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Long Spacings of α,ω-Dicyclohexyl Alkanes and α, ω-Diphenyl Alkanes

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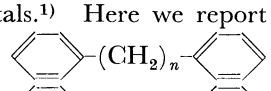
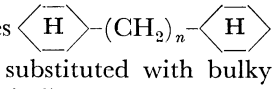
A bulky cyclohexyl group substituted at the chain terminal of *n*-alkanols or *n*-alkanoic acids has been found to cause a marked change in the arrangement of the hydrocarbon chains in crystals.[1] Here we report studies on α,ω-diphenyl alkanes  (I_n) and α,ω-dicyclohexyl alkanes  (II_n) (n=15 to 24) which are substituted with bulky groups at either ends of the chain.[2]

Like many other long chain compounds.[3] the odd (n=odd) and even (n=even) series of both I_n and II_n, crystallized from melt, gave different diffraction patterns. The long spacings also varied in different ways with chain length in the odd and even members.

At temperatures just below melting points the I_n specimens crystallized from melt gave essentially the same diffraction patterns and long spacings as those at room temperature, so that the crystalline forms seemed stable in the temperature range studied.

In II_{even} members a change in the crystalline form took place at II_{20} where the change displayed itself in the diffraction patterns as well as in the value of the long spacing. The II_{20} specimen, obtained by a similar method of preparation as for the lower members, gave two sets of long spacings. The feature of the diffraction patterns of this specimen showed no change up to a few degrees below its melting point, but at just below melting point, the crystalline form with the larger long spacing disappeared. On the other hand, the specimen obtained from melt by very rapid cooling consisted essentially of the form with the larger long spacing, the same as that was obtained for II_{22} and for II_{24}. No such behavior like that of II_{20} was ob-

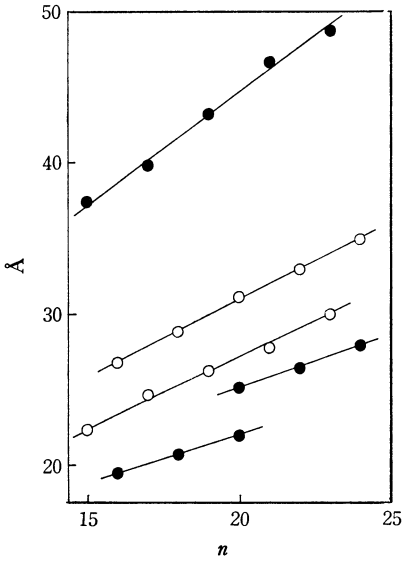
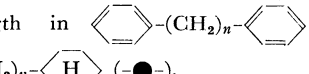
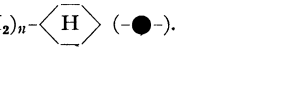


Fig. 1. Dependence of the long spacings on the chain length in  (-○-) and  (-●-).

1) A. Ishizawa, This Bulletin, **44**, 846 (1971).

2) A. Ishizawa, M. Yamamura, and R. Goto, *Nippon Kagaku Zasshi*, **90**, 806 (1969).

3) 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).

Table 1. The long spacings of I_n and II_n (Å)

n	I_n		II_n	
	at room temp.	at mp	at room temp.	at mp
15	22.29	22.28	37.46	37.58
16	26.72	26.86	19.46	19.34
17	24.55	24.33	39.78	40.61
18	28.75	28.71	20.62	20.89
19	26.12	25.86	43.23	43.62
20	31.03	30.87	21.89	21.95
			25.00	
21	27.37	27.54	46.52	46.45
22	32.84	33.21	26.35	26.36
23	29.92	29.67	48.72	49.57
24	34.91	34.85	27.76	27.90

served for any other II members and the crystalline forms once formed seemed stable even at temperature just below melting point.

As is evident from the long spacings of I_n and II_n, the values obtained are considerably shorter than the calculated length of the molecules in which the hydrocarbon chains are stretched in a straight zig-zag form. In crystals, II_n compounds may be considered an analogue to ω-cyclohexyl alkanoic acids and ω-cyclohexyl alkanols which exist in dimeric form by hydrogen bonding between the polar groups. The tilt angle of the hydrocarbon chain in II crystals is found unaffected by the absence of any polar groups and is calculated to be about 30° which is similar to the value obtained for ω-cyclohexyl alaknoic acids and ω-cyclohexyl alkanols.[1] The decrease of the tilt angle of I_n is less marked than that of II_n but is somewhat smaller than those which are not substituted with bulky groups.[3] These observations appear to indicate the importance of the shape and the packing of the end groups on the arrangement of the chain molecules in crystals.