XXXIV.—*An X-Ray Examination of some Salts of the Fatty Acids.*

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X-RAY photographs were taken with the $K\alpha$ rays of copper or iron reflected from thin layers of the salts pressed on a glass strip and mounted on a Müller spectrograph. The salts were in the form of thin flakes, and this method is convenient for obtaining the reflexions from the widely spaced crystal planes parallel to the flake surface. Salts of long-chain compounds of this type crystallise with these planes separated by the lengths of two molecules placed end to end with like groups in contact, and the axis of the chain is usually tilted with respect to the plane. The spacing measured, *i.e.*, the perpendicular distance between the planes, may be conveniently spoken of as twice the *effective* length of the molecule.

Many of the salts, being very deliquescent, were kept in a desiccator provided with windows and maintained at a temperature of 80° during the exposure. The windows were covered with a thin semi-transparent animal membrane prepared by the Badische Fabrik for covering scent-bottle stoppers; as this has no appreciable absorption for X-rays, is impermeable to moisture, and is unaffected at 100°, it is very suitable for the purpose.

The existence of two types of potassium salts was first noticed when a second and larger spacing appeared on the photograph of a specimen of the stearate which had been exposed to the atmosphere for some days. It seemed possible that this spacing was due to the presence of an acid * salt, and preparation of the acid salt immediately confirmed this hypothesis, the photograph showing only the large spacing. Dr. T. Malkin kindly undertook the preparation of several of these acid salts,† and I wish to express my gratitude to him for supplying these and most of the normal salts. It is sufficient to state here that the normal salts and acid salts containing eight or more carbon atoms separate on cooling from a warm alcoholic solution to which has been added the *theoretical* amount of alcoholic caustic potash. Those of less than eight carbon atoms separate on evaporation of the alcoholic solution.

Pure salts give brilliant photographs on which it is possible to measure the orders of reflexion right across the plate, so that an accuracy of 1% is easily obtained, and this may be regarded as the maximum probable error in the individual spacings now given. Traces of impurity give rise to small distorted crystals, the reflexions give few orders and broad ill-defined lines, and the spacings usually differ from those of the pure salt.

The type of reflexion resembles that first obtained by Müller for the fatty acids (J., 1923, **123**, 2043), *i.e.*, strong odd orders and weaker even orders. This effect (see Shearer, *Proc. Roy. Soc.*, 1925, *A*, **108**, 655) is due to the weak reflexions from the planes containing the light methyl groups being in opposite phase to the strong re-

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* Theoretically, of course, an acid salt of a monobasic fatty acid cannot exist. In conformity with other workers, however, we use the term to imply an equimolecular compound of the free acid and the neutral salt.

† The acids used in this work are of the highest degree of purity. Lauric, myristic, palmitic, stearic, and behenic acids were purified by careful fractional distillation of the ethyl esters (compare Piper, Malkin, and Austin, J., 1926, 2312, footnote). With the exception of pentadecoic acid, which was kindly provided by Professor Garner, the acids were obtained by nitrile and malonic ester syntheses, an account of which will be published later. Throughout the latter work, the physical data for intermediates and acids were found to correspond closely with those given by Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 905), which may be regarded as criteria of a high degree of purity.

flexions from the planes containing the heavier active groups. Since active groups containing potassium atoms have a higher scattering power than carboxyl groups, the interference of the reflexions from the CH_3 planes is not so marked as with the acids, and the even orders are stronger. The weakening of the even-order reflexions is slightly more marked in the acid than in the normal salts, as would be expected, for here presumably one hydrogen and one potassium atom take the place of two potassium atoms in the planes which contain the active groups.

In contrast with the acids, which possess a number of crystalline forms (Piper, Malkin, and Austin, J., 1926, 2310; de Boer, *Nature*, 1927, **119**, 634), only one form appears to exist for these pure anhydrous salts at the ordinary temperature. For this reason they are very well suited for X-ray measurements for analytical purposes. The spacings are shown in Table I. Previous measurements on salts of fatty acids are those of Piper and Grindley (*Proc. Physical Soc.*, 1923, **35**, 269) and Trillat (*Compt. rend.*, 1925, **180**, 1838).

TABLE I.

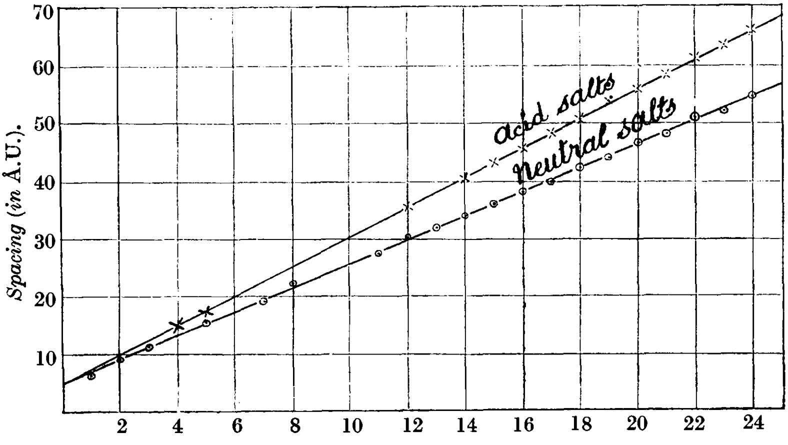
		Spacing, in Å.U.	
Salt.	No. of C atoms.	Normal salt.	Acid salt.
Formate	1	6·4	—
Acetate	2	9·13	—
Propionate ...	3	11·4	—
Butyrate ...	4	—	14·90
Valerate	5	15·55	17·07
Heptoate ...	7	19·16	—
Octoate	8	22·3	—
Undecoate ...	11	27·45	—
Laurate	12	30·2	35·53
Tridecoate ...	13	31·85	—
Myristate ...	14	33·95	40·45
Pentadecoate	15	35·8	42·90
Palmitate	16	37·9	45·29
Margarate ...	17	39·77	48·10
Stearate	18	42	50·47
Nonadecoate	19	43·8	53·03
Eicosoate	20	46·45	55·65
Heneicosoate	21	47·85	58·35
Behenate	22	50·72	60·78
Tricosoate......	23	51·8	63·25
Lignocerate ...	24	54·45	65·94

The spacings are plotted against the number of carbon atoms in the chain in Fig. 1. It appears that, with the exception of potassium formate, the odd and even neutral salts lie on a straight line with an origin at 5 Å.U. The acid salts lie on another straight line starting from the same origin, and the slope of each of these lines gives the *effective* length of two CH_2 groups in the particular type of chain concerned.

The accepted diameter of the carbon atom is 1·54 Å.; and the maximum possible value of the effective length of the CH_2 group, if the lines joining the centre of two successive carbon atoms are inclined at the tetrahedral angle of 109° 28′, is 1·257 Å. (Müller and Shearer, J., 1923, **123**, 3159). I find that the effective length is

1·03 Å. in the normal salts, and 1·275 Å. in the acid salts. The smaller effective length for the normal salts might be explained by assuming that the tetrahedral angle exists in the chain and that the whole chain is inclined at 54° 54′ to the axis. The effective length of 1·275 Å. is slightly too great to be explained on the basis of a tetrahedral angle in the chain; if we assume that the chain is oriented perpendicularly to the reflecting planes, the angle would be 111° 46′, but there is no independent evidence for assuming that the chain is perpendicular. If the chain were tilted, the angle would have to exceed the tetrahedral angle by a still larger amount. Another alternative is that the diameter of the carbon atom is 1·56 Å. instead of 1·54 Å., the chain being perpendicular and the angle tetrahedral, but it is not likely that the diameter of the carbon atom is variable. The choice between these alternatives can only be decided by a complete analysis of single crystals.

FIG. 1.



Müller (*Proc. Roy. Soc.*, 1928, *A*, **120**, 437) concludes that the chain of a normal hydrocarbon is a flat zig-zag in which the tetrahedral angle is conserved within $\frac{1}{2}$%, and it is, therefore, important to decide whether the variation found for these salts is within the limits of experimental error.

The value of 1·275 exceeds the above value of 1·257 by 1·4%; no single spacing has a maximum error of more than ±1%, and most are correct to ±0·5%. In Table II the values of $\Delta s/\Delta n$, the spacing increase per carbon atom, are calculated for eight pairs of values. It will be noticed that all values of $\Delta s/\Delta n$ are greater than 1·257, and only one differs from the mean by as much as 1%. Since an

TABLE II.

No. of C atoms.	Spacing.	Diff.	$\Delta s/\Delta n$.	Difference from mean.	% Variation from mean.
24 17	65·94 48·10	17·84	1·275	0	0
23 16	63·25 45·29	17·96	1·283	+0·008	+0·6
22 15	60·78 42·90	17·88	1·277	+0·002	+0·15
21 14	58·35 40·45	17·90	1·278	+0·003	+0·23
20 12	55·65 35·53	20·12	1·259	−0·016	−1·30
19 5	53·03 17·07	35·96	1·284	+0·009	+0·7
18 4	50·47 14·90	35·57	1·271	−0·004	−0·3
			Mean 1·275		

impurity can alter the spacing, it is possible that the large variation from the mean in this case is due to contamination of one of the salts. The mean value of $\Delta s/\Delta n$ is identical with that measured from the graph.

It appears, therefore, that the difference from the tetrahedral chain is real, and that the chain in these salts differs from the hydrocarbon chain, possibly owing to attractions between the active end groups. The divergence of the *s–n* graph from the line drawn from the same origin for a tetrahedrally spaced chain is quite noticeable when plotted on a large scale, and on the same scale there appears a tendency for the odd-numbered *normal* salts to lie below the even-numbered, although the variations in this case are nearer the possible experimental errors.

Dr. Malkin has also prepared some acid sodium salts. In contrast to the normal sodium salts, these crystallise beautifully, and the spacings obtained are given below. It is noticeable that all three have larger spacings than the corresponding potassium salts, a rather surprising result in view of the smaller size of the sodium atom. The spacings of two normal thallium salts (very kindly given me by Dr. Menzies) are included to bring out the very small change in the spacing that is produced by the addition of a very heavy metallic atom.

TABLE III.

Salt.	No. of C atoms.	Spacing, in Å.U.
Acid sodium laurate	12	35·76
Acid sodium palmitate	16	46·05
Acid sodium stearate	18	50·6
Thallium palmitate	16	38·8
Thallium stearate	18	42·2

Gibbs (J., 1924, **125**, 2622) concludes that a linear relationship of this nature does not exist for the lower members of the fatty acids. It is hoped to show in a further communication that this apparent breakdown of the linear law can, in part at least, be attributed to multiplicity of crystalline form.

Summary.

X-Ray photographs show that the potassium salts of the fatty acids have spacings increasing uniformly with the carbon content from 2 to 24 atoms. Another similar series of spacings exists for acid salts, *i.e.*, equimolecular compounds of free acid and neutral salt. The chain in this type of salt cannot be accounted for by a tetrahedral angle of 109° 28′ between the lines joining the centres of successive atoms—at least 111° 46′ is required.

I am indebted to Mr. T. Howard and Mr. Leacy for taking some of the photographs. Part of the expenses of the work were covered by a grant from the University Colston Research Society.

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[*Received, September* 14*th*, 1928.]