BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1360—1363 (1969)

Synthesis and Physical Properties of Long Chain Compounds. X. Studies on the X-Ray Diffraction Patterns of Normal Higher Primary Amines

Akira WATANABE,* Akio ISHIZAWA,** Masao KOSAKA* and Ryōzō GOTŌ**

* *Department of Chemistry, Faculty of Science and Engineering, Ritumeikan University, Kita-ku, Kyoto*

** *Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto*

(Received August 6, 1968)

For the members of *n*-higher primary amines from C_{12} to C_{20} the crystal structure was studied by X-ray powder method. From the values of long spacings and the splitting of (110) reflections it was concluded that the structure is probably similar to that of fatty acids and that the hydrocarbon chains are tilted with respect to the plane formed by end groups. This structure seems to be stable over the temperature range between room temperature and melting points. The dependence of melting points on chain length was discussed.

X-Ray diffraction patterns of long chain compounds were first studied in detail by Müller[1] whose investigation dealt with normal paraffins with the carbon numbers from C_{18} to C_{44}. Malkin,[2] Francis,[3] and other workers also reported X-ray long spacings for the series of several long chain compounds such as alcohols, fatty acids, esters and iodides. In a previous work in this laboratory normal higher primary alcohols were studied in some detail.[4]

No X-ray study for normal higher primary amines can be found in the literature. Moreover a property of the amines in solid state has not been reported except the work of Smyth[5] who studied dielectric behavior of the amines of even carbon numbers from C_{12} to C_{18}. The present investigation was undertaken in order to study the dependence of solid structure of the amines on carbon numbers and on temperatures by X-ray powder method and to compare the results with those of higher alcohols and other compounds. The amines investigated are odd and even compounds with the carbon numbers from C_{12} to C_{20}.

Experimental

Preparation of the Amines and Their Purity.

The preparation has been reported in a preceding paper,[6] then the procedures will be described briefly. Since an extremely small amount of impurity affects the properties of long chain compounds, great care was taken throughout the preparations. Starting materials were commercial fatty acids and alcohol *e.g.*, lauric, myristic, palmitic, stearic acids and octadecyl alcohol. The acids, which had been converted to methyl esters, and the alcohol were purified by fractional distillation followed by several recrystallizations. The amines of C_{12}, C_{14}, C_{16}, C_{19} and C_{20} were synthesized by lithium aluminum hydride reduction of the corresponding acid amides in tetrahydrofuran. Most of the odd carbon numbered amines were prepared by Schmidt reaction or by Hofmann reaction from the next higher fatty acids. Melting points of the amines are given in Table 1 and Fig. 1. Data of the elemental analysis of *N*-acetylamines are recorded in Table 2. Since the melting point measurement or elementary analysis is not a reliable method to check the impurity in such long chain compounds, the efforts were exerted to find the method to establish the purity of the amines synthesized

TABLE 1. MELTING POINTS OF AMINES

Numbers of carbon atoms	Mp(°C)
12	29.0
13	28.1
14	39.9
15	39.5
16	47.1
17	47.5
18	52.0
19	53.0
20	58.0

1) A. Müller, *Proc. Roy. Soc.*, **A120**, 437 (1928); *ibid.*, **127**, 417 (1930).

2) T. Malkin, *J. Chem. Soc.*, **1931**, 2796; *ibid.*, **1930**, 3739.

3) F. Francis, S. H. Piper and T. Malkin, *Proc. Roy. Soc.*, **A128**, 214 (1930); F. Francis, F. J. E. Collins and S. H. Piper, *ibid.*, **A158**, 691 (1937).

4) A. Watanabe, This Bulletin, **34**, 1729 (1961); *ibid.*, **36**, 336 (1963).

5) J. D. Hoffman and C. P. Smyth, *J. Am. Chem. Soc.*, **71**, 3591 (1949).

6) R. Goto, A. Watanabe, K. Honjo and M. Kosaka, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 1220 (1966).

Table 2. Elemental analysis of *N*-acetylamines

$C_nH_{2n+1}NHCOCH_3$		Calcd %			Found %		
n	Formula	C	H	N	C	H	N
12	$C_{14}H_{29}ON$	73.95	12.87	6.16	73.99	13.10	6.21
13	$C_{15}H_{31}ON$	74.63	12.86	5.80	74.44	12.87	5.81
14	$C_{16}H_{33}ON$	75.32	13.02	5.48	74.97	13.00	5.50
15	$C_{17}H_{35}ON$	75.77	13.09	5.20	75.81	13.35	4.98
16	$C_{18}H_{37}ON$	76.26	13.15	4.94	76.29	13.41	4.94
17	$C_{19}H_{39}ON$	76.70	13.21	4.71	76.66	13.18	4.50
18	$C_{20}H_{41}ON$	77.10	13.27	4.50	77.23	13.50	4.24
19	$C_{21}H_{43}ON$	77.48	13.32	4.30	77.54	13.54	4.39
20	$C_{22}H_{45}ON$	77.81	13.36	4.12	78.06	13.53	4.36

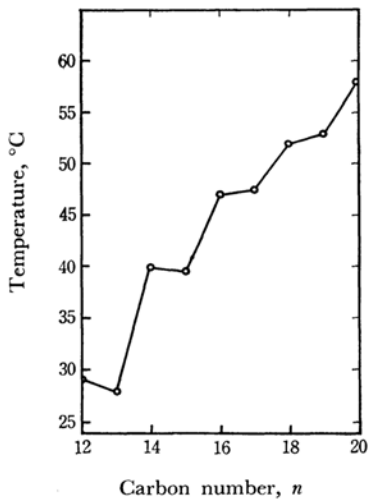

Fig. 1. Melting points of *n*-higher primary amines.

and to obtain the compounds having a suitable purity for X-ray studies.

After preliminary experiments of gas chromatographic analysis it was found that this method is quite reliable for methyl esters, alcohols as well as acetylamines to check the impurities, especially homologous compounds which have been known to cause an important effect on the properties of solid long chain compounds. Methyl esters of starting fatty acids, alcohols and intermediate methyl esters, that is, the esters of C_{19}, C_{20} acids were effectively analyzed by gas chromatography. For example, by the gas chromatography with a flame ionization detector in the best condition, 0.1 to 0.5% of C_{16} compounds in C_{18} compounds could be detected.

The hydrochlorides of the amines were purified by recrystallizing them four to six times from ether-ethanol mixture. Resulting compounds, after being acetylated with acetic acid anhydride, were referred to gas chromatography. Recrystallizations of the hydrochlorides were repeated until a purity of 99% or better was achieved. Selections of the typical chromatograms are shown in Fig. 2 and Fig. 3. Before the X-ray measurements further purifications were carried out for each material as follows. The compound free from hydrogen chloride was heated in a stream of nitrogen at the temperature slightly above its melting point in order to eliminate any carbon dioxide which had been held in the compound. After about two hours heating the compound was distilled from the vacuum system into a tube. After being filled with nitrogen gas the tube was sealed off.

Measurements of X-Ray Patterns. The X-ray photographs were all taken using Cu*K* radiation which was produced at 40 kV and 30 mA. Camera distance was 10 cm. Exposure times were 1.5 to 2.5 hr depending on the chain length of the compounds.

The samples were melted on an electric heater placed in a glove box filled with nitrogen gas, and then drawn into thin walled glass tubes of about 0.5 mm diameter.

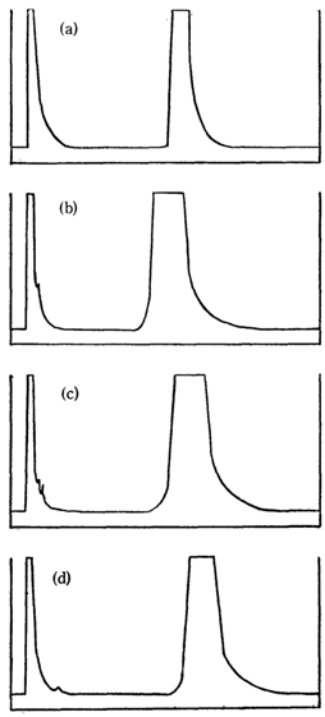

Fig. 2. Gaschromatograms of *N*-acetylamines of C_{17} (a), C_{18} (b), C_{19} (c), and C_{20} (d).
Column: 6 mm × 1 m, 5% Apiezon grease L on 80—100 mesh Celite 545; temp.: 225—245°C; nitrogen flow: 48 ml/min; fuel gas: hydrogen 50—55 ml/min.

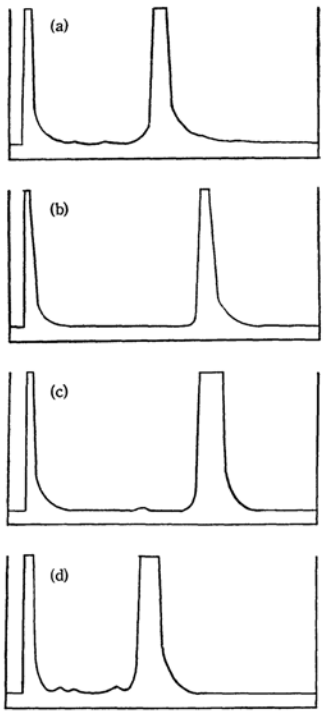

Fig. 3. Gaschromatograms of methyl esters of fatty acids of C_{18} (a), C_{19} (b), C_{20} (c), and octadecanol (d).
Column: 6 mm×2 m, 5% PEG 20 M on 60—80 mesh Celite 545 for the esters; 5% Apiezon grease L on 80—100 mesh Celite 545 for the alcohols; temp.: 155—225°C; nitrogen flow: 47 ml/min; fuel gas: hydrogen 44 ml/min.

The tubes were sealed off at their both ends. During the exposure the tubes were rotated. A brass furnace in which the tube was inserted was used for the measurements at high temperatures.

Results and Discussion

X-Ray diffraction patterns for the series of amines are presented in Fig. 4. The patterns appear to be similar throughout the series. No differences in crystal forms seem to exist between odd and even compounds nor from lower through higher members. The patterns were measured on long spacing reflections and it was found that the values of the spacings are a linerar function of carbon numbers for the series of either odd or even compounds. The data are summarized in Table 3 and illustrated in Fig. 5 together with those of normal higher alcohols quoted from previous papers.[4] The magnitude of the long spacings suggests that the molecules of the amines may be arranged in double molecules in the direction of the long axes, possibly due to the formation of hydrogen-bonding between the nitrogen atoms.

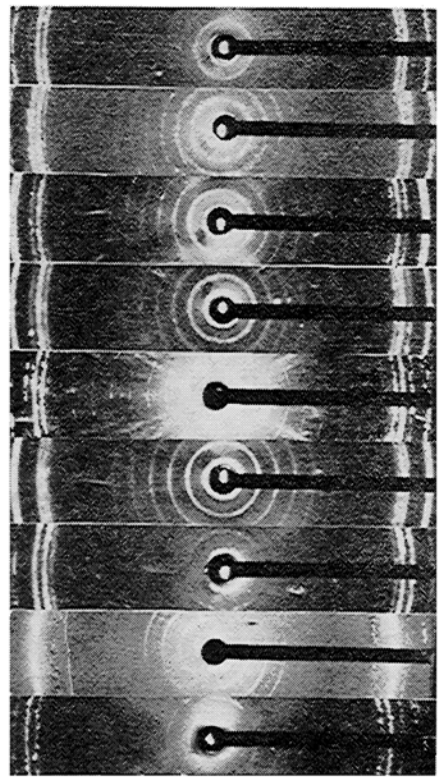

Fig. 4. X-Ray diffraction patterns of amines.
The patterns in discending order are from C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20} amines.

By inspection of the values indicated in Table 3 it can be found that the long spacings of the amines are shorter by about 3 Å than those of the corresponding alcohols of vertical form. In view of the results of the analysis of other long chain compounds it is quite probable that the molecules of the amines extend themselves in straight zig-zag chains in the crystals, hence the shorter long spacings observed in the amines suggest that here the hydro-

TABLE 3. LONG SPACINGS OF AMINES AND ALCOHOLS

Amine		Alcohol	
Carbon number	Long spacing	Carbon number	Long spacing
12	31.01 Å	12	34.9 Å ⊥
13	34.66	13	37.3 ⊥
14	35.85	14	39.6 ⊥
15	39.42	15	42.36 ⊥
16	40.51	16	44.90 ⊥ 37.27 ∠
17	43.87	17	47.46 ⊥
18	45.13	18	41.60 ∠
19	48.40	19	52.82 ⊥
20	49.68	20	45.67 ∠

⊥ : vertical form
∠ : tilted form

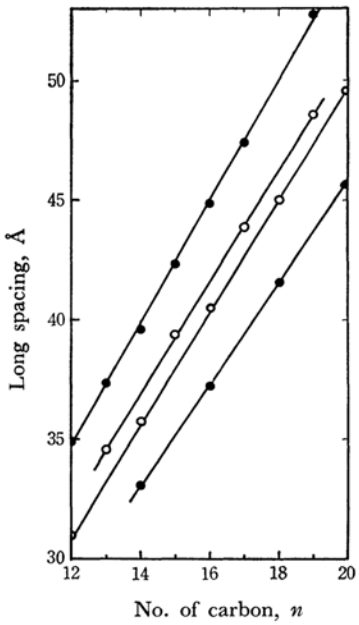

Fig. 5. Long spacings of *n*-higher primary amines and alcohols.
○ amines ● alcohols

carbon chains are inclined to the plane formed by the end groups. Additional evidence of the inclination can be obtained by the inspection of short spacing reflections. As may be seen in Fig. 4, the patterns indicate the splitting of (110) reflections in all the compounds, which is analogous to the case of tilted chain structures of higher alcohols and related compounds. If then, from the fact that the increase of the long spacings by the addition of two carbon atoms is about 4.6 Å, an approximate value of the tilt angle of the amine molecules can be estimated as 60° for both series of odd and even compounds.

Though the results obtained by powder patterns are limited to the general features of the molecular packing, some information on the conformation of the amines may be obtained by considering the intensity of the reflections with long spacings together with that of other compounds which have been analyzed previously. In the vertical form of normal higher alcohol *e. g.*, heptadecyl alcohol, the skew conformation of C–C–C–O bond has been confirmed by Seto.[7] Also it has been shown that, as a result of the existence of the skew conformations, the odd ordered long spacing reflections appear with stronger intensity as compared with those of even order. In the patterns of the amines the intensities of long spacing reflections decay gradually as the order of reflections increase. This behavior is different from that of alcohols mentioned above, and is similar to that of odd carbon numbered paraffin as heneicosane or tricosane which has been confirmed to have a straight zig-zag chain. From the intensity consideration mentioned above it seems probable that the amine molecules in the crystals consist only of transoid conformation of the C–C–C–N bonds.

Transitions in the solid state, which appear at temperatures not far from the melting or freezing points, have been found in paraffins, alcohols, bromides, and fatty acids. Therefore X-ray studies were made at various temperatures, in the hope of finding the same phenomena for the series of amines. However, no abrupt change of spacings was detected in any of the compounds studied. Accordingly, for the amine molecules tilted chain structure seems to be stable over the temperature range between room temperature and melting points.

A well known phenomenon of alternation of melting points could be observed in the series of amines investigated. As may be seen in Fig. 1, melting points of even carbon numbered amines lie on an upper curve similar to the behavior of other long chain compounds. Malkin,[8] in an earlier investigation, postulated a concept that the arrangement of tilted chain molecules makes methyl group packing less tight in odd carbon numbered compounds than in even numbered compounds. Later his concept was verified for the two forms of fatty acids by Sydow[9] with the interpretation based on the structure analysis. As mentioned above, the structure of the amine molecules, existing at the temperature just below their melting points, is the tilted one in both odd and even compounds. From the values given in Table 3 it can be found that the difference in the values of long spacings between odd and even compounds is about 1 Å. This difference will be interpreted reasonably as a result of different orientation of methyl groups, if for the odd numbered amines the C–C bond at the methyl terminal is perpendicular to the plane of methyl groups and if for the even numbered amines the bond in question is inclined at an angle. Thus the general arrangement of the molecules of the normal higher amines may be assumed to be similar to that of fatty acids, and the alternation of the melting points may be accounted for by Malkin's concept.

7) T. Seto, *Memoirs Coll. Sci. Univ. Kyoto*, **A 30**, 89 (1962).

8) T. Malkin, *Nature*, **127**, 126 (1931).

9) E. Sydow, *Arkiv Kemi*, **9**, 231 (1956).