ground in the region between Bragg peaks. Again the region between doublets is also higher than the general background. As in the case of the one-phonon calculation, the major effect relative to correcting for the TDS contribution to measured integrated intensities, is to increase the contribution. In the previous work of Chipman & Paskin, the two-phonon contribution to the apparent integrated intensity was neglected in arriving at a TDS correction in analytic form. It is apparent that in fact there is likely some contribution from the two-phonon TDS as well as the one-phonon. To the degree that the peaking of the two-phonon contribution becomes important, the approximate analytic expression given by Chipman & Paskin becomes in error and their graphical method must be utilized with the velocity term corrections as given by this paper. However, in general for materials such as copper with usual Debye characteristic temperatures, the analytic formula will prove sufficient over the usual region of reciprocal space.

I am pleased to acknowledge many valuable discussions with Dr D. R. Chipman pertaining to the problem of TDS in cubic powders.

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The Crystal Structure of Orthorhombic Hexatriacontane C36H74

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Single crystals of the orthorhombic form of hexatriacontane $C_{36}H_{74}$ have been shown to have space group $Pca2_1$ with unit-cell dimensions $a = 7\cdot42$, $b = 4\cdot96$, $c = 95\cdot14$ Å. The crystal structure has been determined from Fourier syntheses of the electron density projected down the three principal crystallographic axes and from observations of the agreement between observed and calculated structure factors. The molecular chains are regular and periodic within experimental error, with a C–C bond length of $1\cdot533$ Å and a zigzag bond angle of $112°$. The side-by-side packing of chains is identical with that found in the monoclinic form and in polythene. Intermolecular distances are given and discussed briefly in relation to the polymorphism, the stability and the anisotropic thermal vibrations and expansion coefficients of long chain hydrocarbons.

Introduction

The structure of the monoclinic form of hexatriacontane has recently been described by Shearer & Vand (1956). The investigation described here was in progress at the same time as the work of these authors, and the results are now presented as a contribution to the study of long-chain hydrocarbons and their polymorphism. The crystals examined in this investigation were part of the original batch of material used by Vand (1953) and Shearer & Vand (1956), and were originally prepared by Dr McGowan of I.C.I. (Alkali) Ltd., by a Wurtz synthesis from octa–decyl iodide $C_{18}H_{37}I$. When the original material was recrystallized from high-boiling petroleum only small, poor-quality crystals were obtained. Crystals satisfactory for X-ray intensity measurements were

finally grown by dissolving the recrystallized material in hot petroleum ether and cooling slowly over a period of a few days in a large water-filled Dewar vessel. Orthorhombic plate-like crystals were obtained with inter-edge angles of 67° 30'. The large plane surfaces are (001) faces and the edge surfaces are (110) and (1$\bar{1}$0) faces. In subsequent experiments it was found that monoclinic crystals were obtained by crystallization from benzene and that the orthorhombic form was usually obtained from petroleum ether. These observations will be discussed later in the light of Smith's (1953) and Vand & Shearer's work, but at the time we chose to examine the crystal structure of the orthorhombic form because of its closer analogy to the crystal structure of polythene described by Bunn (1939). The crystallographic data for this form has already been used in the derivation of bond polarizabilities (Bunn & Daubeny, 1954).

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Determination of the unit-cell dimensions and space group

The unit-cell dimensions were determined from oscillation and zero-layer Weissenberg photographs taken with Ni-filtered Cu $K\alpha$ radiation. The c-dimension determination was based on the measurement of thirty $(00l)$ reflexions on Weissenberg photographs and of the (0074) and (0076) reflexions on powder photographs. In addition the first eight $(00l)$ reflexions from a single crystal were recorded on a counter diffractometer of 14·5 cm. radius. The values obtained:

$$a = 7·42 \pm 0·01, \quad b = 4·96 \pm 0·01, \quad c = 95·14 \pm 0·20 \text{ Å}$$

(Vand gave

$$a = 7·44 \pm 0·02, \quad b = 4·955 \pm 0·01, \quad c = 47·61 \pm 0·10 \text{ Å})$$

are in excellent agreement with those of Vand, provided that the latter's c dimension (determined from powder photographs) is doubled. The calculated density with four molecules of $C_{36}H_{74}$ is $0·960 \pm 0·001$ g.cm.$^{-3}$ in satisfactory agreement with the observed value of 0·961 g.cm.$^{-3}$ and with Vand's observed value of 0·9609 g.cm.$^{-3}$.

The following systematic absences were observed:

$$0kl \text{ for } l = 2n+1,$$
$$h0l \text{ for } h = 2n+1 \text{ and } 0k0 \text{ for } k = 2n+1$$

and indicated that the space group was either $Pca2_1$–C_{2v}^5 or $Pcam$–D_{2h}^{11}. The former was chosen because a simple packing could be obtained with it, whereas none could be obtained with $Pcam$. The accidental $0k0$ absences are accounted for by the structure suggested.

Intensity measurements

$hk0$, $h0l$ and $0kl$ intensity data were obtained from zero layer Cu $K\alpha$ Weissenberg photographs with the use of the multiple-film technique. Collection of the $hk0$ intensity data was difficult because of the 95 Å spacing, and required the use of a layer line screen slit width of $\frac{1}{100}$ in., so the intensities are less accurate. Low angle $00l$ reflexions were recorded independently with a flat plate camera and were later related to the Weissenberg intensities. No additional reflexions could be observed on Weissenberg photographs taken with Mo $K\alpha$ radiation.

The intensities were estimated visually by two observers and corrected by the Lorentz and polarization factors. No corrections were made for absorption or extinction.

Determination of the structure

The preliminary structure determination and the calculation of $h0l$ and $0kl$ structure factors were greatly facilitated by the use of a molecular-transform technique devised by Dr E. R. Howells. The derivation of the structure factor expressions may be summarized as follows:

First, the Fourier transform of an isolated C_2H_4 group is written down with origin at the centre of symmetry. The corresponding expression is then deduced for one hexatriacontane chain (minus one H atom at each end) by setting down 18 such C_2H_4 groups with the appropriate distance between neighbours. Finally, the transform of the isolated chain is modified according to the space-group relations between the four molecules of the unit cell to give the transform, and hence the structure factors, of the structure.

For the use of this method an accurate value of 2γ, the difference of the fractional z co-ordinates of two successive carbon atoms in the main chain, is required. For the preliminary calculations the mean was taken of the following values obtained in earlier structure analyses. (The values have been corrected for the less accurate wavelengths used by the early workers).

Müller (1928)	$C_{29}H_{60}$	1·271
Hengstenberg (1928)	$C_{35}H_{72}$	1·273
Kohlhaus (1938)	$C_{30}H_{62}$	1·263
Bunn (1939)	$[CH_2]_n$	1·270

giving a γ value of 0·00667. The γ value was also determined from a one-dimensional Fourier synthesis calculated with 30 non-zero $00l$ values. The sampling of the projected electron density by the $\frac{1}{120}$ Beevers–Lipson strips is not fine enough for this unit cell with a half-length of 47 Å ($l = 2n$ only), so some peaks were sampled at intervals of $\frac{1}{1000}$ with the use of Buerger's Structure Factor Tables (1941). The value of γ determined by this method was 0·00669, and in subsequent calculations the mean of this value with that of the earlier workers was used, implying a carbon–carbon distance projected onto the chain axis of $1·270 \pm 0·01$ Å.

The preliminary x and y co-ordinates of the atoms were determined by a consideration of the end packing of the molecules and of the implications of the $0k0$ non-space-group absences. These absences indicate that the centres of gravity of the molecules must lie very close to $\frac{1}{4}$ and $\frac{3}{4}$ of b. In the first trial structure model the plane of the zig-zag carbon-chain made an angle (φ) of 51° with the b, c plane, and the agreement factor, defined in the conventional manner, for the $0kl$ reflexions was 31%. In these preliminary assessments of the accuracy of the structure the $00l$ reflexions were omitted in the calculation of the agreement factor, since good agreement (14%) between observed and calculated structure factors had already been obtained. All hydrogen atoms except the two terminal ones were included in all the structure-factor calculations.

Refinement of the trial structure then began by observing the effect on the agreement factor for the $0kl$ reflexions of rotating the plane of the molecule about its projected centre of gravity towards the b, c plane. The calculated signs given by Model 4, which had a φ angle of 45° and an $0kl$ agreement factor of 24% were used in a Fourier synthesis of the pseudo-centrosymmetric (100) projected electron
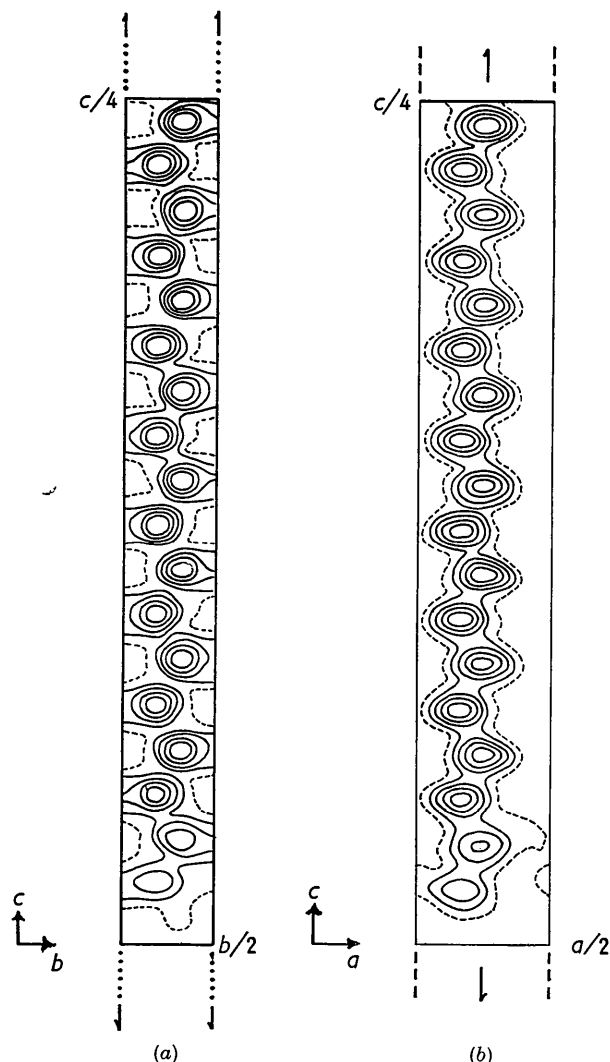
Fig. 1. Projected electron density. (a) (100) and (b) (010).
Contours at arbitrary equal intervals (approx. 1 e.Å^{-2}).
The 1 e.Å^{-2} contour is broken.

factor of 24% when compared with the observed values. The calculated phase angles were then used in a Fourier synthesis of the non centro-symmetric (010) projected electron density (Fig. 1(b)). To obtain the necessary fine sampling in the c-axis direction with the set of $\frac{1}{120}$ punched cards available from the National Physical Laboratory, a technique suggested by Dr E. R. Howells was used. The intermediate $\frac{1}{240}$ sampling points were obtained by calculating a second $\frac{1}{120}$ Fourier synthesis with the origin offset by $\frac{1}{240}$. Unfortunately this requires the summation of additional Fourier syntheses with coefficients modified by factors of $\sin 2\pi\frac{l}{240}$ and $\cos 2\pi\frac{l}{240}$ but it does offer a practical procedure when no alternative methods of finer sampling are available. The (010) electron-density projection showed very much better resolution than the (100) projection, due to the greater separation of the molecules in the former, and indicated that a further tilt of the plane of the molecule towards the b, c plane, together with a bodily shift of the molecule in the x-direction, would be desirable. These small adjustments were made, and the final model, whose group co-ordinates are listed in Table 1, gave reliability factors of 18% for the $0kl$ reflexions and 16% for the $h0l$ reflexions.

Table 1. *Group co-ordinates*

	x	y	
C	0·039	0·064	Co-ordinates of the CH_2 sub-
H_1	0·181	0·044	group atoms relative to the
H_2	0·008	0·274	group origin O_G
O_G	0·053	0·250	

As a final check on the proposed structure, these co-ordinates were used in $hk0$ structure factor calculations, and an agreement factor, R_{hk0}, of 29% was obtained. This value is poor in comparison with those for the $h0l$ and $0kl$ zones, but the difficulties in the collection of the $hk0$ intensities are such that less reliance can be placed upon them. The (001) projected electron-density map was calculated with these signs and the observed $hk0$ structure amplitudes, and showed the expected appearance (see Fig. 2) with the plane

density. $0kl$ reflexions occur only for $l = 2n$, and so the sampling interval with the Beevers–Lipson strips was decreased from $\frac{1}{120}$ to $\frac{1}{240}$ of c by halving the l values. The resulting electron-density map (see Fig. 1(a)) showed well resolved atomic peaks from which the peak centres were obtained by Megaw's method (1954). The y co-ordinates were then adjusted according to these indications, particular attention being paid to the peak positions given by the better resolved, more circular atomic peaks near the centre of the chain. The $0kl$ agreement factor decreased to 21% after these small adjustments had been made. The y co-ordinates of this model were then used in conjunction with the accepted bond lengths and angles to work out the x co-ordinates for $h0l$ structure-factor calculations. The structure factors calculated using these atomic co-ordinates had an agreement
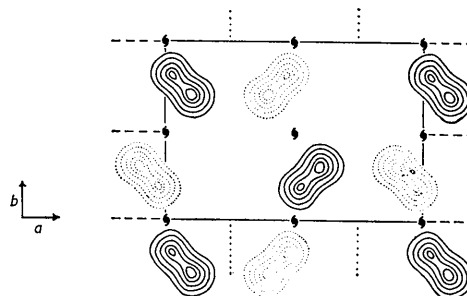

Fig. 2. (001) Projected electron density. Molecules dotted are at $z + \frac{1}{2}$. Contours at arbitrary equal intervals.

of the molecule making an angle of 43° with the b-axis.

Atomic co-ordinates

The sub-group co-ordinates listed in Table 1 can be combined with the value of γ to give a complete set of atomic co-ordinates.

The fractional atomic co-ordinates of the $(2n+1)$th carbon atom with its attached hydrogen atoms are

	x	y	z
C	0·014	0·186	$0·01638+n\times0·02672$
H_1	0·872	0·206	$0·01638+n\times0·02672$
H_2	0·045	0·976	$0·01638+n\times0·02672$

and of the $2n$th carbon atom with its attached hydrogen atoms are

	x	y	z
C	0·092	0·314	$0·02973+(n-1)\times0·02672$
H_1	0·061	0·524	$0·02973+(n-1)\times0·02672$
H_2	0·234	0·294	$0·02973+(n-1)\times0·02672$

Accuracy of the structure determination

Observed and calculated structure factors are listed in Table 4. The standard deviations of the atomic co-ordinates, bond lengths and bond angles were calculated by Cruickshank's formulae (1949), and are given in Table 2. To avoid excessive computation,

Table 2. *Standard deviations*

$\sigma(x)\ =\ 0·0167\ \text{Å}$
$\sigma(y)\ =\ 0·0172$
$\sigma(z)\ =\ 0·0137$
$\sigma\ \text{(Bond length)}\quad=\ 0·022\quad\text{Å}$
$\sigma\ \text{(Bond angle)}\quad=\ 1·8°$

the curvatures were not calculated from differential syntheses or directly from the electron-density maps. Instead a mean value of -40 electrons Å^{-2} obtained from several comparable structures was assumed for all three directions. The standard deviations of the bond lengths and angles were obtained by the well-known formulae (Cruickshank, 1949, 1953).

The structure-factor calculations in this analysis were made with the implicit assumption of perfectly regular molecules (having the ideal planar configuration as regards C atoms) all lying with their axes parallel to the c direction. No estimate was made of the effect on the reliability factors of departures from this regularity.

Bond lengths, angles and intermolecular distances

The atomic co-ordinates given above correspond to a carbon–carbon bond length of 1·533 Å and a bond angle of 111·9°. The carbon–hydrogen bond length was 1·07 Å and the H–$\hat{\text{C}}$–H angle was close to 107°. This value was deduced from the graphs given by Coulson (1948). The bond lengths and bond angles quoted, are those actually used in the transform calculations.

The carbon–carbon contacts between adjacent chains are of two types (see Fig. 3), and are such
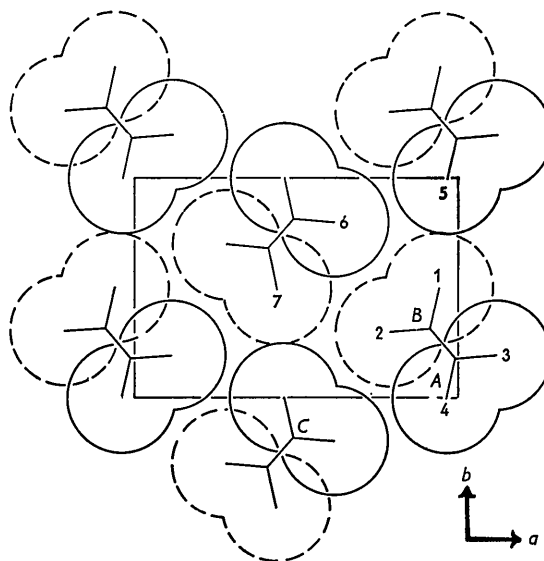
Fig. 3. Interchain contacts within a layer. Atoms outlined with broken lines are at $z\pm1·270$ Å.
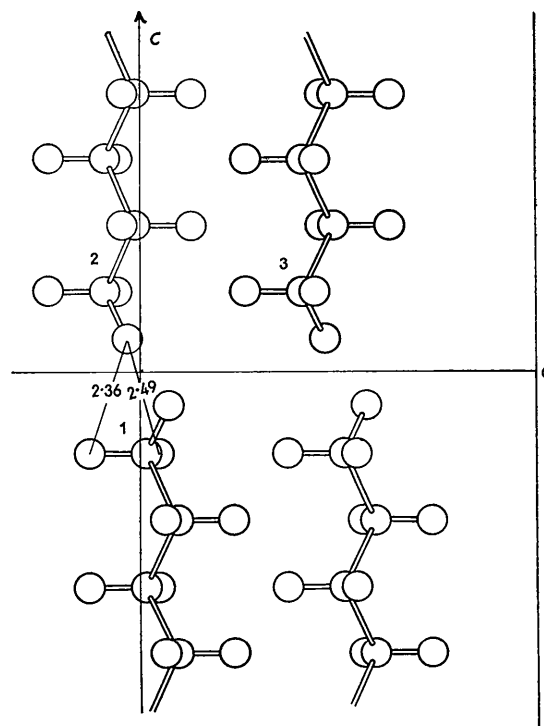

Fig. 4. End contacts between chains.

that $A-C = 4·15$ Å and $B-C = 4·19$ Å. (Shearer & Vand gave 4·14 and 4·20 Å respectively). The carbon–carbon end contacts between chains are also of two types (see Fig. 4) such that 1–2 = 4·06 Å, and 1–3 = 4·32 Å. The closest hydrogen contacts between chains are also shown in Fig. 3. They are:

$$H_1-H_5 = 2\cdot58, \quad H_2-H_7 = 2\cdot6 \text{ Å},$$
$$H_1-H_6 = 2\cdot95, \quad H_2-H_6 = 2\cdot97 \text{ Å}.$$

When the hydrogen atoms of the methyl groups at the ends of the molecules are placed in the *trans* staggered position the shortest end-to-end hydrogen contact distances (see Fig. 4) are 2·36 and 2·49 Å. These distances are less than twice the normally accepted Van der Waals radius of hydrogen atoms (1·25), and it is therefore implied that this particular instantaneous arrangement of hydrogen atoms is forbidden. Either the terminal hydrogen atoms are in a more favourable spatial position or, more probably, they are in some form of intermeshing or hindered rotation.

The plane of the carbon–carbon zig-zag makes an angle of 42·3° with the b, c plane.

Discussion of the structure

Interatomic and intermolecular distances and thermal vibrations

The side-by-side packing of the planar zig-zag chains of carbon atoms is very closely similar to that found in the comparable structures of polythene (Bunn, 1939), and monoclinic hexatriacontane. Table 3 lists the atomic x and y co-ordinates in the three structures, all referred to an equivalent origin, and shows that they are identical within the limits of the experimental errors.

Table 3. *Atomic co-ordinates*

	Polythene		Orthorhombic $C_{36}H_{74}$		Monoclinic $C_{36}H_{74}$	
	x	y	x	y	x	y
C	0·038	0·065	0·039	0·064	0·038	0·065
H_1	Not given		0·181	0·044	0·179	0·049
H_2	Not given		0·008	0·274	0·010	0·273

All three structures are based on the familiar rectangular packing of planar chains, with the central molecule having its plane approximately perpendicular to the molecules at the corners of the rectangle. The translations of the molecules in their axial directions are such that the hydrogen atoms of nearest neighbour molecules interleave exactly. In the orthorhombic form of hexatriacontane there are no abnormally short intermolecular contacts; indeed, the structure appears to be rather loosely packed, with regard to the end contacts in the a, c plane, as the carbon–carbon distances approximately parallel to this plane are 4·32 Å compared with the distance of 4·06 Å in the b, c plane. These distances are both greater than the end-pack distance of 3·91 Å given by Shearer & Vand (1956), and thus account for the lower density of the orthorhombic form.

The atomic scattering factors used for the structure factor calculations were those given by Robertson (1935) with no further corrections for anisotropic

thermal vibrations. It is known that the use of an isotropic scattering factor cannot possibly represent the thermal vibrations actually occurring in the hexatriacontane structure, as it is likely that vibrations in the c-direction will be practically negligible, while those in the a-direction may be much greater than those in the b-direction. A series of measurements is at present in progress on the expansion coefficients and thermal motions of hexatriacontane and of several different ethylene polymers, and will form the subject of a separate publication (Holmes & Cole, 1958). The electron-density maps in Fig. 1 certainly show considerably lower peak electron densities for the last two carbon atoms at each end of the chain, but part of this effect may be due to the omission of high order terms from the Fourier series (although these high-order reflexions were not recorded in the photographs taken with molybdenum radiation). The long intermolecular contact distances at the ends of the chains would certainly point to the possibility of rather greater molecular motion at these points than in the body of the chains where the carbon–carbon contact distances are only about 0·15 Å greater than those normally found. Alternatively, the lower electron density at the chain ends might be due to the gaps left by shorter molecules present as impurities.

Polymorphism

The identical side-by-side packing found in the orthorhombic and monoclinic crystal forms confirms Schoon's (1938) original prediction. What then is the reason for this polymorphism, which involves translation of adjacent chains by integral multiples of 2·54 Å? Ubbelohde (1938) and Smith (1953) have recently thrown considerable light on the problem with their observations that about 2% impurity of neighbouring homologues is necessary for the formation of the orthorhombic form, but no mechanism has yet been suggested. However, their work does provide a possible explanation for our observation that monoclinic crystals were obtained from benzene and orthorhombic crystals from high-boiling petroleum–ether solutions. The latter would contain paraffins up to hexane at least, and might well contain higher members of the series in solution.

There can be no doubt that the monoclinic form is the energetically stable one, as it has the higher calculated crystal density (0·964 compared with 0·960) because of the more efficient packing of the ends of the molecules. At present it is not possible to suggest a detailed mechanism for the transition from monoclinic to orthorhombic symmetry, although it seems likely that a crystal composed of a random distribution of chain lengths might have a statistical orthorhombic symmetry.

Intermolecular forces and the structure of hydrocarbons

There are two interesting properties of orthorhombic

Table 4. *Observed and calculated* (h0l), (0kl) *and* (hk0) *structure amplitudes*

hkl	Obs.	Calc.	hkl	Obs.	Calc.	hkl	Obs.	Calc.	hkl	Obs.	Calc.
002	47.4	41.4	2,0,16	6.0	12.9	4,0,75	64.0	67.5	040	18.1	27.8
004	47.3	41.1	2,0,17	4.3	6.7						
006	44.6	38.6				600	17.6	24.1	0,5,32	7.1	9.9
008	43.5	37.1	2,0,29	4.9	2.9	601	22.0	35.8	0,5,34	12.1	14.5
0,0,10	40.2	35.1	2,0,30	11.0	13.8	603	11.8	11.7	0,5,36	27.0	31.8
0,0,12	33.4	33.2	2,0,31	5.1	5.8				0,5,38	48.7	75.6
0,0,14	30.3	31.5	2,0,32	14.6	16.1	6,0,36	37.5	45.7	0,5,40	4.9	13.7
0,0,16	30.6	29.6	2,0,33	7.4	10.5	6,0,37	25.7	50.1			
0,0,18	27.8	27.7	2,0,34	25.4	21.9	6,0,38	68.0	108.5	060	32.8	45.3
0,0,20	22.8	25.9	2,0,35	19.3	22.5						
0,0,22	19.2	23.9	2,0,36	41.6	45.6	800	19.0	27.7	*110	173.6	159.8
0,0,24	17.8	21.9	2,0,37	145.6	138.0				210	77.3	62.2
0,0,26	16.6	20.2	2,0,38	111.7	105.7	8,0,37	36.6	62.2	310	151.9	139.8
0,0,28	15.1	18.3	2,0,39	47.3	43.5	8,0,38	26.9	31.8	410	70.6	75.7
0,0,30	13.6	16.5	2,0,40	12.7	19.1	8,0,39	16.8	20.0	510	61.5	78.5
0,0,32	12.0	14.6	2,0,41	30.4	21.3				610	41.3	57.6
0,0,34	9.9	13.1	2,0,42	10.1	9.1	0,1,18	2.6	8.8	710	9.6	12.4
0,0,36	8.4	12.1	2,0,43	22.2	14.5	0,1,20	3.8	9.8	810	12.1	14.7
0,0,38	7.6	11.1	2,0,44	6.0	5.3	0,1,22	6.6	10.9	910	8.5	4.9
0,0,40	6.3	8.4	2,0,45	14.9	11.2	0,1,24	7.0	12.1			
0,0,42	6.6	6.8	2,0,46	6.2	3.2	0,1,26	9.8	13.6	120	88.9	83.1
0,0,44	3.8	5.4	2,0,47	10.8	9.4	0,1,28	13.0	15.5	220	130.9	86.5
0,0,46	3.9	4.0				0,1,30	18.9	18.2	320	69.5	61.3
0,0,48	4.0	2.5	2,0,69	7.5	5.2	0,1,32	25.5	22.8	420	27.3	9.8
0,0,50	4.2	1.1	2,0,70	15.6	14.0	0,1,34	39.6	32.7	520	48.5	8.9
0,0,52	4.3	0.3	2,0,71	11.2	5.7	0,1,36	87.0	70.1	620	9.8	1.9
0,0,54	4.4	1.8	2,0,72	26.3	23.3	0,1,38	183.9	162.7	720	35.0	46.7
0,0,56	4.5	3.3	2,0,73	17.8	7.4	0,1,40	33.7	28.7	820	10.8	31.4
0,0,58	4.6	5.0	2,0,74	81.4	74.9	0,1,42	10.5	13.1	920	6.0	21.2
0,0,60	4.7	6.8	2,0,75	90.9	79.2	0,1,44	3.9	7.1			
0,0,62	4.9	8.9	2,0,76	67.4	58.1				130	50.1	34.0
0,0,64	4.9	11.4	2,0,77	8.1	0.5	020	188.6	206.5	230	63.0	65.1
0,0,66	22.1	14.7	2,0,78	18.1	20.3	022	11.2	8.0	330	44.6	33.8
0,0,68	24.4	19.7				024	10.3	8.3	430	88.5	87.8
0,0,70	29.4	28.0	2,0,111	14.6	13.7	026	9.3	8.1	530	13.7	32.5
0,0,72	41.0	47.1	2,0,112	23.2	22.1	028	8.1	8.0	630	49.6	76.8
0,0,74	158.9	152.0	2,0,113	26.7	24.6	0,2,10	6.6	7.8	730	8.1	0.3
0,0,76	127.5	116.6				0,2,12	3.3	7.6	830	17.2	19.4
0,0,78	39.7	40.5	400	32.9	44.1	0,2,14	3.4	7.4			
0,0,80	23.3	23.3	401	90.0	122.2				140	38.7	51.3
0,0,82	13.6	15.5	402	6.0	1.8	0,2,66	5.2	4.9	240	15.7	5.6
0,0,84	5.8	11.0	403	39.5	39.4	0,2,68	5.3	6.6	340	47.9	39.7
			404	6.0	2.2	0,2,70	10.7	9.4	440	9.6	2.3
200	314.9	360.7	405	20.5	22.9	0,2,72	19.4	15.8	540	42.0	6.6
201	193.5	191.2	406	6.0	2.5	0,2,74	64.6	50.9	640	7.7	5.2
202	20.2	14.0	407	11.2	15.7	0,2,76	58.0	39.3	740	23.2	39.0
203	58.5	61.6				0,2,78	19.6	13.7			
204	20.3	14.6	4,0,28	12.5	11.0	0,2,80	10.9	7.9	150	13.2	14.7
205	31.1	36.1	4,0,29	6.7	1.0	0,2,82	5.4	5.3	250	23.6	28.5
206	18.9	14.2	4,0,30	16.2	13.1				350	12.1	28.7
207	21.4	25.1	4,0,31	6.7	1.8	0,3,28	4.6	10.8	450	37.1	38.7
208	14.4	14.2	4,0,32	23.2	16.7	0,3,30	9.4	12.9	550	6.3	12.2
209	13.9	18.6	4,0,33	6.8	2.8	0,3,32	14.1	16.4	650	13.6	36.1
2,0,10	11.4	13.9	4,0,34	35.2	24.2	0,3,34	22.4	23.8			
2,0,11	8.1	14.3	4,0,35	6.9	5.4	0,3,36	57.8	52.0	160	6.0	15.0
2,0,12	9.2	13.5	4,0,36	58.1	52.9	0,3,38	132.2	123.0	260	12.6	28.4
2,0,13	7.2	11.2	4,0,37	35.8	31.2	0,3,40	15.7	22.1	360	10.3	8.6
2,0,14	8.4	13.3	4,0,38	109.3	124.6	0,3,42	5.0	10.3			
2,0,15	6.0	8.6	4,0,39	5.8	10.2						

* For accuracy of hk0 intensity data, see comment on p. 295 under intensity measurements.

crystalline hydrocarbons which still require some comment.

(1) The large anisotropy of the thermal expansion coefficients in the temperature range between 0 °C. and the melting points. For both polymeric and monomeric hydrocarbons the expansion of the a-axis is more than 50 times that of the b axis (Müller, 1928; Bunn & Alcock, 1945; Holmes & Cole, 1958).

(2) There is quite strong evidence that the polythene crystal lattice can accommodate a limited number of methyl groups, provided that a small expansion in the a-lattice dimension occurs. This was shown by the work of Walter & Reding (1956), presumably on copolymers of propylene and ethylene, in which an increase of 0·32 Å in the a-dimension was reported for a sample containing 8 CH_3 groups per 100 carbon

atoms. Similar increases in the a-dimension have been observed in methyl-branched polymethylenes prepared from mixtures of diazoethane and diazomethane (unpublished). It would be very valuable to have comparable information for methyl-branched monomeric hydrocarbons, but the author is not aware of any published work on this subject.

Both these observations might be interpreted as indicating that the intermolecular forces in the a-direction in the orthorhombic hydrocarbon crystal lattice are weaker than those in the b-direction. But the equality of the side-by-side chain hydrogen contacts in the a and b directions lends little support to this suggestion. Admittedly Fig. 4 does appear to show a rather obvious gap in the structure in the a-direction, but the projection diagram is misleading in this respect, as the hydrogen contacts in the b-direction are interleaved. Elastic modulus measurements for the a and b directions would be the most direct method of settling whether there is any anisotropy of molecular forces.

A more plausible suggestion to account for the anisotropic thermal expansion made by Bunn (1957) is that the change in axial ratio $a:b$ with increasing temperature is brought about by a twist of the mean plane of the zig-zag carbon chain towards the a, c plane of the unit cell. This rotation may be associated with an increase in amplitude of the rotational oscillations of the molecules, which would cause the packing of the chains to approach a hexagonal arrangement $(a = 3^{\frac{1}{2}}b)$ with rise of temperature; this would involve an increase of a relative to b. This transition to a hexagonal arrangement has been observed in orthorhombic hexatriacontane at a few degrees below the melting point by both dilatometric (Vand, 1953) and X-ray methods (Holmes & Cole, 1958), but it does not occur in the high polymers. Experiments are in hand to check the validity of Bunn's suggestion by measuring the variation with temperature of the $hk0$

structure amplitudes. Until this information becomes available, judgement on the mechanism responsible for the anisotropic thermal expansion must be withheld.

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