NOTES

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Long Spacings of ω-Cyclohexyl Alkanoic Acids

Akio Ishizawa

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

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In almost all the long chain compounds studied the chain ends are either both methyl or one of the ends is substituted with a group different in nature but similar in size with the chain constituent.[1] Studies of the long chain compounds substituted with a bulky group at the chain end in comparison with the results from such compounds as long chain *n*-paraffins or *n*-alkanoic acids will clarify the influence of the end groups on the properties of these long chain crystals. Reported here are some results from the examination of solid ω-cyclohexyl alkanoic acids $\langle\mathrm{H}\rangle$-(CH$_2$)$_n$COOH (n=13 to 33)[2] by X-ray powder method.

The specimens crystallized from solution (acetic acid) and those from melt gave essentially the same diffraction patterns except that in some of those obtained from solution two or more crystalline forms were observed concomitantly. The odd (n=even) and even (n=odd) members of the acids crystallized from melt, like many long chain compounds studied, differed not only in the general appearance of the diffraction patterns but also in the relation between the long spacing and the chain length.[3] Examination of the specimens crystallized from melt at temperatures just below their melting points gave the long spacings identical with those obtained at room temperature within experimental error.[4] In the thermal analysis of the specimens, the time-temperature curves increased monotonously with temperature until the temperature reached about 1 °C below their melting points, where the slope of the curves became gradual. Thus, the crystalline forms obtained from melt seems stable in the range from room temperature to near their melting points.

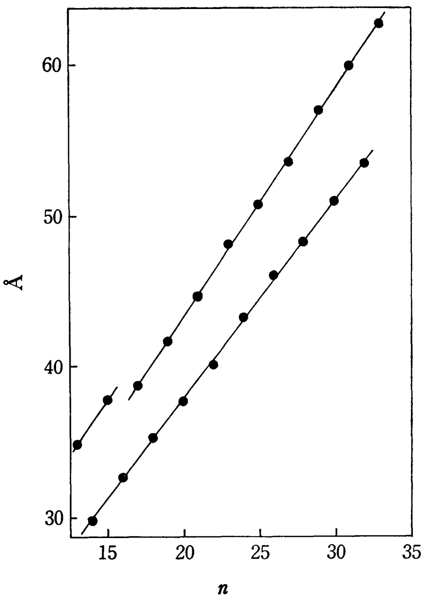

Fig. 1. Dependence of the long spacings on the chain length in $\langle\mathrm{H}\rangle$-(CH$_2$)$_n$COOH.

The effect of a bulky end group is evidently demonstrated in the long spacings. The values obtained are considerably smaller than the calculated length of the hydrogen-bonded dimeric molecule in which the chain is stretched in a straight zig-zag form. The tilt angle which refers to the angle between the chain axis and the basal plane is estimated to be about 30°

Table 1. The long spacings of cyclohexyl alkanoic acids

$\langle\mathrm{H}\rangle$-(CH$_2$)$_n$COOH

n	(Å)	*n*	(Å)
13	34.79	14	29.74
15	37.75	16	32.53
17	38.56	18	35.17
19	41.72	20	37.46
21	44.61	22	40.01
23	48.03	24	43.16
25	50.72	26	46.00
27	53.50	28	48.21
29	56.85	30	50.92
31	59.85	32	53.31
33	62.67		

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[1] A. Müller, *Proc. Roy. Soc.*, **A 114**, 542 (1927); **A 120**, 437 (1928); **A 127**, 417 (1930); A. A. Schaerer, C. J. Busso, A. E. Smith, and L. B. Skinner, *J. Amer. Chem. Soc.*, **77**, 2017 (1955); F. Francis, F. J. E. Collins, and S. H. Piper, *Proc. Roy. Soc.*, **A 158**, 691 (1937); E. von Sydow, *Ark. Kemi*, **9**, 231 (1957); T. Malkin, *J. Amer. Chem. Soc.*, **52**, 3739 (1930); A. Watanabe, This Bulletin **34**, 1728 (1961); **36**, 336 (1963); A. Watanabe, A. Ishizawa, M. Kosaka, and R. Goto, *ibid.*, **42**, 1360 (1969).

[2] R. Goto, A. Ishizawa, and M. Yamamura, *Nippon Kagaku Zasshi*, **88**, 678 (1967); A. Ishizawa, M. Yamamura, M. Ichii, Y. Sakashita, and R. Goto, *ibid.*, **89**, 516 (1968); A. Ishizawa, M. Yamamura, and R. Goto, *ibid.*, **89**, 815 (1968).

[3] The samples were examined using Ni filtered Cu*K*α radiation (45 kV, 40—50 mA, camera distance=100 mm or 110 mm).

[4] All the measurements at high temperatures were carried out within 1°C below the melting points.

from the increment of the value of the long spacing with the two additional chain units divided by twice the theoretical increase in the chain length, 2 × 2.515 Å. Almost all the long chain compounds studied are known to pack themselves in crystals with the chain axis inclined about 60° at most to the basal plane.1) The marked inclination of the hydrocarbon chain of these acids seems to show the intrinsic importance of the packing of the large end groups on the arrangement of the chain molecules in crystals.