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The Crystal Structure of Form *A* of Potassium Caprate

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Potassium caprate, $\text{KC}_{10}\text{H}_{19}\text{O}_2$, form *A*, is monoclinic. The cell contains four molecules and has the dimensions $a=8.119$, $b=5.650$, $c=28.907$ Å., $\beta=108^\circ 2'$; density calculated 1.108, observed 1.123 g.cm.⁻³. The space group is $C_{2h}^2-P2_1/a$. Two-dimensional Fourier projections show that the hydrocarbon chains cross each other and that the average distance between two alternate carbon atoms in the chain is 2.598 Å. This is significantly greater than the commonly assumed distance 2.522 Å., derived from the diamond structure. The angle of tilt of the molecules is $57^\circ 30'$.

Introduction

A preliminary report on the crystal structure of potassium caprate has been published by Vand, Lomer & Lang (1947). There exist at least three forms, *A*, *B*, *C*, of anhydrous and three forms, *D*, *E* and *F* of hydrated neutral even-numbered potassium soaps. The form *A* is monoclinic and was obtained for soaps with from 4 to 12 carbon atoms in the chain. According to Lomer (to be published), the form *B* is triclinic; it was obtained for soaps with from 12 to 18 carbon atoms per molecule. The form *C* was observed only at higher temperatures. The form *D* is suspected to be a crystalline hydrate stable at lower temperatures; it has not yet been studied in detail. The forms *E* and *F* are liquid-crystalline, stable at room temperature within narrow ranges of high humidities. Piper (1929) reports only one form each of neutral and acid potassium soaps, and the neutral soaps of longer chain length investigated by him are most probably identical with our form *B*.

The long spacings, d , of every form obey a linear law $d=pN+q$, where N is the number of carbon atoms in the chain, and p , q are two constants. Their values, determined by the method of least squares, are given for forms *A*, *B*, and *C* in Table 1.

Table 1. Values of p and q

Form	p (Å.)	q (Å.)
<i>A</i>	2.156 ± 0.017	5.82 ± 0.14
<i>B</i>	2.052 ± 0.018	5.24 ± 0.28
<i>C</i>	2.152 ± 0.011	6.56 ± 0.15

The angle of tilt τ between the chain axes and the (001) plane can be calculated from the long spacings of a homologous series of soaps all in the same form.

Assuming a C-C bond length of 1.54 Å. and the angle between successive bonds in the chain to be tetrahedral, the calculated increment per two carbon atoms in the length of the molecule is 2.522 Å.

Since, for the form *A*, the observed increment in long spacing is 2.156 Å., we have $\sin \tau = 0.8550$, whence $\tau = 58^\circ 45'$.

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Preparation

The potassium caprate was prepared by neutralization of an alcoholic solution of capric acid with alcoholic potash containing a little water. Phenolphthalein was used as indicator. The capric acid used was obtained in these laboratories by fractional distillation of palm-kernel fatty acids, and was subsequently twice recrystallized from alcohol. Its (corrected) melting-point was 31.8° C., setting point 30.6° C., and mean equivalent molecular weight by titration (saponification value) 172.0. The neutral solution was evaporated to dryness in a vacuum desiccator over calcium chloride, and the soap was obtained as a mass of very thin white platelets, easily visible under the microscope.

The single crystals used for X-ray analysis were then grown from solution in ethanol by very slow evaporation over calcium chloride. They are extremely thin plates with malformed edges, the large face being {001}. They are stable on exposure to dry air, but disintegrate (forming the probably hydrated form *D*) when exposed to air of unknown humidity at temperatures below room temperature. Dehydration experiments showed them to be anhydrous.

Determination of crystal data

Rotation, oscillation and moving-film photographs were prepared using Ni filtered $Cu K\alpha$ radiation from a Metrovick 'Raymax' tube. The moving-film photographs were taken using Robertson's (1934) moving-film camera. Photographs were taken with the crystal rotating about its *a* and *b* axes, and, in order to obtain some general reflexions, about the diagonal of the *a-b* face. The moving-film photographs were indexed by a method described by Vand (1947). The unit-cell dimensions agreed well with those determined from a powder photograph, taken in a 12.5 cm. diameter focusing camera of the Frevel (1937) type. Details of the camera are given by Vand (1948*b*). The dimensions derived from powder data, however, were considered to be of greater accuracy, and the values given below are those determined from the powder photograph by the method of least squares. The camera was calibrated against quartz and rock salt, and the results are expressed in Ångström units, using $1 \text{ Å} = 1.00202 \text{ kX}$.

The following data were used in determining the structure:

Molecular formula $KC_{10}H_{19}O_2$. Molecular weight = 210.35.

Form *A*, monoclinic prismatic.

$$a = 8.119 \pm 0.016, \quad b = 5.650 \pm 0.011,$$

$$c = 28.907 \pm 0.037 \text{ Å};$$

$$\beta = 108^\circ 2' \pm 4'; \quad c \sin \beta = 27.488 \pm 0.034 \text{ Å}.$$

4 molecules per unit cell. Density calculated

$$1.108 \pm 0.005 \text{ g.cm.}^{-3},$$

density observed

$$1.123 \pm 0.005 \text{ g.cm.}^{-3}.$$

Absent reflexions: (*h*0*l*) when *h* odd; (0*k*0) when *k* odd. Space group $C_{2h}^5 - P2_1/a$. Total number of electrons = 456 per unit cell.

Estimation of the intensities

The intensities were estimated visually, using the multiple-film technique of de Lange, Robertson & Woodward (1939). The lowest orders of (00*l*) reflexions were recorded on a flat film at a distance of 8 cm. The (00*l*) reflexions which occurred both on the (*h*0*l*) and (0*k**l*) photographs served as a link which ensured that the intensity scale was the same for both photographs.

The intensities were corrected for the oblique angle of incidence by the factor D_2 , given by Cox & Shaw (1930). As the crystal was very small, no absorption or extinction corrections were applied. The values of the structure factors were brought on to an absolute scale by comparison with the calculated values F_0 at a later stage of the calculations.

Calculation of structure factors

The calculation of structure factors involves long periods of computation, and methods of shortening the labour are invaluable. The following technique was found adequate for this problem:

The expression for the structure factor is

$$F(hkl) = \sum f_i \cos 2\pi(hx_i + ky_i + lz_i).$$

The quantities $(hx_i + ky_i + lz_i)$ were first calculated for values of *h*, *k*, *l* on an electrical adding machine; the summation of the cosine terms, of which the above quantities are the arguments, was done on a simple machine (Vand, 1948*c*) similar to that described by Booth (1947*a*). Values of f_i were obtained from the scattering curves, published by Booth (1946), which have the same shape for all atoms irrespective of atomic number. Hydrogen-atom positions were neglected, and the curves for CH_2 and CH_3 groups were obtained assuming effective atomic numbers of 8 and 9 respectively.

Preliminary analysis of the structure

As no similar structure has been determined previously, the solution of the structure presented considerable difficulties, and a technique suitable for long-chain compounds had to be developed. Among the (*h*0*l*) reflexions by far the strongest is the (200) reflexion. This indicates that the chain axes lie approximately parallel to the (200) planes. If it is assumed that the chains are all parallel to each other, a discrepancy arises in that the angle of tilt, obtained from long spacings, is 58° 45', whereas the angle of tilt of the (200) planes is 72°. When it was realized that this difference was real, it followed that the chains must have a component of tilt when viewed along the *a* axis. Space-group considerations require that if the chains are not perpendicular to the (001) plane in this projection, then they form a criss-cross pattern and cannot be parallel with each other. This conclusion is strengthened by the fact

that neither the (020) nor the (040) reflexion is as strong as it would be if the molecules were all parallel to these planes. We thus formed a rough idea of the structure from these considerations; in the projection along the b axis, the chains are parallel to each other and have an angle of tilt of approximately 72° , and in the projection along the a axis they form a criss-cross pattern and have angles of tilt of alternately 60° and 120° approximately. Steric considerations show that the chains will be seen approximately edge-on in the projection along the b axis, while the zigzag nature of the chains will be apparent in the other projection.

Determination of the signs of the structure factors

The signs of the (00 l) reflexions were determined first. The shape of the molecule was assumed to be a plane zigzag with the usual bond dimensions and angles: C-C bonds 1.54 Å., C-O bonds 1.25 Å., the angle between C-C bonds $109^\circ 28'$, and the O-C-O angle 125° .

The values of the $F(00l)$ then depend on only four variables:

- (1) the z co-ordinate of the potassium atom,
- (2) the z co-ordinate of the centre of the chain,
- (3) the angle of tilt of the chain,
- (4) the angle of twist of the chain, i.e. the angle between the plane of the molecule and the plane containing the axis of the molecule and the normal to the (001) plane.

Several trials were made with the z co-ordinate of the potassium atom zero, but no satisfactory agreement was obtained. When the z co-ordinate of the potassium atom was changed, however, better agreement between observed and calculated F 's resulted; approximate z co-ordinates were obtained for all the atoms and the signs of the (00 l) reflexions calculated.

Patterson maps of both the a and b projections were prepared, but these showed little except the peaks due to the interatomic vectors between potassium atoms, which confirmed that the z co-ordinate of these atoms is not zero.

Electron density projected on plane perpendicular to b axis

After several unsuccessful trials at the preparation of an electron-density map, the following technique of the addition of successive ripples proved successful. The first synthesis consisted only of the three strong reflexions

(hkl)	$ F $
(200)	219
(20 $\bar{2}$)	151
(40 $\bar{2}$)	161

There are in all eight electron-density maps which result from the combination of these reflexions according to the signs given to the F 's. Of these, four are the same map with the origin moved and the remaining four are the inverse of the first four; thus only one map need be

prepared. If this map shows a ridge of high electron density on a reasonably flat, low background, all is well, but if it shows a valley with a flat, high background, all the signs must be changed. It is then relatively simple to choose the signs so that the origin coincides with that used in determining the sign of the (00 l) reflexions. The second synthesis consisted of the three above reflexions and all the long spacings. This crude map already showed the outline of the hydrocarbon chain and an indication of the position of the potassium atom in agreement with the position obtained from the Patterson map. These atomic co-ordinates were used to calculate the signs of the next strongest reflexions which were then added to the previous synthesis. The procedure of adding in succession the strongest reflexion not previously included has these advantages:

(1) A ripple added with the wrong sign distorts a synthesis twice as much as if left out; it is thus better to leave out ripples of unknown sign.

(2) The addition of one or two ripples to a synthesis involves much less labour than to change the whole synthesis.

(3) Sometimes it is not necessary to complete the addition of the ripple to the whole map before it can be recognized that the new ripple is being added with the wrong sign.

The completed map showed that in this projection the angle of tilt was approximately 80° , and therefore that in the b - c projection the angle of tilt was approximately 60° .

Electron density projected on plane perpendicular to a axis

Steric and space-group considerations suggested that the potassium atoms lay on one glide plane (say $y = \frac{1}{2}$), and that the polar end-groups of the soap chain lay on the second glide plane (say $y = \frac{3}{2}$). It was thus easy to guess a structure for the preliminary calculation of signs of the $F(0kl)$. The method of addition of successive ripples was not applicable to this projection because there were no reflexions very much stronger than the average. Several electron-density maps were prepared using signs calculated with varying angle of tilt of the chain, and with slight movements, both in y and z , of the chain as a whole. None of these gave a satisfactory map, but some of them suggested that the assumed values of the molecular dimensions were wrong. In particular, it appeared that the length of the chain or, more precisely, the distance between alternate carbon atoms was greater than assumed. This distance was therefore next assumed some 4% greater, and the signs of the structure factors were recalculated. A new electron-density map was prepared, and an improvement in the appearance of the map was immediately apparent. Refinement of the co-ordinates by the usual successive approximations was continued until no changes in signs of the structure factors resulted.

The resulting final electron-density maps are shown

in Figs. 1 and 2; Fig. 1 represents the projection of the electron density along the b axis on the a - c plane, and Fig. 2 represents the projection along the a axis. The

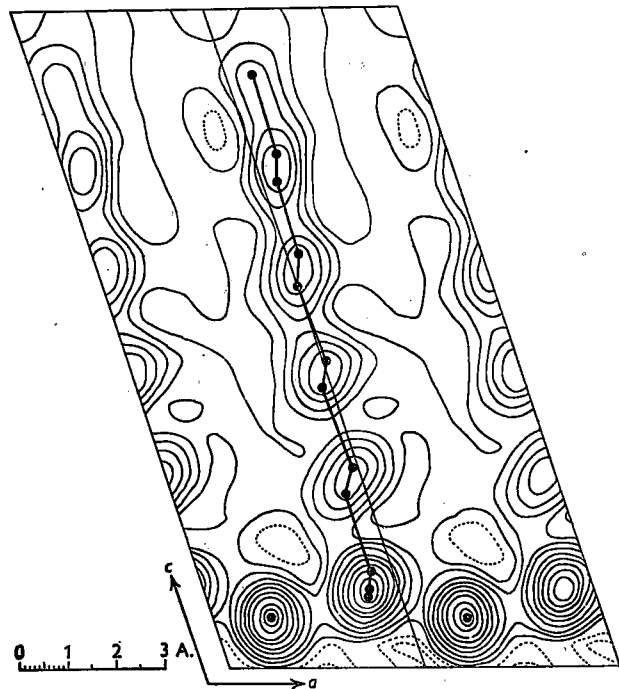


Fig. 1. A Fourier projection of electron density on a plane perpendicular to the b axis. Contours are drawn at levels of 0, 2, 4, etc., e.A.⁻². Negative contours dotted.

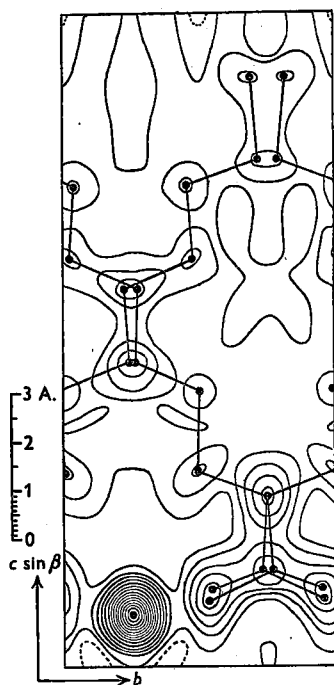


Fig. 2. A Fourier projection of electron density on a plane perpendicular to the a axis. Contours (except for potassium) are drawn at levels of 0, 4, 8, etc., e.A.⁻². Negative contours dotted.

positions of the atoms deduced from the electron-density maxima are represented by black circles.

In order to see better the kind of packing of the molecules, the projections are represented schematically in Figs. 3 and 4. The co-ordinates obtained from the electron-density maps are given in Table 2. The observed and calculated structure factors are given in Table 3.

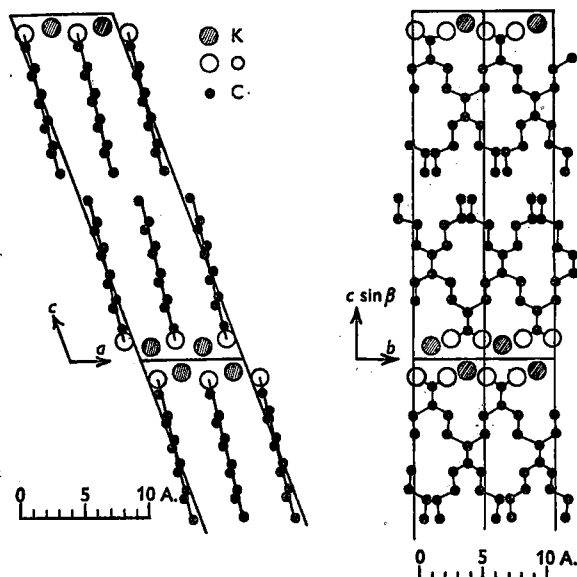


Fig. 3.

Fig. 4.

Fig. 3. Schematic representation of the projection of the structure on a plane perpendicular to the b axis. Hydrogen atoms are not shown.

Fig. 4. Schematic representation of the projection of the structure on a plane perpendicular to the a axis. Hydrogen atoms are not shown.

Table 2. Co-ordinates from Fourier projections

(Co-ordinates in brackets are of lower accuracy.)

Atom	x/a	y/b	z/c
K	0.148	0.250	0.039
O ₁	0.425	0.545	(0.059)
O ₂	0.412	0.960	(0.051)
C ₁	(0.445)	(0.722)	0.073
C ₂	0.442	(0.743)	0.130
C ₃	0.480	0.490	0.150
C ₄	0.476	0.509	0.211
C ₅	0.510	(0.256)	(0.232)
C ₆	0.500	(0.277)	(0.290)
C ₇	0.530	0.022	0.312
C ₈	0.540	0.045	0.369
C ₉	0.562	(0.790)	0.389
C ₁₀	0.566	0.811	0.450

The agreement between observed and calculated structure factors does not compare well with that usually obtained with other substances. The discrepancies may at least partly be due to the treatment of the CH₂ groups as spherically symmetrical scattering units, whereas it is well known that the hydrogen contributions are not negligible.

Table 3. Comparison of the observed and calculated structure factors

<i>hkl</i>	$ F_o $	F_o	<i>hkl</i>	$ F_o $	F_o	<i>hkl</i>	$ F_o $	F_o	<i>hkl</i>	$ F_o $	F_o
000	—	456	0.1.19	21	30	0.3.10	0	15	203	0	17
001	113	104	0.1.20	22	18	0.3.11	0	— 5	204	56	— 32
002	35	39	0.1.21	22	17	0.3.12	0	— 11	205	0	17
003	68	69				0.3.13	0	— 12	206	0	0
004	0	0	020	65	— 49	0.3.14	0	— 23	207	0	17
005	0	9	021	0	— 5	0.3.15	0	— 14	208	32	0
006	54	— 42	022	38	— 46	0.3.16	32	— 53	209	39	9
007	51	— 42	023	0	— 6	0.3.17	32	— 41	2.0.10	34	— 8
008	98	— 67	024	32	— 32				2.0.11	49	2
009	106	— 75	025	0	11	040	101	117	2.0.12	15	— 29
0.0.10	118	— 95	026	15	81	041	69	46	2.0.13	130	95
0.0.11	133	— 118	027	0	— 41	042	69	— 5	2.0.14	107	94
0.0.12	141	— 160	028	42	— 34	043	69	15			
0.0.13	35	49	029	0	4	044	0	4	400	0	43
0.0.14	0	9	0.2.10	5	19	045	0	1	401	0	— 34
0.0.15	35	— 23	0.2.11	13	19	046	0	— 6	402	0	19
			0.2.12	19	29	047	0	— 12	403	0	1
010	0	0	0.2.13	26	11	048	0	— 18	404	19	44
011	35	— 19	0.2.14	27	29	049	0	— 28	405	27	26
012	35	— 5	0.2.15	20	— 7	0.4.10	22	— 24	406	20	45
013	82	104	0.2.16	11	0	0.4.11	22	— 31	407	20	43
014	91	— 84	0.2.17	0	— 17				401	0	— 49
015	70	— 59	0.2.18	0	— 20	200	219	245	402	161	— 242
016	83	— 60	0.2.19	32	77	201	0	— 12	403	65	— 66
017	74	— 47	0.2.20	9	6	202	0	18	404	65	— 71
018	75	— 40				203	0	— 21	405	65	— 55
019	59	— 31	030	0	— 5	204	11	— 12	406	0	— 29
0.1.10	58	— 22	031	0	4	205	43	— 28	407	0	— 18
0.1.11	53	— 14	032	56	39	206	71	— 36	408	0	— 3
0.1.12	16	— 10	033	0	— 25	207	57	— 22	409	0	25
0.1.13	0	— 4	034	68	56	208	59	— 29	4.0.10	0	36
0.1.14	0	— 5	035	110	95	209	46	— 28	4.0.11	18	58
0.1.15	0	— 12	036	79	58	2.0.10	73	— 18	4.0.12	41	62
0.1.16	76	76	037	65	48	2.0.11	33	— 44	4.0.13	75	116
0.1.17	45	32	038	51	32	201	0	12	4.0.14	81	140
0.1.18	28	31	039	20	10	202	151	— 164			

Lattice errors of the structure

Study of the general reflexions obtained from photographs about the diagonal of the *a-b* face revealed that the reflexions (11 \bar{l}) and (33 \bar{l}) are diffuse, whereas (22 \bar{l}) reflexions are sharp. Diffuseness of certain reflexions is an indication that the periodic nature of the crystal does not extend in certain directions over large distances. The fact that all the (*h*0 \bar{l}) and (0 \bar{k} *l*) reflexions are sharp means that these lattice errors are invisible on the projections along the *a* and *b* axes, but that they become apparent when the crystal is viewed along the *a-b* diagonal. Consideration of the molecular packing shows that mistakes might easily occur in the order of crossing of the hydrocarbon chains. Fig. 5 shows an ordered structure. Fig. 6 shows a structure with randomly disordered crossing of chains from layer to layer, obtained by tossing a coin to determine the chain orientation within each successive layer. Such a structure would give the same projections along the *a* and *b* axes as the structure in Fig. 5, but certain general reflexions, such as (11 \bar{l}), (33 \bar{l}), etc., would be diffuse. Occurrence of disorder in soap crystals is not surprising as, during the crystal growth, the arrangement of the deeper layers of the crystal might have but small influence on the structure of a new layer.

The observational material is insufficient to determine whether the disorder from layer to layer is completely random, or whether a certain degree of order

extends over several layers, as the diffuse reflexions merge into one another; however, the order, if present, cannot extend over more than about 10 layers at a time.

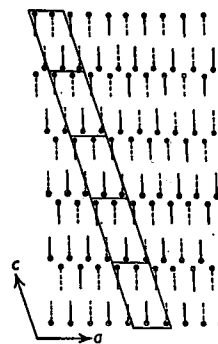


Fig. 5.

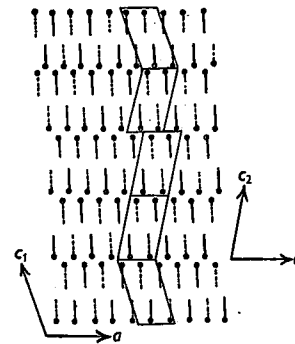


Fig. 6.

Fig. 5. Schematic representation of a lattice without mistakes. There is a rigorous repetition of the pattern. Chains represented by a full line are inclined above the level of the paper, dashed chains are inclined below the level of the paper.

Fig. 6. Schematic representation of a layer structure, in which the succession of inclinations of the chains from layer to layer is at random.

Refinement of the parameters by the Booth method of steepest descents

The Booth method of steepest descents (Booth, 1947*b*; Vand, 1948*a*) was applied to the refinement of the parameters in the hope of obtaining more accurate co-

ordinates, and also as a test of the method itself. However, it was found that different answers were obtained when assumptions regarding the weights of observed structure factors were altered. Although co-ordinates obtained from various assumptions of weighing might be more probable than those obtained from Fourier synthesis, it was felt advisable to postpone their publication until deeper insight has been gained into the accuracy of the method of steepest descents as compared with the more orthodox methods.

Determination of the bond lengths and angles

As the atoms of the carboxyl groups overlapped on both Fourier projections, the bond lengths and angles within these groups cannot be discussed with any accuracy, and only a general outline of the structure of the ionic sheet will be given.

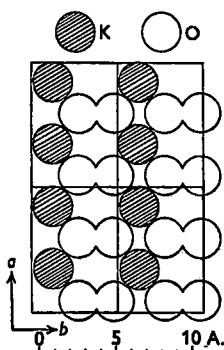


Fig. 7. Schematic representation of the packing of oxygens and potassium ions within one, say the top, half of the double ionic sheet.

The hydrocarbon chains attached to the carboxyl groups make it impossible for the ionic structure of the type *AB* to be continued in all three dimensions, so that only an electrically balanced double ionic layer of positively charged potassium ions and negatively charged carboxyl groups is built. The packing within one, say the top, half of the layer is shown in Fig. 7. The potassium ions of the bottom sheet are approximately under the carboxyl groups of the top sheet, and vice versa.

The only accurate data which can be obtained from our material concern the length of the hydrocarbon chains.

Assuming equal weight of all the atomic co-ordinates and that the hydrocarbon chain is a periodic structure, so that the co-ordinates of the even and odd carbon atoms obey a linear law, the application of the least-squares method gave components of the average vector between alternate carbon atoms. They are given in Table 4 with their probable errors, expressed as fractions of the cell edges and also transformed to a rectangular co-ordinate system. Errors in the cell constants and in the calibration of the camera were taken into account. From the rectangular components, the

modulus of the vector, which is equal to the distance *s* between two alternate carbon atoms, is obtained as $2.598 \pm 7 \times 10^{-3}$ Å.

Table 4. Components of the average vector *s* between two alternate carbon atoms

Co-ordinate	Fractional components	Rectangular components (Å.)
<i>x</i>	$0.0298 \pm 6 \times 10^{-4}$	$0.471 \pm 6 \times 10^{-3}$
<i>y</i>	$-0.2326 \pm 1.8 \times 10^{-3}$	$-1.314 \pm 11 \times 10^{-3}$
<i>z</i>	$0.0797 \pm 1.5 \times 10^{-4}$	$2.191 \pm 5 \times 10^{-3}$

According to Riley (1944), the carbon bond length in diamond is $1.54453 \pm 9 \times 10^{-5}$ Å. If we assume that in a hydrocarbon chain, the carbon bond length is the same as in diamond, but that the bond angle is strained from its tetrahedral value of $109^{\circ}28'$, we obtain from our value of *s* an angle of $114^{\circ}30'$ between the C-C bonds in a hydrocarbon chain. This is in good agreement with the angle of 115.3° , deduced by Ingold (1921) from purely steric considerations.

In a hydrocarbon chain, the hydrogens occupy a smaller volume than the carbon atoms, so that the C-C valency angle is strained from its tetrahedral value. If the angle remained tetrahedral, then a value of *s* equal to 2.52217 Å. should be expected, as found in diamond. The value obtained by us is 0.076 Å. greater, which exceeds our experimental probable error by over ten times, so that the result is significant.

Using our value of $s = 2.598$ Å., we obtain for the angle of tilt, when calculated from the increment from Table 1,

$$\sin \tau = 2.156/2.598 = 0.8300,$$

whence $\tau = 56^{\circ}6'$.

The same angle can be calculated from the components of the vector between alternate carbon atoms. We obtain thus

$$\sin \tau = 2.191/2.598 = 0.8433,$$

whence $\tau = 57^{\circ}30'$, which is probably the most reliable value of tilt obtained from our experimental material, as no special assumptions, such as the constancy of τ in a homologous series, are involved in its derivation.

The disagreement between these two angles of tilt can be judged from the disagreement between the increment and the *z* component of the vector *s*; these values differ by 0.035 ± 0.018 Å., or the probable error is exceeded twice. This is not significant, and it is thus doubtful whether this discrepancy is real; if it is, it may be accounted for either by an assumption that the angle of tilt varies slightly with the chain length, or that *s* varies slightly from compound to compound. Some degree of such variation is to be expected; however, from the above discussion it is evident that such variations, if present, are too small seriously to affect the accuracy of calculations of the angle of tilt.

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