Average Increase in Chain Length of Crystalline Long Chain Compounds per Carbon Atom

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ABSTRACT

A comprehensive survey has been made of published crystal X-ray diffraction data in order to select an authentic overall value for d_{90}, the average increase in chain length of crystalline long chain compounds per carbon atom, for general use in calculating angle of tilt. Data were available for 10 isomorphous homologous series including the normal hydrocarbons, alkanoic acids, primary alcohols, ketones, dicarboxylic acids, symmetrical saturated triglycerides, potassium acid salts, quarter-hydrates of Na-1-alkanesulfonates, hydrazides and the dihydrazides of dicarboxylic acids. The results, supported by data for other specific long chain derivatives show that (a) 1.27 Å is the best value for this constant, and (b) there is no justification for the value 1.30 Å, which has been used in the recent literature as the accepted value in estimating the angle of tilt. The information developed can be used to predict the effective length of one molecule in the crystal of any specific long chain member of any of the homologous series studied.

INTRODUCTION

The distance d_{90} represents the average increase in chain length of crystalline long chain compounds per carbon atom measured along the axis of the zigzag hydrocarbon chain. This is an important constant for use in elucidating the orientation of the molecules in crystals of long chain compounds from long spacing data. It is equal to half the linear distance between alternate carbon atoms in the chain.

The long spacing, L, determined by X-ray diffraction measurements of the crystals, is the distance between the "reflecting planes" passing through the opposite ends of the repeating units in the crystal lattice, i.e., the distance between the 001 planes through the ends of the crystal unit cells.

The long spacings for the crystals of an isomorphous series of homologous compounds show a linear relationship to the number of carbon atoms, n, in the molecule. This can be represented by equation 1, where m represents the number of molecules lined up

$$L = (md) n + k \qquad [1]$$

end to end, contributing to the length of the repeating unit; d equals the increase in the long spacing per carbon atom per molecule measured along a line perpendicular to the 001 planes of the crystal lattice; and k is a constant.

The angle of tilt, θ, of the hydrocarbon chains in the crystal lattice, i.e., the angle they make with respect to the 001 planes of the crystal, can be calculated from the expression

$$\sin \theta = d/d_{90} \qquad [2]$$

No definite agreement has yet been reached on the selection of a value for d_{90}. The two most commonly accepted values used at different times by different investigators are ca. 1.27 (1) and 1.30 Å (2-5). The preferred value was 1.27 Å (6) until the early 1950's when Vand et al. (7) and Morley and Vand (8) reported 1.299

and 1.305 Å for potassium caprate and strontium laurate, respectively, based on single-crystal measurements. As a result, 1.30 Å has been accepted and used by recent investigators for calculating the angle of tilt from long-spacing data (3,9-13). The purpose of the present investigation was to select an authentic value for d_{90} on the basis of a systematic survey of the pertinent literature data.

SURVEY OF PERTINENT LITERATURE DATA

The value of d_{90} was calculated from the published X-ray diffraction data for a number of homologous series of isomorphous crystals. When the hydrocarbon chains and the long axis, c, of the unit cell are both normal to the 001 planes, the long spacing, L, is equal to c. Thus the slopes of the L vs. n plot and the c vs. n plot are both equal to md_{90}. This is generally true also for homologous series showing no alternation of melting point (14). The value of md_{90} can also be obtained from the c vs. n plot for monoclinic crystals. The only requirement is that the long chains be parallel or almost parallel to the c axis, as is known to be the case for the following monoclinic crystals: the C form of the n-alkanoic acids (26); the β form of the dicarboxylic acids (42), and the quarter-hydrates of the sodium-1-alkanesulfonates (53). If the chains are not exactly parallel to the c axis (or normal to the 001 planes), the resulting error in the value of d_{90} obtained from the linear equation for the c vs. n plot will be negligible for small angular differences. For a deviation of 5°, for example, the error in d_{90} will be only 0.4% or 0.005 Å.

The method of least squares was used to determine the equation of the best straight line through the L vs. n or the c vs. n data. The calculations were made by a digital computer which gave the values for md and k of equation 1, i.e., md_{90} and k_{90}, as well as the standard error of estimate. The latter, with the average and maximum deviations of the individual values of L or c from the linear equation, gave an indication of the self-consistency of the data and the reliability of the calculated constants. In some instances, more reliable results were obtained by omitting one or more obviously inconsistent points and recalculating. Consideration of the composite data of two or more authors usually resulted in much larger deviations of the calculated from the experimental values.

Table I summarizes the results. Unless otherwise specified, they are based on long spacing data including both the odd and even carbon members of the series.

The results for the n-hydrocarbons (item 1) are based on both L and c values reported in 12 publications for 39 samples. They represent 22 different odd and even carbon hydrocarbons containing from 11 to 60 carbon atoms. Only three values had to be rejected because of obvious inconsistency. The value of d_{90}, 1.268 Å, is in excellent agreement with that reported by Broadhurst (57), 1.270 Å, on the basis of a less extensive survey. It is almost identical with that obtained from the data of Müller (15) (item 2).

Attention is called to the erroneous report (58), apparently based on a misinterpretation of reports of Piper et al. (59), and perpetuated by later reviews (60-61), that the A and A' forms of the long chain saturated fatty acids possess vertical chains. Actually none of the polymorphic forms of these acids has vertical chains. Therefore L vs. n data cannot be used for the direct determination of d_{90}. However, as mentioned above, the value of d_{90} can be

TABLE I

Mean Square Calculations for d_{90}

Item no.	Homologous series	References	No. of values[a]	Range,[b] n	md_{90}, Å	k_{90}, Å	d_{90}, Å	SE of estimate, Å	Deviation[c] Ave., Å	Deviation[c] Max., Å	Crystals[d]	Ave. d_{90} Å
1	Hydrocarbons (α)	(6,15-25)	39[e]	11-60	1.268	2.02	1.268	0.11	0.08	0.24	N(25)	1.268
2		(15)	11	11-30	1.267	2.09	1.267	0.18	0.11	0.40	M(26)	
3	Alkanoic acids (C form)	(26)	5[f]	12-26g	2.538	5.12	1.269	0.08	0.05	0.09		1.271
4		(26-31)	10[f]	12-26g	2.543	5.06	1.272	0.08	0.08	0.13	N(39)	
5	Primary alcohols	(32)	4	29-50	2.530	4.49	1.265	0.07	0.04	0.06		
6		(33-37)	21	11-18	2.530	4.37	1.265	0.12	0.09	0.19		
7		(32-37)	25	11-50	2.535	4.29	1.268	0.11	0.08	0.19	N(40)	1.270
8	Ketones	(6)	6[f]	18-35	1.273	1.76	1.273	0.06	0.04	0.06		
9		(40)	11[h,i]	13-23	2.542	3.66	1.271	0.06	0.04	0.13		
10		(6,40)	17[h,e]	13-35	1.268	1.88	1.268	0.05	0.04	0.08	M(42)	1.271
11	Dicarboxylic acids (β)	(41)	7[f]	6-18k	1.268	2.33	1.268	0.13	0.10	0.17		
12		(43)	8[f,j]	6-13k	1.263	2.40	1.263	0.07	0.05	0.08		
13		(41-45)	20[f]	5-18k	1.265	2.37	1.265	0.09	0.07	0.18		1.265
14	Sym-saturated triglycerides (α)	(46-50)	12	11-18m	2.541	4.96	1.270	0.16	0.12	0.35	N(48)	1.270
15	Potassium acid salts	(51,52,65)	16[e]	10-24l	2.542	4.83	1.271	0.12	0.08	0.19	N(52)	1.271
16	Na-1-alkanesulfonates to 25% H_2O	(53)	6[f]	8-18g	5.106	14.58	1.276	0.04	0.03	0.06	M(53)	1.276
17	Hydrazides	(54-55)	5[f]	6-12	5.096	12.86	1.274	0.10	0.06	0.16	N(55)	1.274
18	Dihydrazides of dicarboxylic acids	(56)	6[f]	6-12	1.273	2.04	1.273	0.02	0.02	0.02	N(56)	1.273

Final Ave. 1.271

a L values.
b Total number of carbons, both odd and even.
c Deviation of individual values from linear equation.
d N,c axis and chains normal to 001 planes; M, monoclinic; chains parallel to c axis.
e L and c values.
f c values.
g Even carbon members.
h Used 0.5L values for methyl ketones (see text).
i Methyl ketones only.
j Disregarding extrapolated values.
k Used 0.5 c for odd carbon members (see text).
l Total carbons, odd and even, in acid residue.
m Total carbons, odd and even, in each acid residue.

estimated from the linear relationship between c and n. The data of Abrahamson and von Sydow (26) for even carbon members show almost perfect linearity, covering a range from C_{12} to C_{26}, and give a value of 1.269 Å for d_{90} (item 3). Good agreement is also obtained from a composite of these data with the individual values of five other authors (item 4).

The d_{90} values for primary alcohols are based on data for the polymorphic form possessing vertical chains, variously designated as the α, β and sub-α forms by different authors (35,36,38). The data of Ställberg et al. (32) for the C_{29}-C_{50} range (4 values) give a d_{90} value of 1.265 Å (item 5), the same as that of item 6 for the C_{11}-C_{18} range (21 values) reported by five different authors (33-37). The excellent mutual consistency of the data for these two ranges is indicated by the almost identical d_{90} value, 1.268 Å, calculated from a composite of all 25 values (item 7). To adjust all the C_{11}-C_{18} data to the same scale, 0.10 Å was subtracted from the values for the four (solvent crystallized) samples of Malkin (34) and 0.20 Å added to the six values of Wilson and Ott (35).

The ketones of items 8 and 10 include symmetrical, unsymmetrical and methyl ketones. The methyl ketones (item 9) differ from the rest by having a repeating unit involving the length of two molecules instead of one. Therefore, when methyl ketones were considered with the others, $L/2$ values were used in conjunction with the L values for the other members of the series in calculating d_{90}. The data of MacArthur (6) and Stenhagen (40), separately and as a composite, show very low average and maximum deviations from a straight line (item 10).

Good agreement was found in the d_{90} values for dicarboxylic acids derived from the data of Caspari (41) (item 11) and Housty (43) (item 12), separately and as a composite with the data of two other authors (item 13). In order to adjust for the fact that the repeating unit of the odd carbon members involves the length of two molecules instead of one, $c/2$ values were used in conjunction with the c values of the even carbon members in calculating the d_{90} values.

The published long spacing data for the α crystalline forms of the symmetrical saturated triglycerides (item 14) are not entirely consistent. The values for the C_{14} triglyceride (46,47) seem to be at least 0.7 Å too high compared to the other data and were therefore not used in our calculations. The fact that m equals 2 is in harmony with the proposed (62-64) shape and arrangement of simple triglyceride molecules in the crystal.

The potassium acid salts (item 15) are actually 1:1 molecular compounds of the free acid and the neutral salt. Therefore, as would be expected, m, the number of long chain residues contributing to the length of the repeating unit, equals 2.

Crystals of the quarter-hydrate of the Na-1-alkanesulfonates (item 16) show a repeating unit involving the length of four alkane-sulfonate residues. This is not surprising since n was taken as the number of carbons in the alkanesulfonate residue and since these compounds are really molecular compounds of the formula $4RSO_3Na \cdot H_2O$.

The fact that m equals 4 for the hydrazide series (item 17) is difficult to explain. It indicates that the repeating unit involves the length of four carboxylic acid residues instead of two.

The results for the various homologous series listed in Table I give an overall average of 1.271 Å for the value of d_{90}. They indicate that the early data on ketones, alcohols and hydrocarbons, on which Malkin (2,3) based his value of ca. 1.30 Å, lacked sufficient precision. This is apparently true also of the data which gave a value of 1.32 Å for ethyl esters (2). Aleby (66) has recently calculated the average dimensions of the subcell of ethyl stearate from single-crystal measurements and reports the distance between

alternate carbons to be 2.51 Å, i.e., $d_{90} = 1.255$ Å.

Further evidence supporting the 1.27 Å rather than the 1.30 Å value is supplied by values reported for the n-paraffin portion of molecules, based on the structural analysis of other specific long chain derivatives, e.g., dihexadecyl ether, 1.27 Å (67); methyl stearate, 1.265 Å (68); palmityl palmitate, 1.27 Å (67); lauric acid, 1.261 Å (27); dihydromalvalic acid, 1.272 Å (69); and the 1,3-diglyceride of 11-bromoundecanoic acid, 1.27 Å (71).

The only remaining arguments for Malkin's 1.30 Å value are the single-crystal data on anhydrous potassium caprate and strontium laurate by Vand et al. (7) and Morley and Vand (8). The extreme difficulty of preparing single crystals of anhydrous soaps is well known. It is interesting to note, therefore, that Lewis and Lomer (70), using very carefully prepared crystals of potassium caprate, obtained a d_{90} value of 1.279 ± 0.0045 Å instead of 1.299 Å from new measurements. It would seem logical, therefore, to question the validity of the d_{90} value, 1.305 Å, reported for strontium laurate (8) and to accept the overall average, 1.27 Å, obtained from Table I, as the value for this constant.

An important byproduct of these calculations is the fact that the values in Table I can be used to predict the effective length of one molecule in the crystal of any specific long chain member of any of these homologous series. The values md_{90}, d_{90} and k_{90} are the constants for the special case of equation 1 (rearranged): $L_{90}/m = d_{90}n + k_{90}/m$, where L_{90}/m is the effective length of a molecule containing n carbon atoms (n being defined as in Table I and the footnotes), measured along the axis of the long chain, and k_{90}/m is that portion of the length of the molecule contributed by (a) the substituents on the terminal carbons, (b) the gaps between the ends of the molecules, and (c) the difference in the distance between alternate carbon atoms especially near substituent and terminal groups.

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