be considered proved.

### Discussion of Results

(1) **The Fiber Periods.**—Examination of Table III shows that in the case of all the decamethylene polyesters studied, the observed fiber periods and the fiber periods calculated on the basis of a planar zigzag chain agree within 0.2 Å. The chains in these compounds therefore conform very closely indeed to the planar zigzag model. A somewhat greater deviation (0.4 Å.) has been reported previously<sup>1</sup> for the higher members of the ethylene series of polyesters. This is in support of the view advanced at the time that the ethylene glycol portion of these esters may vary somewhat from the planar configuration. The closeness of these differences to the experimental error, however, makes further investigation of this point desirable. It is entirely possible that a slight shortening of the identity periods can occur as a result of atomic vibrations in the plane perpendicular to the chains as Huggins<sup>5</sup> has suggested. A value of 1.51 Å. for the C-C distance would likewise bring about agreement between the calculated and observed results.

In view of the possibility of resonance in the oxalate ester a shortening of the fiber period due to a shortening of the C-C bond between the two carbonyl groups is to be expected.<sup>6</sup> Table III shows, however, that the oxalate fiber period deviates no more than the other esters. This is probably explained by the small magnitude of the shortening and by the fact that the increased angle between the C-C and C-O bonds partially compensates for the smaller C-C distance.

(2) **The Equatorial Reflections.**—As pointed out in a previous paper<sup>2</sup> the equatorial reflections for the modification of the ethylene polyesters possessing the zigzag type of chain configuration agree well in spacing with those corresponding to the (*hk*0) planes reported for the lower molecular long-chain paraffins<sup>7,8</sup> and esters.<sup>9,10</sup> This is in general true of the decamethylene polyesters also and indicates that the chain molecules pack together in the plane perpendicular to the chain axes in the same fashion in all of these cases.

There are, however, certain deviations from this rule for the oxalate, as can be seen from Table II. This indicates that the distribution of polar groups along the chains influences to some extent the effective cross-section of the chains. With the exception of the oxalate, however, the interchain spacings are constant for all the esters within the experimental error and practically the same as have been found for aliphatic hydrocarbon chains ( $ab \sin \beta = 37.0 \text{ \AA.}^2$ ).

(3) **Layer-Line Reflections.**—In the decamethylene series as in the ethylene series strong second-order meridian reflections are observed in the case of the odd esters (Fig. 1C and F). These in the case of decamethylene azelate fall very close to the primary beam and are barely visible in the reproduction. These reflections agree with the twofold screw axis present in the structure and constitute further proof of the zigzag chain configuration. Unlike polyethylene azelate, however, polydecamethylene azelate shows, in addition to the second-order meridian reflections, reflections of large spacing which arise from planes inclined to the fiber axis (IV<sub>1</sub> Table II). Since the presence of the strong second-order meridian reflection requires an alignment of the carbonyl groups of neighboring chains in planes perpendicular to the fiber axis, these strong layer-line reflections indicate that in the case of some of the chains the carbonyl groups fall in planes inclined to the fiber axis. This also is true of decamethylene glutarate in which pyramidal spacings (II<sub>1</sub> Table II) occur on the same layer-line as the meridian reflections. The best interpretation of these patterns at present is that the chain molecules fit two forms of lattice. In one of these the C=O groups are aligned in planes perpendicular to the fiber axis, whereas in the other they lie in planes which form an angle with this axis.

In the case of the even decamethylene esters (Fig. 1 A, B, D, E and G) certain differences as compared with the ethylene esters are also evident. The oxalate, succinate, and sebacate behave normally in that no low-order meridian reflections are present. The adipate and suberate esters, however, show second-order reflections on the meridian. These reflections are weak in the case of the adipate and are accompanied by pyramidal reflections on the first layer-line. The suberate is unique in possessing very strong meridian reflections on the second layer-line together with weak pyramidal reflections on the third layer-line.

(5) M. L. Huggins, private communication.

(6) Robertson and Woodward, *J. Chem. Soc.*, 1817 (1936).

(7) A. Müller, *Proc. Roy. Soc. (London)*, **120A**, 437 (1928), *et seq.*

(8) Kohlhaas and Soremba, *Z. Krist.*, **100**, 47 (1938).

(9) C. Shearer, *J. Chem. Soc.*, **123**, 3152 (1923), *et seq.*

(10) R. Kohlhaas, *Z. Krist.*, **98**, 419 (1938).

In view of the fact that the zigzag structure of the chain holds in the case of the suberate, as shown by the agreement of the observed and calculated fiber periods, we are forced to assume that in this ester a twofold screw axis or a glide plane exists but that it does not coincide with the chain axis. In other words, a displacement of one-half the fiber period parallel to the chain direction must occur in the case of some of the chains. Because of the high intensity of this reflection it is probable that half of the chains are shifted this amount. An analogous situation exists in the adipate. The much lower intensity of the corresponding meridian reflection in this case suggests that the halving of the fiber period may not occur as often. However, the general fuzziness of the pattern indicates that the chain arrangement is less perfect than in the case of the suberic ester.

As in the case of the odd esters the best interpretation of the fiber patterns produced by the adipate and suberate esters is that more than one form of crystalline arrangement is present. It is possible that the sebacate ester also is complicated by more than one form. The patterns of the oxalate and succinate on the other hand can be explained on the basis of one form of crystal (monoclinic). In the case of these patterns the strong pyramidal planes arise from the fact that all of the carbonyl groups fall in inclined planes. As will be seen in the next paragraph, these findings are capable of a general interpretation.

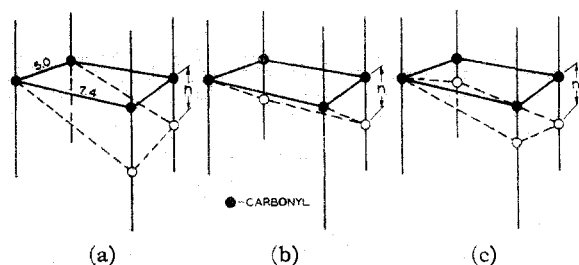


Fig. 2.—Possible types of gliding in polyesters.

The patterns of the even esters other than the adipate and suberate agree with the behavior of the even ethylene polyesters in showing no low order meridian reflections.<sup>11</sup> The pyramidal planes observed in these compounds are best interpreted as arising from the fact that a pre-

(11) Compare K. H. Storks, *THIS JOURNAL*, **60**, 1753 (1938). As pointed out in ref. 2, most of the polyesters undoubtedly possess meridian reflections on the layer-line corresponding to the number of chain atoms in the repeating unit. Because of the comparatively long wave length employed, however, these reflections are not observed in this work.

dominance of carbonyl oxygen atoms fall together with chain carbon atoms in these planes.

**General Theory of the Crystalline Structure of Polyesters.**—The determination of the positions of the atoms in the crystals composing the polyesters is too complex an undertaking to be solved by means of the present X-ray data. Because of the known chemical structure and the zigzag nature of the chains, however, the problem is simplified considerably. The X-ray results show that the polyester chains having the zigzag type of structure assume the same relative positions in the plane perpendicular to their long axes as do the lower molecular long-chain compounds.<sup>12</sup> As mentioned previously, this is strong evidence that the long chains in the polyesters have the same cross-sectional area and shape as in these lower molecular chain structures and that they behave like rigid rods in so far as packing in the crystal is concerned. Because of the great length of the chains in the polyesters and therefore the negligible influence of the end-groups on the structure, we may consider the repeating unit as the unit of packing, and attempt to work out the crystal structure on this basis.

In a bundle of chain molecules all having a common repeating unit it is evident that various crystal structures will arise depending on the relative displacement of the repeating units in the direction of the chain axis. Thus, corresponding atoms in adjacent parallel chains will assume various positions in the structure depending on the amount of gliding these chains undergo with respect to one another in the direction of their lengths. In this manner orthorhombic, monoclinic and triclinic lattices may arise. If no gliding occurs in the case of identical chains, an orthorhombic cell is possible. If, on the other hand, a glide parallel to the *ac* plane takes place as shown in Fig. 2a, a monoclinic cell may be formed. An alternative monoclinic cell may be produced by a glide parallel to the *bc* plane (Fig. 2b). Finally, a glide parallel to the diagonal plane as illustrated in Fig. 2c may result in a triclinic cell. It is possible, therefore, that all of these lattices will be observed in crystals composed of chain structures of this nature.<sup>13</sup>

In order to show that the crystalline polyesters

(12) As pointed out, in the oxalate ester the interchain spacings are somewhat different from the higher decamethylene esters.

(13) It is possible to draw up unit cells in which the chain axis is always perpendicular to one face. These large cells, however, turn out to be multiples of the smaller cells considered in the present treatment. The latter are, therefore, to be regarded as the true unit cells.

so far examined can be explained on the basis of the theory briefly outlined above, let us consider those chain structures which are essentially zigzag in form and in which the chains fall on a Müller net ( $a = 5.0$ ,  $b = 7.4$ ). The assumption is made that when gliding occurs, its magnitude is always an integral multiple of the distance between chain atoms as measured parallel to the chain. In the case of the esters this distance is obtained by dividing the observed identity period along the fiber axis by the number of bonds composing the repeating unit. For the ethylene polyesters<sup>14</sup> the distance averages 1.19 Å., whereas for the decamethylene polyesters the average distance is 1.23 Å. Decamethylene oxalate<sup>15</sup> has a slightly lower value, 1.21 Å. By multiplying this distance by  $n$  the total displacement in the chain direction is obtained.

TABLE IV

Ester	Reflection	Obsd.	Calcd. for	Glide $n$
Decamethylene oxalate	I <sub>1</sub>	49	49.2	5(ac) <sup>a</sup>
			47.5	4(bc)
Succinate	I <sub>1</sub>	42	40.7	7(ac)
			39.1	5(bc)
Glutarate	II <sub>0</sub>	90	90.0	Zero
	II <sub>1</sub>	40	40.7	7(ac)
Adipate	I <sub>1</sub>	43	39.1	5(bc)
			45.1	6(ac)
			45.5	4(bc)
Suberate	II <sub>0</sub>	90	90.0	Zero <sup>b</sup>
	III <sub>1</sub>	45	45.1	6(ac)
			45.5	4(bc)
Azelate	II <sub>0</sub>	90	90.0	Zero
	IV <sub>1</sub>	49	50.3	5(ac)
Sebacate	II <sub>1</sub>	62	47.5	4(bc)
			63.8	2(bc)
Ethylene adipate	I <sub>1</sub>	65	63.5	3(ac)
			64.3	3(ac)
Suberate	I <sub>1</sub>	65	64.7	2(bc)
			64.3	3(ac)
Azelate	II <sub>0</sub>	90	90.0	Zero
Sebacate	I <sub>1</sub>	65	64.7	2(bc)
			64.3	3(ac)
$\omega$ -Hydroxy-decanoic ester	II <sub>0</sub>	90	90.0	Zero

<sup>a</sup> (ac) designates glide parallel to  $ac$ -plane. <sup>b</sup> In these cases as noted in the text a screw axis non-coincident with the chain is supposed to be present.

Table IV shows the agreement obtained between the observed angles and angles calculated

(14) The present argument applies only to zigzag chain configurations.

(15) For the oxalate  $a = 5.28$  Å.,  $b = 7.00$  Å. have been employed.

on the basis of the above glides. In the second column are given important low order reflections for each of the esters employing the designations of Table II. Reflections for the ethylene polyester and  $\omega$ -hydroxydecanoic ester taken from previous publications are also included. The angles which the planes causing these reflections make with the fiber axis are given in the third column. These angles have been calculated from the observed fiber periods and the  $d$ -values corresponding to the planes in question. In column 4 are listed the angles calculated on the basis of the glides in column 5. Only values of  $n$  which agree best with the observations are recorded. Glides parallel to the diagonal planes as shown in Fig. 2c have not been considered since the angles corresponding to these cannot be calculated on the basis of the available data. The possible solutions in column 5 therefore are not to be considered as inclusive. The agreement between the observed and calculated angles is, however, confirmatory of the gliding theory. The choice of the proper lattice and unit cell from among the various possibilities must await more complete experimental results. It is planned to present a more detailed analysis in the case of some of the structures in a later publication.

The general theory given above to account for the various polyester structures is essentially that given by T. Schoon<sup>4</sup> to explain the various polymorphic forms of the lower molecular weight chain compounds. In this way Schoon accounts nicely for the various monoclinic and orthorhombic forms shown by these compounds. On this same basis one might expect that the polyesters would also exhibit a variety of stable modifications in the case of each compound. From the results presented above on the decamethylene polyesters this appears to be the case.

The authors wish to thank Mr. N. R. Pape for his assistance in the X-ray work.

### Summary

1. Decamethylene polyesters of average molecular weight above 10,000 have been prepared from the following acids: oxalic, succinic, glutaric, adipic, suberic, azelaic and sebacic.

2. X-Ray fiber patterns have been obtained on oriented fibers of these compounds. Complete measurements of the patterns are given and it is shown that in all cases the molecules conform closely to the planar zigzag model. Except in the

case of the oxalate ester, all of the structures conform to the same lateral packing as is shown by the lower molecular chain compounds.

3. A discussion of the origin of the various fiber patterns is given. It is shown that in the

case of certain esters the presence of different crystal forms is indicated. A general interpretation of these forms on the basis of the theory of Schoon is presented.

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## Kinetics of the Exchange of Oxygen between Benzoic Acid and Water<sup>1</sup>

BY IRVING ROBERTS AND HAROLD C. UREY

The organic compounds which thus far have been found to exchange their oxygen with that of water are aldehydes, ketones, carboxylic acids, and a few very reactive alcohols.<sup>2</sup> A kinetic study of the exchange of oxygen between acetone and water in the medium 90% acetone-10% water was made by Cohn and Urey,<sup>3</sup> who demonstrated a general acid catalysis which is significant for the mechanisms of both the hydration and the enolization of acetone. The obvious structural similarity of the acid catalyzed esterification and ester hydrolysis reactions to the oxygen exchange reactions of carboxylic acids indicates that a kinetic study of the latter should yield results at least as interesting as those obtained in the acetone exchange.

Benzoic acid exchanged both its oxygen atoms with that of water, the reaction being catalyzed by acids, as is the case for the exchange of carboxylic acids in general.<sup>4-6</sup> The usual method for following exchange, that of mixing comparable amounts of the reacting substances, cannot be used at ordinary temperatures in the case of benzoic acid since the compound is not sufficiently soluble in water to cause an appreciable change in the heavy oxygen content of the water. Rather than introduce the complication of a mutual solvent, we have devised a method of determining the heavy oxygen content of benzoic acid and have carried out the kinetic experiments in dilute aqueous solution.

(1) Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) For a summary of the literature on this subject, see Reitz, *Z. Elektrochem.*, **45**, 100 (1939).

(3) Cohn and Urey, *THIS JOURNAL*, **60**, 679 (1938).

(4) Roberts, *J. Chem. Phys.*, **6**, 294 (1938).

(5) Senkins and Brown, *J. Org. Chem.*, **2**, 569 (1938).

(6) The present work shows that the statement of Koizumi and Titani [*Bull. Chem. Soc. Japan*, **13**, 607 (1938)] that only one oxygen atom of benzoic acid is readily exchangeable cannot be correct. Such a statement is quite unreasonable in the light of our present knowledge of the rapid dissociation of the hydrogen ion from a carboxylic acid and of the symmetrical structure of a carboxylate ion.

### Experimental

**Decarboxylation Apparatus.**—The determination of the O<sup>18</sup> content of benzoic acid depends upon the observation of Sabatier and Mailhe<sup>7</sup> that benzoic acid will be converted almost quantitatively into benzene and carbon dioxide when passed over reduced copper at 500°. For the present work, it was necessary to construct an apparatus which would perform the decarboxylation of a few milligrams of benzoic acid in a stream of nitrogen gas, and which would be free of traces of oxygen, carbon dioxide, water, or copper oxide. In addition, after each conversion, the apparatus should be easily made ready for the succeeding one, since many samples must be converted for each kinetic experiment.

The apparatus finally used is shown in Fig. 1. Tank nitrogen was admitted at the left through a flowmeter (A) and successively through a tube of copper at 350° (B), a bubbler containing sulfuric acid (C), and tubes D and E, filled with potassium hydroxide and anhydrous calcium sulfate, respectively. At this point the nitrogen can be made to take one of two paths; if stopcock K is closed, it can pass through J into the decarboxylation tube (I) containing copper at 500° and into the air through stopcock F. On the other hand, with stopcock J closed, the nitrogen could enter tube I through stopcock F and pass successively through K, a trap (L), and into the air through stopcock O. Tube I was made of temperature-resistant glass (Corning 172), and sealed directly to the Pyrex tubing at either side. Tube H was 1.5 cm. in diameter and contained a ring seal with an opening of about 2 mm. diameter. The apparatus also contained a safety seal (G), a manometer (M), a sample tube fitted with a break seal (N), and a trap (P) surrounded with solid carbon dioxide to protect a Hyvac pump connected at the right.

After sweeping out with hydrogen gas to reduce the oxides of copper, the entire apparatus was evacuated and filled with nitrogen. Trap L was surrounded with liquid nitrogen. The nitrogen stream was then adjusted to 30 cc./min., and directed through J, through tubes I and H and into the air through F (stopcocks K and O being closed). The plug in tube H was removed, the tube containing the benzoic acid inserted around the ring seal and the plug replaced. The benzoic acid sample tubes, which were 10 mm. in diameter and of the shape shown in the upper left of Fig. 1, were first wiped with chamois to

(7) Sabatier and Mailhe, *Compt. rend.*, **159**, 219 (1914).