Modifications of Normal Fatty Acid Amides

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Introduction

It is well known that A. Müller[1] concluded, from his X-ray measurements, that molecules of normal paraffines with carbon numbers ranging from 21 to 27 rotate around their long axis above certain critical temperatures which are several degrees below their melting points. Similar rotational transformation has also been found in the experiments of X-ray diffractions[2,3], specific heats[4] and dielectric properties[5,6,7] of some normal alcohols. It seems interesting to confirm such transformation in some other long chain compounds, especially in those containing hydrogen bonds. The object of the present experiment is to examine if any discontinuous changes occur in X-ray diffraction lines of normal fatty acid amides of even carbon number from 4 to 18 between room temperature and the individual melting points.

Experimental

The acid amides were all synthesized by the following reaction.

$$2RCOOH + H_2NCONH_2 \longrightarrow RCONH_2 + CO_2 + RCOONH_4$$

After heating the mixture of equivalent fattty acid and urea for several hours in a flask, the amide was separated by distillation. All amides thus obtained were purified by vacuum distillation and by repeated recrystallization from adequate solvents, their melting points being shown in Table I.

The powdered specimens were enclosed in thin walled glass capillary tubes and their X-ray diffraction photographs were taken with the Cu K_α radiation filtered by nickel foil. The distance between the specimen and the film was 8.03 cm. The time of exposure was about five to ten minutes at about 30 *k*V. and 60–70 MA. using rotating copper anode.

The specimen was heated to the required temperature by a small electric furnace, which was placed so as to surround the capillary tube at the

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[1] A. Müller, *Proc. Roy. Soc. A.*, **138**, 514 (1932).

[2] J.D. Bernal, *Nature*, **123**, 870 (1932).

[3] K. Sano and Y. Kakiuchi, *J. Phys. Soc. Japan*, **4**, 365 (1949).

[4] Y. Kakiuchi, T. Sakurai and T. Suzuki, *J. Phys. Soc. Japan*, **5**, 369 (1950).

[5] Y. Kakiuchi, *Proc. Japan Acad.*, **23**, 65 (1947).

[6] T. Sakurai, *J. Phys Soc.*, **6**, 431 (1949).

[7] J.D. Hottman and C.P. Smyth, *J. Am. Chem. Soc.*, **71**, 431 (1949).

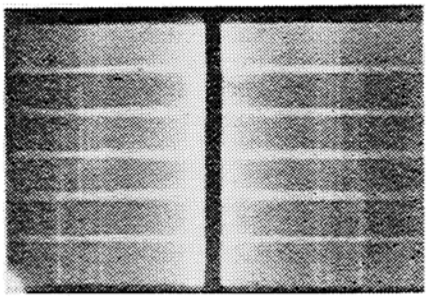

Photo. 1. C_{12}-amide

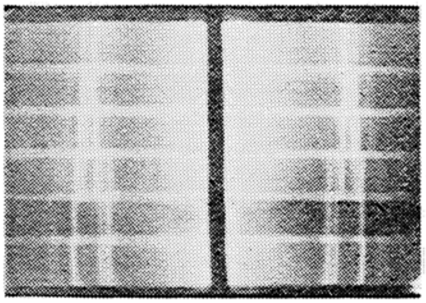

Photo. 2. C_{16}-amide Type I.

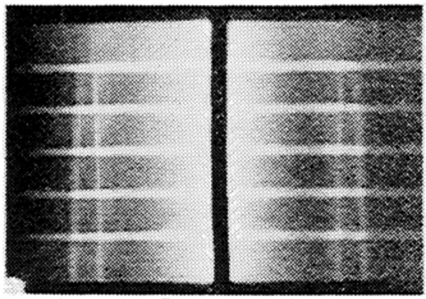

Photo. 3. C_{18}-amide Type II.

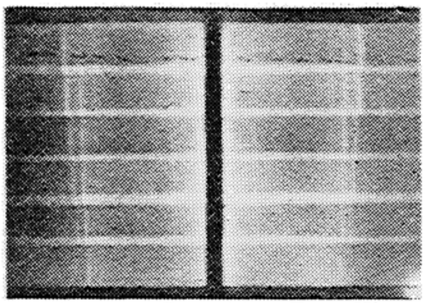

Photo. 4. C_{18}-amide Tpye II′.

center of the camera. The temperature of the specimen was measured by the thermometer, the bulb of which was close to the specimen. It was kept constant during the exposure within about 2°C. In order to find easily small shifts of diffraction lines due to the variation of temperature, the temperature of the specimen was varied stepwise and a whole series of photographs was recorded on the same film as shown in the Photos. 1–4.

Experimental Results and Discussion

Modification at Room Temperature.—The measured values of short and long spacings at room temperature are summarized in Table I, their relative intensities of reflections estimated visually being given in five degrees as usual. In the cases of lower amides than C_{16} the specimens crystallized from solvents show the same diffraction lines as those crystallized from the molten states. The general behaviours of the diffraction lines are close to those obtained by F. W. Matthews, G. G. Warren and J. H. Michell[8], though the individual values of reflection lines do not perfectly coincide.

In the case of C_{16} amide four types of modifications exist at room temperature. The

TABLE I

THE X-RAY DIFFRACTION DATA ON THE ACID AMIDES

Acid amide		m.p. (°C)	Type	Short spacing (Å)							Long spacing (Å)
Butyric acid amide	C_4	113		3.79(s)	4.05(m)	4.20(w)	4.68(vs)				9.95
Caproic acid amide	C_6	98		3.56(s)	4.30(vw)	4.39(w)	4.88(vs)				13.92
Caprylic acid amide	C_8	110		4.07(s)	4.36(m)	4.55(m)	4.94(s)				17.41
Capric acid amide	C_{10}	96		3.33(w)	3.48(vw)	3.70(vs)	4.19(m)	4.45(s)	4.94(s)		20.63
Lauric acid amide	C_{12}	97		3.68(s)	4.12(m)	4.53(m)	4.95(m)				24.32
Myristic acid amide	C_{14}	102		3.51(vw)	3.59(vw)	3.76(w)	3.96(s)	4.51(m)	4.92(m)		27.73
Palmitic acid amide	C_{16}	106	I	3.82(vs)	4.58(s)	4.95(s)					30.62
			II	3.39(vw)	3.49(vw)	3.78(vs)	3.94(w)	4.18(m)	4.52(vs)	5.02(w)	32.41
			II′	3.26(vw)	3.77(s)	4.16(vw)	4.46(w)				32.46
			III	3.82(vs)	4.34(m)	4.53(w)					44.50
Stearic acid amide	C_{18}	107	II	3.77(s)	3.86(m)	4.54(s)	5.09(vw)				36.22
			II′	3.26(vw)	3.71(s)	3.87(m)	4.10(vw)				36.26
			III	3.80(vs)	4.32(m)	4.52(w)					49.65

The symbols, vs., s., m., v., vw. show the relative intensities of reflections estimated visually, very strong, strong, medium, weak, very weak, respectively.

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[8] F.W. Matthews, G.G. Warren and J.H. Michell, *J. Anal. Chem.*, 22, 514 (1950).

specimen crystallized from solvents generally shows Type I, while that crystallized from the molten state show Type II (Table I). The relation between the long spacing and the number of carbon atoms in the chain is shown in Fig. 1. The linear relation existing usually in many other long chain compounds is seen also in the present case. It is noted, however, that the long spacing of Type I lies just on the linear extension of those of lower amides, while that of Type II shows a little greater value. T. Sakurai has recently concluded from his structural analysis that C_{16} amide has two types[9], parallel chain and cross chain types, the former appearing in the crystal from molten state and the latter in that from solvents, and also suggested that in lower amides the cross chain type only may exist. Although this suggestion should be confirmed by the structural analysis of lower amides, the present result does not seen to contradict it. In the case of C_{18} amide the distinction between Types I and II is not observed. The observed value of the long spacing, however, seems to correspond to that of Type II of C_{16} amide as seen in Fig. 1.

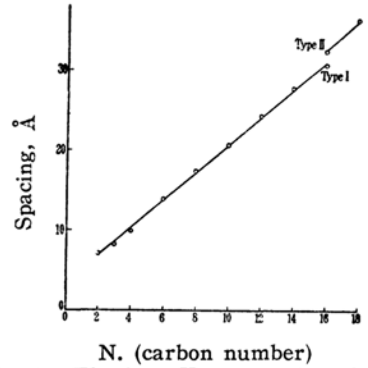

Fig. 1. The long X-ray spacings for acid amides as a function of the number of C atoms.

Type II' appears when the molten C_{16} and C_{18} amides are solidified very slowly as written in the next section. Type III is observed in a thin flake obtained when the acetic acid solution of C_{16} and C_{18} amides are evaporated slowly on a glass plate. From their great values of long spacings it is considered that in the crystal of Type III the dimer linked together by hydrogen bonds between the amide ends stands perpendicular to the basal plane. If this is the case, the long spacing of C_{18} amide will be greater than that of C_{16} amide by four times the C-C distance projected on the chain axis; viz. $1.27\times4=5.08$ **Å**, the observed value 5.15 Å agreeing nearly with it. Among the four types, Type II seems to be the most stable from as seen below.

Temperature Effects.—In the cases of C_{14}-C_{10} amides the diffraction lines do not present any discontinuous changes with temperatures up to the melting points. The long spacings increase continuously with the rise of temperature, while in short spacings some expand and some others contract. The amounts of these shifts are in the order of some per-

TABLE II

THE TEMPERATURE EFFECTS ON THE X-RAY DIFFRACTION DATA OF C_{12} AND C_{14}-AMIDES (SHORT SPACINGS)

temp. (°C)	Short spacings (Å)						
	C_{12}-amide						
13	4.95(m)		4.53(m)	4.12(m)	3.68(s)		
31–32	4.93		4.51	4.09	3.67		
39	4.90		4.48	4.11	3.67		
45–46	4.91		4.48	4.11	4.66		
50–51	4.91(m)	4.65(vw)	4.46(w)	4.19(s)	3.74(w)	3.61(vw)	
68	4.90	4.68	4.47	4.20	3.76	3.63	
84–86	4.90	4.69	4.48	4.22	3.77	3.63	
99–100	4.93	4.69	4.47	4.24	3.78	3.64	
	C_{14}-amide						
16	4.92(m)	4.51(m)	3.96(s)	3.76(w)	3.59(vw)	3.51(vw)	
34	4.91	4.50	3.96	3.76	3.58	3.52	
48–50	4.91	4.50	3.97	3.76	3.59	3.52	
55	4.89	4.49	3.95	3.75	3.57	3.50	
59	4.89	4.48	3.95	3.74	3.58	3.50	3.41(vw)
63	4.90	4.48	3.95		3.60	3.51	3.43
66	4.89	4.51	3.97		3.60	3.53	3.46
86	4.91	4.52	3.98		3.61	3.52	3.46
94–96	4.92	4.53	3.99		3.61	3.53	3.45

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[9] T. Sakurai, *J. Phys. Soc. Japan*, (to be published soon).

centages between room temperature and the melting points and are completely reversible with temperature.

The long spacing as well as short spacings of C_{12} amide present abrupt changes at about 48°C as shown in Table II and Photo. 1. This transformation is reversible with temperature. In the case of C_{14} amide the expansion of long spacing is not observed, while in the reflection of short spacings one diminishes its intensity with the increase of temperature, disappearing at about 59°C and another one appears at the same time. These changes, however, are gradual and reversible with temperature, not showing a distinct transition point. (Table II)

Type I of C_{16} amide and Type III of C_{16} and C_{18} amides both transform into Type II at high temperature. The former shows a distinct transformation point at 76°C, while the latter does not change abruptly. The very long spacing of the latter contracts gradually with temperature accompanying the gradual appearance of the characteristic long spacing of Type II, and Type II only remains above 80°C. It may be considered that in Type III the chain axis standing perpendicularly to the basal plane begins to tilt on heating, partially forming Type II. Type II, once formed by heating, does not return to Type I or III without recrystallization from solvents.

When Type II of C_{16} amide is heated, the long spacing expands continuously. Among the short spacings the one which shows strong reflection at 3.78 Å, splits into a doublet between 49°C and 85°C, becoming again a singlet of 4.00 Å near the melting point as shown in Fig. 2. Another one, which shows strong reflection at 4.52 Å, contracts continuously, decreasing to 4.30 Å near the melting point. This approach of two strong reflection lines on heating appears to be similar apparently to the tendency observed by Müller in the case of paraffine. In the present case, however, the distinct transformation point to become a single reflection line can not be observed below the melting point.

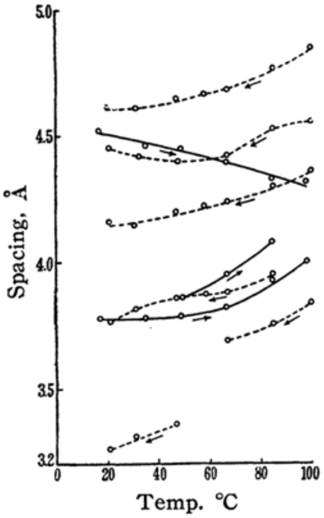

Fig. 2. The temperature effects on the X-ray spacings of C_{16}-amide. (Type II. & II′.)

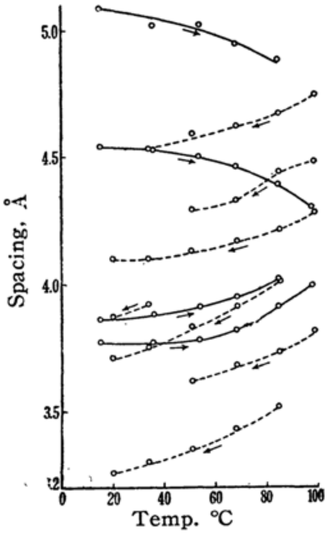

Fig. 3. The temperature effects on the X-ray spacings of C_{18}-amide. (Type II. & II′.)

It is interesting to note that contrary to the cases of lower amides a phenomenon of hysteresis is observed in the case of C_{16} amide. When Type II is cooled after heating up to near the melting point, the temperature effects are just reversed with those of heating. When it is cooled slowly, however, after heating up to the molten state, new short spacings appear and they change continuously on cooling, forming a different type, Type II', at room temperature (Fig. 2). If it is cooled rapidly to room temperature from the molten state, Type II always appears. As to the long spacing Type II' is not very different from Type II. The analogous phenomenon of hysteresis is observed also in the case of C_{18} amide as shown in Fig. 3.

These phenomena are probably due to the following reasons: that the molecules are more loosely bound in higher amides than in lower amides, and also that different arrangements of atoms in the amide groups may occur on solidification from the molten state. The detailed discussion, however, must be postponed until the complete structural analysis, now in progress, is accomplished.

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