BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 846—847 (1971)

Long Spacings of ω-Cyclohexyl Alkanols

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(Received June 15, 1970)

It has been found that substitution of a bulky cyclohexyl group at the end of long chain alkanoic acids caused a marked change in the arrangement of the hydrocarbon chain in crystals.[1] Reported here is another similar observation on the effect of a bulky group which is introduced at the end of normal alkanols.

ω-Cyclohexyl alkanols $\langle\overline{\text{H}}\rangle$-$(CH_2)_n$OH($n$=14 to 34) were synthesized by the reduction of ethyl (or methyl) ω-cyclohexyl alkanoates with excess lithium aluminum hydride in refluxing ether. After treatment with boiling ethanolic potassium hydroxide solution, the resulting mixture was evaporated to dryness under reduced pressure, extracted with anhydrous benzene, and the products were repeatedly recrystallized from benzene or toluene solution.

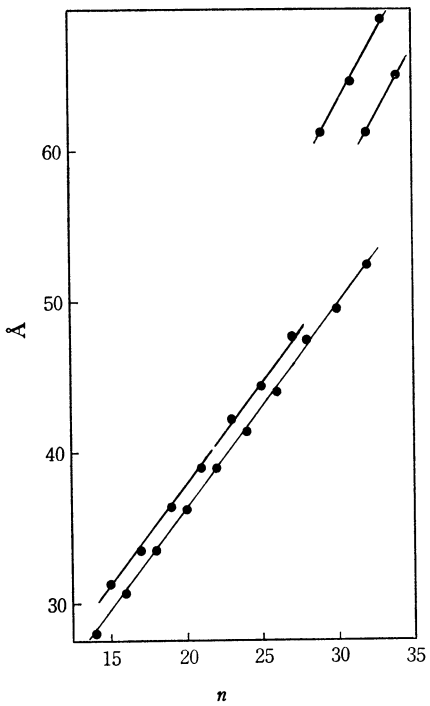

Fig. 1. Dependence of the long spacings on the chain length in $\langle\overline{\text{H}}\rangle$-$(CH_2)_n$OH.

1) A. Ishizawa, This Bulletin, **44**, 845 (1971).

As in the case of ω-cyclohexyl alkanoic acids[1] and many other long chain crystals,[2] the odd (n=odd) and even (n=even) alkanols crystallized from melt differed not only in the general appearance of the powder patterns but also in the variation of the long spacings with the chain length. As is evident from the values of long spacings, the crystalline forms of the alkanols changed at n=29 in the odd series and at n=

Table 1. Long spacings, melting points and elemental analyses of cyclohexyl alkanols

$\langle\overline{\text{H}}\rangle$-$(CH_2)_n$OH

n	Long spacing (Å)	mp (°C)	Elemental analysis (%) Calcd C	Calcd H	Found C	Found H
14	27.99	53.4—53.7	81.00	13.60	81.17	13.79
15	31.24	46.4—46.6	81.21	13.63	81.13	13.61
16	30.65	61.1—61.3	81.41	13.66	81.25	13.75
17	33.71	54.9—55.3	81.58	13.69	81.73	13.89
18	33.47	67.1—67.3	81.74	13.72	81.75	13.57
19	36.28	62.1—62.2	81.89	13.75	81.78	14.01
20	36.20	71.8—72.1	82.03	13.77	82.02	13.79
21	38.90	68.0—68.4	82.16	13.79	82.02	13.67
22	38.96	76.7—77.1	82.27	13.81	82.39	13.68
23	42.19	72.7—73.0	82.39	13.83	82.44	14.06
24	41.36	79.6—80.0	82.49	13.85	82.43	13.64
25	44.28	77.1—77.5	82.59	13.86	82.35	14.08
26	43.90	82.8—83.2	82.68	13.88	82.53	13.86
27	47.65	80.4—80.7	82.77	13.89	82.71	13.95
28	47.38	85.4—85.6	82.85	13.91	83.02	14.16
29	61.13	83.6—83.8	82.92	13.92	82.97	14.07
30	49.64	88.3—88.7	83.00	13.93	83.00	13.67
31	64.46	86.5—86.9	83.07	13.94	83.04	14.08
32	52.30 61.17	90.4—90.5	83.13	13.95	83.17	13.98
33	68.65	89.6—89.9	83.19	13.96	83.40	13.71
34	64.85	92.5—92.9	83.25	13.97	83.51	13.91

2) A. Müller, *Proc. Roy. Soc.*, **A 120**, 437 (1928); **A 127**, 417 (1930); F. Francis, F. J. E. Collins, and S. H. Piper, *ibid.*, **A 158**, 691 (1937); E. von Sydow, *Ark. Kemi*, **9**, 231 (1957); A. Watanabe, This Bulletin, **34**, 1728 (1961), **36**, 336 (1963).

32 in the even. Formation of a crystalline form with $n=32$ was found to be sensitive to the method of preparation. Rapid cooling, in general, gave the form with larger long spacing. In the other members no such behavior was observed. When the specimens were examined at temperatures immediately below their melting points,[3] those with $n\leqq 28$ gave essentially the same diffraction patterns and long spacings as were obtained at room temperature, but with the higher members ($n\geqq 29$), though the reflections at higher angles were similar to those obtained at lower temperatures, the intensity of the reflections corresponding to the long spacings became too weak to be measured. In thermal analysis, the time-temperature curves of these specimens increased linearly 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 of the alkanols seemed stable in the range from room temperature to just below their melting points.

The effect of a bulky cyclohexyl end group on the chain arrangement was clearly seen in the values of the long spacings of the alkanols. The long spacings are considerably shorter than the theoretical length of the hydrogen-bonded dimeric molecule in which the chain is stretched in a zig-zag form and the tilt angle of the chain axis to the basal plane is estimated to be about 30°. The effect is similar to that observed in ω-cyclohexyl alkanoic acids and the packing of the bulky end group seems to be responsible for the change in the arrangement of the hydrocarbon chains in crystals.

3) All the measurements at high temperature were carried out within 1°C below the melting points.