161. *Built-up Films of Unsaturated and Substituted Long-chain Compounds.*

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A number of long-chain compounds, particularly *cis-trans*-unsaturated and α-substituted acids, have been built up from monolayers on water into multilayers on polished chromium. The optical thickness per layer was compared with the spacing determined by *X*-rays. The results support previous findings that multilayers are microcrystalline and that the method is excellent for obtaining oriented crystals of long-chain compounds which may be difficult to crystallise in other ways. Some chemical reactions in multilayers have also been studied.

THE early *X*-ray examination of built-up films of stearic acid and of calcium and lead stearates (Clark and Leppla, *J. Amer. Chem. Soc.*, 1936, **58**, 2199) showed that the long spacings (d) so obtained corresponded closely with those given by the crystalline material. With barium stearate (Holley and Bernstein, *Physical Rev.*, 1937, **52**, 525; Holley, *ibid.*, 1938, **53**, 534; Fankuchen, *ibid.*, p. 909) and with long-chain esters (Stenhagen, *Trans. Faraday Soc.*, 1938, **34**, 1328), the d values are independent of the method of deposition and, where comparison is possible, correspond with those from known crystalline modifications, thus showing that such films, even when optically clear, are in reality microcrystalline.

Since the optical thickness of these layers depends upon the type of deposition and upon the piston pressure employed, there should be no exact correlation between this optical thickness (t_B) and the long spacing (d) as found by *X*-ray analysis. In all the cases previously examined the differences in t_B due to a different tilt of the molecule on the water surface, have been quite small (up to *ca.* 6%), whereas in this investigation very much bigger differences (up to *ca.* 50%) have been encountered. The conditions which obtain in built-up films, as might be anticipated from the completely regular orientation which exists in the monolayer on water, seem excellent for inducing crystallisation, even in compounds such as the unsaturated, α-hydroxy-, and α-methyl acids, which normally are very reluctant to do so. Another great advantage of the multilayer method is the very minute amount of substance required, since if necessary a complete *X*-ray determination could be carried out on about 0·01 mg.

The compounds which have been examined can be divided into the following groups :

(a) cis-trans-*Isomers*. Alcohols : oleyl and elaidyl. Acids : *cis*- and *trans*-dihydroxybehenic; oleic, elaidic; *cis*- and *trans*-petroselinic; erucic, brassidic.

(b) α-*Substituted acids*. α-Bromostearic, α-triazopalmitic, α-aminopalmitic, α-hydroxystearic, α-methylpalmitic.

(c) *Benzene derivatives*. *p*-Hexadecylphenol, 2 : 6-dibromo-4-hexadecylphenol.

The multilayers were built up in the usual manner on polished chromium plates by the methods developed by Blodgett and Langmuir (*J. Amer. Chem. Soc.*, 1935, **57**, 1007), except that when the film came out hydrophilic and hence covered with a thick layer of water (*e.g.*, α-amino- and α-hydroxy-acids), the latter was removed " in a vacuum " at room temperature. Except for the benzene derivatives, the best substrate was found to be the ordinary Cambridge tap-water, filtered before use. Its p_H was rather high (*ca.* 8·0), and it contained approximately 2 × 10^{-5}M-calcium as bicarbonate. A synthetic substrate of the same p_H and calcium concentration was comparatively poor for multilayer building, but the reason for this marked difference has not been investigated. Rather strangely, stearic acid gave beautiful *Y* deposition from this tap-water substrate with no tendency at all to the *X* type, although Blodgett (*loc. cit.*) has shown that the optimum conditions for *X* deposition of stearic acid are obtained by using a substrate containing *ca.* 10^{-4}M-calcium, p_H 8·8. With the exception of oleic and *cis*-petroselinic acids, which showed *X* deposition, all films came on as the *Y* type, although in some cases there was a marked tendency towards the former at low piston pressures.

The optical thickness was measured by comparison of the interference colours with those given by a known number of *Y*-deposited stearate layers from the same substrate, and also with barium stearate films of known thickness for which t_s = 24·4 A. (Blodgett, *J. Physical Chem.*, 1937, **41**, 975). No allowance was made for any differences in refractive index, but the error introduced is probably less than 1%. A comparison of the multilayers of stearic acid from tap-water and from a standard barium solution as used by Blodgett showed that the former was appreciably thicker (5%), but the reason for this difference has not been investigated. Accordingly, with the exception of *p*-hexadecylphenol, which was deposited from a standard barium solution, all optical thicknesses may have been correspondingly increased. The deposition ratio (*i.e.*, area of slide covered/area of monolayer removed) was measured and found in all cases to be 0·99—1·00, in agreement with the results of Langmuir, Schaefer, and Sobotka (*J. Amer. Chem. Soc.*, 1937, **59**, 1751) and of Stenhagen (*loc. cit.*).

For measuring the long spacings by *X*-ray diffraction, monochromatic copper-*K*α radiation (wave-length 1·54 A.) was employed to give freedom from background, and the experimental details followed those of Fankuchen (*loc. cit.*). One very satisfactory modification is to build the film on a thin sheet of mica, which calibrates the photographic plate directly, since it possesses a layer lattice with a spacing of about 10·1 A. between the lattice planes. In one experiment a calcium stearate multilayer of 51 layers was built up quite easily and gave four fairly weak lines and one very strong one, corresponding presumably to the first orders of the stearate and the lattice spacing of the mica. This was confirmed on measuring the spacings, which were found to be 51·4 A. for the stearate and 10·18 A. for the mica, in excellent agreement with the known values.

Table I summarises the results obtained for the optical and *X*-ray spacings, and gives the physical state of the monolayer from which the film was built up and the piston pressure used. As previously mentioned, all films except oleic and *cis*-petroselinic acids showed *Y* deposition, and all, even including these, gave a *Y* type (*i.e.*, double molecules) from *X*-ray diffraction, so the optical spacings have been doubled for comparison purposes. All films were built up from a tap-water substrate except *p*-hexadecylphenol which gave best results from a standard barium solution. In col. 4 the letters have the following significance : L. = liquid, V.L. = viscous liquid, S. = solid, S.B. = " solid board," *i.e.*, very great rigidity.

TABLE I.

Compound.	*t*, A.	*d*, A.	Nature of monolayer.	Piston.
Calcium oleate	33·4	47·0	L.	Triolein
,, elaidate	51·2	50·0	S.B.	,,
,, *cis*-petroselinate	42·2	43·7	L.	,,
,, *trans*- ,,	51·2	51·5	S.B.	,,
,, erucate	57·3	55·5	S.	Oleic acid
,, brassidate	62·1	60·7	S.B.	Triolein
,, α-methylpalmitate	36·3	41·2	V.L.	,,
,, ,, ,,	37·4	41·6	V.L.	Oleic acid
,, α-bromostearate	48·8	48·4	L	Triolein
,, α-triazopalmitate	32·2	26·2	L.	,,
,, ,, ,,	34·9	39·6	L.	Oleic acid
,, α-aminopalmitate	—	38·9	S.B.	Castor oil
,, α-hydroxystearate	—	49·6	S.B.	Oleic acid
p-Hexadecylphenol	54·0	46·3	S.	Triolein
2 : 6-Dibromo-4-hexadecylphenol	—	29·7	L.	—
Calcium stearate	51·2	51·3	S.	Oleic acid

In Table II the multilayer *X*-ray spacings are compared with the values found in bulk for the same or closely related substances, the latter being taken from Clark (" The Fine Structure of Matter," 1937, Chapman and Hall).

TABLE II.

Compound.	Multilayer spacing.	Bulk spacings.	
Calcium stearate	51·3	Lead stearate	51·3
*Barium ,,	51·5	Potassium stearate	42·0
		Thallium stearate	42·2
		Potassium acid stearate	50·5
		Sodium acid stearate	50·6
Calcium oleate	47·0	Sodium oleate	43·5
		Oleic acid	37·5, 36·2
,, elaidate	50·0	Elaidic acid	48·3
,, erucate	55·5	Erucic acid	46·3
,, brassidate	60·7	Brassidic acid	59·9
		Potassium acid behenate	60·8
,, α-bromostearate	48·4	α-Bromostearic acid	36·2, 46·5
p-Hexadecylphenol	46·3		

* Fankuchen, *Physical Rev.*, 1938, **53**, 909.

Direct comparison is only possible with the long-chain phenol, but the agreement is undoubtedly as good with the stearate, since the effect of changing the metal atom is very small (cf. potassium and thallium stearates, and the acid stearates). For the *trans*-elaidic and brassidic acids the agreement is quite good, whereas for the *cis*-isomers there is a very big difference between the calcium salt in the multilayer and the pure acid.

The more detailed results for each class of compound are given below.

(a) cis-trans-*Isomers*.—Neither oleyl nor elaidyl alcohol gave multilayers, the former being liquid at room temperature and the latter giving too solid a film.

cis-Dihydroxybehenic acid gave fairly good multilayers from a tap-water substrate (triolein piston) which showed an *X*-ray spacing of 35·6 A. (*i.e.*, a very tilted molecule), whereas the *trans*-acid, owing to its unusually great solidity, gave very poor ones. Attempts to diminish this solidity by alteration of the p_H over the range corresponding to that between N-hydrochloric acid and 0·1N-sodium hydroxide all failed, the film remaining a " solid board " throughout. The reason for this great difference between the two forms has been discussed by Marsden and Rideal (J., 1938, 1163).

The isomeric unsaturated acids gave excellent multifilms, and the evidence from these films is consistent with the usually accepted *cis*- or *trans*-form and agrees with the conclusions drawn by Marsden and Rideal (*loc. cit.*) from their monolayer studies. As they pointed out, the *cis*-forms can pack much less readily than the *trans*-, in which the ease should be little different from that of a saturated chain. This was well shown in the physcial state of the monolayers on a tap-water substrate, since, whereas all the *trans*-acids gave " solid board " films, oleic and *cis*-petroselinic gave perfectly fluid films, and erucic acid, with its extra four carbon atoms, gave a viscous liquid film at triolein pressure, becoming solid under oleic acid pressure. Closely related to this was the very pronounced difference in the visible crystallisation on the water surface, for although the *trans*-compounds withstood very much higher pressures than the *cis*-, yet they crystallised very much more readily (crystallisation always appearing to take place from the edges of the trough). Elaidic and *trans*-petroselinic acids even showed a greater tendency for crystallisation than did stearic acid—a rather surprising fact, since it would appear to indicate an easier packing in the *trans*-unsaturated acids. It may be suggested that the great stability and ease of crystallisation of these *trans*-acids is due to the interaction between the double bonds *via* either water or oxygen molecules as intermediaries, or the effect may be a purely mechanical one due to the rigid double bond reducing lateral vibrations in the chain. That there exists some considerable difference between the saturated and the *trans*-unsaturated acids which greatly influences their aggregation is shown by the crystal structure of the free acids, since the former exist with inclined and the latter with vertical chains (see Table II).

The *trans*-acids showed only Y deposition, and the *cis*-acids X, although with erucic acid a change over to the Y type occurred at oleic acid pressure. From the optical spacings (Table I) it is seen that, as expected, the *trans*- are much more stretched than the *cis*- and approximate to the length of the saturated acids, and that the difference between the *cis*- and the *trans*-forms depends upon the position of the double bond and upon the chain length.

Müller and Shearer (J., 1923, **123**, 3156), in their early work upon the X-ray structure of long-chain compounds, measured the spacings of oleic, elaidic, erucic, and brassidic acids, but no measurements appear to be recorded for *cis*- and *trans*-petroselinic acids. Their values for the acids, given in Table II, show a close agreement with the multilayer spacing (*i.e.*, with the calcium salt) for the *trans*-acids, and a very pronounced difference with the *cis*-. This is readily understood if the saturated and *trans*-acids are assumed to be vertical, and the *cis*- very much inclined (as the monolayer experiments indicate), since formation of the calcium salts would condense and therefore lengthen the *cis*-forms but would have little effect on the *trans*-.

(b) *α-Substituted Acids.*—These gave excellent multifilms except the α-amino- and α-hydroxy-compounds which came out hydrophilic and so were dried " in a vacuum " as described above. It is very significant that when the α-group was large ($-CH_3$, $-N_3$, $-Br$), the films were always liquid, even on tap-water, whereas when it was smaller ($-OH$, $-NH_2$), they were extremely solid, indicating that close-packing of the long-chains throughout their whole length is one condition for solidity.

With α-methylpalmitic acid, changing the piston from triolein to oleic acid increased the optical thickness but did not alter the X-ray spacing, whereas with α-triazopalmitic acid a similar change produced an entirely new crystalline modification. The photograph obtained when using the oleic acid piston showed two sets of spacings quite distinctly, the weaker being exactly the same as obtained by using triolein ($d = 26{\cdot}2$ A.), and the stronger corresponding to a new, much less inclined molecule ($d = 39{\cdot}6$ A.). Such a transition brought about by alteration of the piston pressure would appear to be quite possible, but this appears to be the first recorded example.

(c) *Benzene Derivatives.*—The 2 : 6-dibromo-4-hexadecylphenol multilayer was obtained from one of *p*-hexadecylphenol by direct bromination with moist bromine vapour. This caused a colour shift corresponding to an increase either in thickness or in refractive index, and some irregularities became apparent in the film. Nevertheless, it gave quite a good X-ray diffraction pattern corresponding to a spacing of 29·7 A., indicating that the molecules lie in very inclined doublets. Now it is known that bromination of this phenol in the monolayer (Alexander, J., 1938, 729) is accompanied by a very great increase (*ca.* 40%) in the molecular area and liquefaction of the previously solid film, and the stability pressure is decreased to such small values (*ca.* 3—4 dynes/cm.) that no multilayers can be obtained by the usual methods. However, the conditions in the multilayer seem to promote crystallisation of this new compound, and so perhaps this method may be applicable to other cases.

An attempt was made to determine the structure of the saturated dibromo-oleic and -elaidic acids by brominating the multilayer of the calcium salt in a similar manner to the above, but in these cases the films visibly collapsed on bromination, and then gave no sign of an *X*-ray diffraction pattern, indicating a complete disorder. It is probable that in this case the bromine not only adds on to the double bond, but also liberates the free acid from the calcium salt, and the disruption brought about by the combined effects completely destroys the regular orientation in the multilayer.

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