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The Crystal Structure of the Monoclinic Form of *n*-Hexatriacontane

BY H. M. M. SHEARER AND V. VAND*

Chemistry Department, The University, Glasgow W. 2, Scotland

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The unit cell of the monoclinic form of *n*-hexatriacontane, $C_{36}H_{74}$, was determined by X-rays. It is $a = 5.57$, $b = 7.42$, $c = 48.35$ Å, $\beta = 119^\circ 6'$, with two molecules per cell and space group $C_{2h}^2-P2_1/a$. Fourier projections were prepared and atomic co-ordinates determined with the aid of the subcell theory. The chains pack essentially in an orthorhombic subcell with $a_0 = 4.945$, $b_0 = 7.42$, $c_0 = 2.546$ Å, space group $D_{2h}^{16}-Pbnm$, but a monoclinic subcell is needed for structure-factor computations. The chain is regular and periodic within experimental error, with an average single C-C bond length 1.534 ± 0.006 Å and the zigzag bond angle $112^\circ 1' \pm 21'$.

Introduction

The interest in accurate crystal-structure determination of *n*-paraffins is twofold: the effect of environment on the bond lengths and angles of carbon deserves study and the details of polymorphism need elucidation. Considerable advance has recently been made by Smith (1953), who showed that the space group of the odd orthorhombic hydrocarbons described by Müller (1928) is $D_{2h}^{11}-Pbcm$ instead of $D_{2h}^{16}-Pnam$. Smith has also shown that for even orthorhombic hydrocarbons the $(00l)$ long spacings are halved, a point also confirmed by Bunn (private communication), so that the c axis of the orthorhombic $n-C_{36}H_{74}$, obtained by Vand (1953) from powder data, needs to be doubled. Smith also found that pure even paraffins above $n-C_{26}$ normally crystallize as monoclinic at room temperature, whereas about 2% impurity of neighbouring homologues changes them to the orthorhombic form, the amount of impurity decreasing with increasing chain length. As our monoclinic crystals were obtained by recrystallization of the orthorhombic material used by Vand (1953) for density determination, one can infer from Smith's data that during recrystallization some purification took place and that the original orthorhombic material was probably less than about 98–99% pure, whereas the monoclinic crystals used in the present work were of a higher purity. However, it proved impossible to check this in a mass spectrograph owing to the experimental difficulties.

Monoclinic crystals of *n*-hexatriacontane, $C_{36}H_{74}$, were grown slowly from light petroleum solution by evaporation at room temperature. They were flat lozenge-shaped plates with an inter-edge angle of about 75° , with the $\{001\}$ and $\{110\}$ faces well developed. Most of the crystals were twinned about (001) , but it was possible to select under polarized light a few untwinned crystals.

Determination of the unit cell

Rotation, oscillation and zero- and first-layer Weissenberg photographs were taken about the a and b axes using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.542$ Å). The axial lengths a and b were measured from rotation photographs, carefully calibrated by powder lines of copper. The Weissenberg photographs were calibrated by powder lines of NaCl, so that cell dimensions so obtained should be free of systematic camera and film-shrinkage errors.

The long spacing was obtained by measuring Bragg angles θ of all the observable $00l$ reflexions and by taking the weighted average of its reciprocal c^* ,

$$c^* = 2\sum \sin \theta_{00l} / \sum l,$$

and calculating the standard deviation from the residuals. The value $c^* = 0.03650 \pm 0.00006$ was obtained, from which

$$c \sin \beta = \lambda / c^* = 42.25 \pm 0.07 \text{ Å}.$$

The best value of the monoclinic angle β has been evaluated by least squares from Weissenberg photo-

* Present address: Physics Department, Pennsylvania State University, University Park, Pennsylvania, U.S.A.

graphs, using a modification of a method originally developed for powder data by Vand (1948).

For a monoclinic cell, the reciprocal spacing D^* of a reflexion of Miller indices hkl is given by

$$D_{hkl}^{*2} = H_{hk}^{*2} + K_{hk}^{*2} + 2K_{hk}^*lc^* + l^2c^{*2},$$

where

$$H_{hk}^* = ha^* \sin \beta^* \quad \text{and} \quad K_{hk}^* = ha^* \cos \beta^*$$

are two constants for a festoon of reflexions of common indices h and k .

By writing

$$(D^*/c^*)^2 - l^2 = y, \quad l = x, \\ (H^*/c^*)^2 + (K^*/c^*)^2 = q, \quad 2K^*/c^* = p,$$

one obtains n linear equations of the form

$$y_i = px_i + q, \quad i = 1, 2, \dots, n,$$

where x is a whole number and y is known from measurement. These equations can now be solved by the usual least-squares procedure, assuming that all the equations have equal weight. This leads to formulae for p and q :

$$p = (n\Sigma xy - \Sigma x \Sigma y) / M, \quad q = (\Sigma x^2 \Sigma y - \Sigma x \Sigma xy) / M,$$

and for their standard deviations:

$$\sigma(p) = \{n\Sigma \delta^2 / (n-2)M\}^{\frac{1}{2}}, \\ \sigma(q) = \{\Sigma x^2 \Sigma \delta^2 / (n-2)M\}^{\frac{1}{2}},$$

where

$$M = n\Sigma x^2 - (\Sigma x)^2 \quad \text{and} \quad \delta = y' - y,$$

y' being the calculated value of y using the above p and q .

Then H^* can be calculated from

$$H^* = c^*(q - \frac{1}{4}p^2)^{\frac{1}{2}},$$

and, from this, the cell edge a can be obtained from $a = \lambda h / H^*$, using appropriate H^* . In our case, $a = 5.572 \pm 0.011$ Å. Also

$$K^* = \frac{1}{2}pc^*, \quad \cot \beta^* = p/2(q - \frac{1}{4}p^2)^{\frac{1}{2}},$$

whence

$$\beta^* = 60^\circ 54' \pm 4' \quad \text{and} \quad \beta = 119^\circ 6' \pm 4'.$$

Also $c = 1/c^* \sin \beta$ and $c = 48.35 \pm 0.08$ Å.

Summarizing the results, we have:

n-Hexatriacontane, $C_{36}H_{74}$. Molecular weight = 507.00, m.p. = 75.5° C.

Monoclinic prismatic,

$$a = 5.57 \pm 0.01, \quad b = 7.42 \pm 0.01, \quad c = 48.35 \pm 0.08 \text{ Å}, \\ c \sin \beta = 42.25 \pm 0.07 \text{ Å}, \quad \beta = 119^\circ 6' \pm 4'.$$

Two molecules per unit cell. Molecular symmetry, centre. Density calc. 0.964, meas. 0.961 g.cm.⁻³.

Absent reflexions: ($h0l$) when h odd, ($0k0$) when k odd. Space group $C_{2h}^5-P2_1/a$. Absorption coefficient for X-rays ($\lambda = 1.542$ Å) $\mu = 4.52$ cm.⁻¹. Total number of electrons per cell $F(000) = 580$.

Determination of the structure of the subcell

The intensities of reflexions of the main cell were estimated by eye, using the multiple-film technique, and the structure factors were evaluated using the Lorentz and polarization factors. Absolute intensity values were obtained at a later stage by comparison with the calculated structure factors.

The structure of the subcell was determined by considering the reciprocal sublattice in three dimensions. A sublattice was found connecting the regions of strong main lattice reflexions. The subcell reciprocal axes a_s^* , b_s^* , c_s^* were situated as follows: The b_s^* coincided with b^* of the main cell in magnitude and direction, the c_s^* and c^* coincided in direction and a_s^* was at an angle with a^* . In real space, this corresponds to a_s and a and also b_s and b being identical, but permits c_s being inclined to c . The comparison of dimensions revealed that the number N^j of subcells in the c_s direction is 18 and unity in the other two directions, so that the interference function T becomes, according to Vand (1951),

$$T = \sin 18\pi L / \sin \pi L,$$

where the subcell indices are (HKL).

The centre of gravity of subcell region coincides with the origin of the main cell, so that $x_m = 0$. All the atoms can be included in the subcells except the two terminal hydrogens of the methyl end groups, which can be neglected. The structure-factor relation between the main cell and the subcell is given by

$$F(hkl) = T(L)F(HKL), \quad (1)$$

where $F(HKL)$ is the structure factor of the subcell (HKL may be fractional).

With the aid of a graph of T against L it was possible to locate the subcell reciprocal-lattice points more accurately. The following subcell dimensions were obtained:

$$a_s = 5.57, \quad b_s = 7.42, \quad c_s = 2.548 \text{ Å}, \quad \beta_s = 117^\circ 26'.$$

Space group $C_{2h}^5-P2_1/a$ with four CH₂ groups per subcell. (Note that β_s differs slightly from β .)

The next step was to postulate a trial structure and to evaluate $F(HKL)$. A trial structure was comparatively easily found and after some refinement by trial and error, the figure of merit of ($H0L$) and of ($0KL$) subcell reflexions was brought down to 16.4 and 12.0% respectively, using McWeeny (1951) atomic scattering factors and applying a temperature factor $B = 3.0$ Å². Fourier syntheses of the subcell along b_s and a_s were prepared and are shown in Fig. 1. They indicate presence of hydrogen atoms. These were therefore included in further calculations, assuming C-H bond length 1.09 Å and tetrahedral valence angles. The inclusion of the hydrogens brought down the figure of merit to 12.7 and 9.3% respectively. The same B value was used for the hydrogens as for the carbons.

The subcell atomic co-ordinates so obtained are

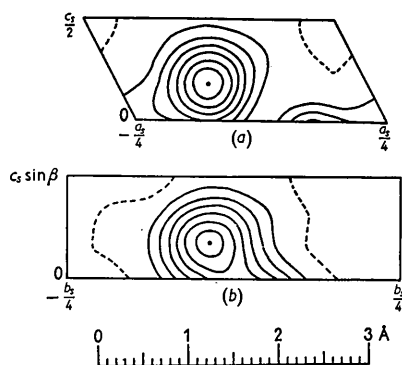


Fig. 1. Electron-density projection of the subcell (a) along the b_s axis, (b) along the a_s axis. Each contour line represents a density increment $1 \text{ e.}\text{\AA}^{-2}$. The one-electron contour is broken.

Table 1. Preliminary co-ordinates of the subcell atoms, referred to subcell axes and centre

	X/a_s	Y/b_s	Z/c_s	X	Y	Z
C	0.068	0.036	-0.181	0.38	0.27	-0.46
H ₁	0.061	0.183	-0.188	0.34	1.36	-0.48
H ₂	0.280	0.000	0.012	1.56	0.00	0.03

given in Table 1. They refer to subcell axes and subcell centre as origin.

Determination of the structure of the main cell

Values of T were calculated for all the observed main cell reflexions and their structure factors were calculated using formula (1). The transformation between the main cell and subcell indices was effected by using the equation $H_k = s_k^i h_i$, where

$$s_k^i = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ s_1^3 & 0 & s_3^3 \end{bmatrix}$$

with $s_1^3 = 0.01526$ and $s_3^3 = 0.05353$.

Although comparatively good agreement was effected near integral values of L , the agreement between the observed and calculated structure factors was poor for intermediate values of L . It became apparent that, as the subcell contains centres of symmetry at $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$, either can be taken as the origin, but only one will coincide with the subcell centre which must be taken as the origin on building up the molecule. The choice of the second subcell origin

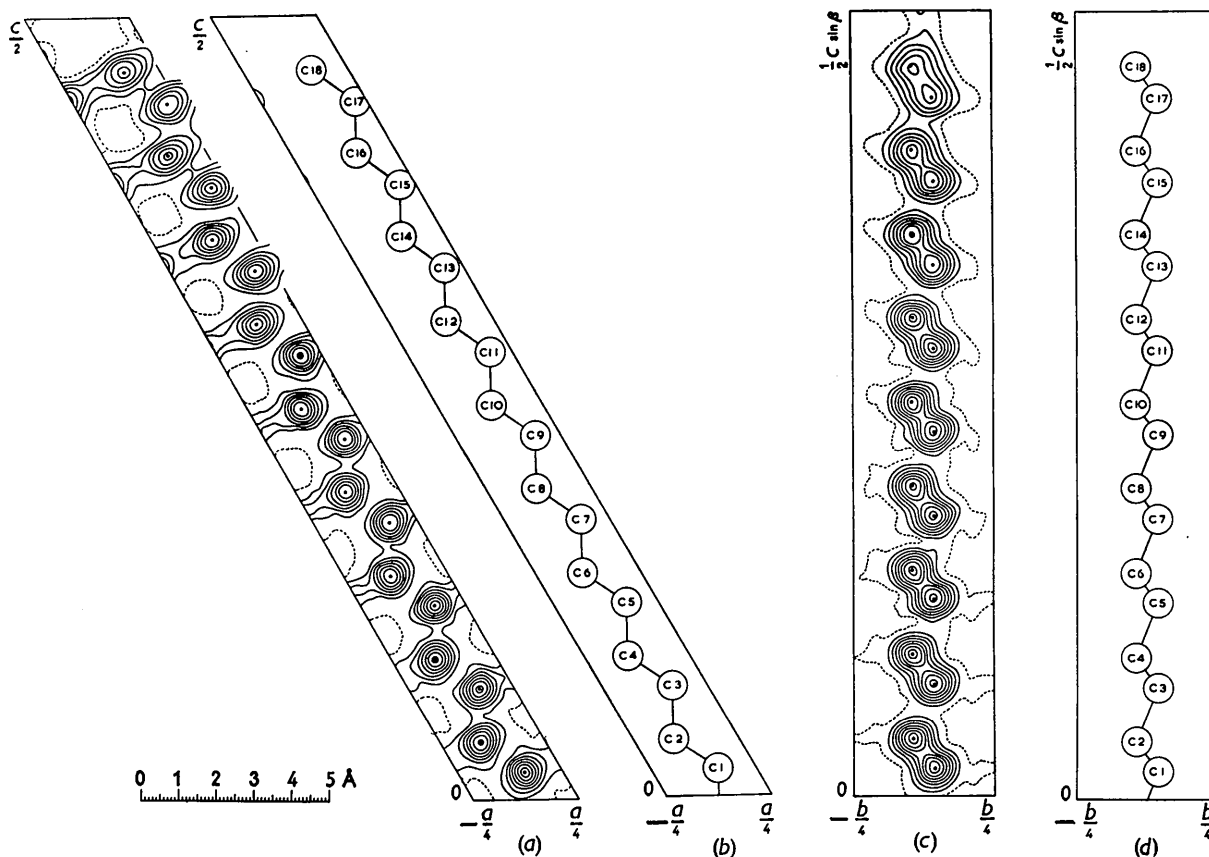


Fig. 2. (a, c) Electron-density projections of the main cell along the b and a axes. Contours at $1 \text{ e.}\text{\AA}^{-2}$, the one-electron contour being broken. (b, d) Numbering of the atoms corresponding to (a) and (c).

Table 2. *Atomic co-ordinates*

(Centre of symmetry as origin)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	<i>x'</i> (Å)	<i>z'</i> (Å)
C ₁	0.070	0.038	0.0173	0.39	0.28	0.84	-0.02	0.73
C ₂	-0.056	-0.038	0.0364	-0.31	-0.29	1.76	-1.17	1.54
C ₃	0.084	0.037	0.0705	0.47	0.28	3.41	-1.19	2.98
C ₄	-0.041	-0.040	0.0898	-0.23	-0.30	4.34	-2.34	3.79
C ₅	0.102	0.038	0.1243	0.57	0.28	6.01	-2.35	5.25
C ₆	-0.025	-0.040	0.1432	-0.14	-0.30	6.92	-3.51	6.05
C ₇	0.115	0.036	0.1775	0.64	0.27	8.58	-3.53	7.50
C ₈	-0.009	-0.040	0.1970	-0.05	-0.30	9.52	-4.68	8.32
C ₉	0.131	0.038	0.2312	0.73	0.28	11.18	-4.71	9.77
C ₁₀	0.005	-0.040	0.2506	0.03	-0.30	12.12	-5.86	10.59
C ₁₁	0.145	0.036	0.2843	0.81	0.27	13.75	-5.87	12.01
C ₁₂	0.020	-0.038	0.3040	0.11	-0.28	14.70	-7.04	12.84
C ₁₃	0.160	0.038	0.3377	0.89	0.28	16.33	-7.05	14.27
C ₁₄	0.040	-0.039	0.3580	0.22	-0.29	17.31	-8.20	15.12
C ₁₅	0.178	0.039	0.3911	0.99	0.29	18.91	-8.21	16.52
C ₁₆	0.057	-0.036	0.4114	0.32	-0.27	19.89	-9.35	17.38
C ₁₇	0.196	0.038	0.4444	1.09	0.28	21.49	-9.36	18.77
C ₁₈	0.074	-0.034	0.4647	0.41	-0.25	22.47	-10.52	19.63

as centre will give a different structure but will change only slightly the moduli of the structure factors near integral values of *L*. On transferring the subcell centre to $(0, 0, \frac{1}{2})$, the figure of merit of the main cell fell from 28.7 and 21.5% to 19.1 and 14.9%. The subcell coordinates of Table 1 refer to this centre as origin.

Fourier syntheses (Fig. 2) were carried out along the *b* and *a* axes using calculated signs. As the 001, 002 and 003 planes were obscured by the beam trap and 021 by the very intense 020, their calculated values were used in the syntheses. Carbon atoms are well resolved and there is some indication of the hydrogens. The electron density at the centres of the main peaks, consisting of a carbon and one superimposed hydrogen, falls from over 8 e.Å⁻² at the centre of the chain to over 6 e.Å⁻² at the ends. This suggests increasing thermal motion of the ends, although some of it may be due to the series-termination error.

Atomic co-ordinates were assigned to the atoms from the electron-density maps and are given in Table 2, where *x*, *y*, *z* refer to monoclinic axes and *x'*, *y*, *z'* to orthogonal axes *a*, *b*, *c'*. The molecular dimensions are given in Table 3.

Table 3. *Dimensions of the molecule*

Bond lengths between carbon atoms in the order C₁'-C₁, C₁-C₂, C₂-C₃, ..., C₁₇-C₁₈:

1.57, 1.52, 1.55, 1.52, 1.57, 1.52, 1.56, 1.52, 1.56, 1.53, 1.53, 1.55, 1.53, 1.55, 1.51, 1.53, 1.50, 1.54 Å.

Bond angles in the order C₁'-C₁-C₂, C₁-C₂-C₃, C₂-C₃-C₄, ..., C₁₆-C₁₇-C₁₈:

112.3, 111.7, 111.8, 111.3, 110.6, 111.0, 112.1, 112.1, 111.7, 110.9, 111.6, 111.7, 112.5, 112.0, 112.5, 113.1, 113.3°.

Redetermination of the structure of the subcell

The data of Tables 2 and 3 were obtained directly with reference to the Fourier syntheses, i.e. without any

assumption of chain periodicity. They may now serve to detect whether there are any deviations from periodicity and, if not, to obtain averaged bond lengths and angles.

If a regular structure is assumed for the chain, the co-ordinates *x*, *y*, *z* of the atoms will obey a linear law each, i.e.

$$x = m_x v + w_x, \text{ etc. ,}$$

where *m_x* is the displacement of each succeeding subcell in the *x* direction, *v* is the subcell number ranging from -9 to +8 and *w_x* is the subcell *x* co-ordinate of the atom.

The three groups of eighteen equations in each were solved by least squares and the following constants obtained, expressed in fractional main cell co-ordinates:

$$\begin{aligned} m_x &= 0.01549 \pm 0.00010, & w_x &= 0.06978 \pm 0.00053, \\ m_y &= 0.00001 \pm 0.00008, & w_y &= 0.03811 \pm 0.00044, \\ m_z &= 0.053496 \pm 0.000014, & w_z &= 0.016926 \pm 0.000077. \end{aligned}$$

Transforming these values into Ångström units, we obtain for the co-ordinates *x*₁, *y*₁, *z*₁ of the subcell point (001) the values

$$\begin{aligned} x_1 &= 0.08630 \pm 0.00058, & x'_1 &= -1.1715 \pm 0.0034, \\ y_1 &= 0.00007 \pm 0.00062, & & \\ z_1 &= 2.5865 \pm 0.0044, & z'_1 &= 2.2601 \pm 0.0041, \end{aligned}$$

and for the co-ordinates of the carbon atom in the subcell, both being referred to the main cell axes and orthogonal axes and origin:

$$\begin{aligned} x_2 &= 0.3887 \pm 0.0030, & x'_2 &= -0.0093 \pm 0.0037, \\ y_2 &= 0.2828 \pm 0.0033, & & \\ z_2 &= 0.8184 \pm 0.0040, & z'_2 &= 0.7151 \pm 0.0035. \end{aligned}$$

From the above data, the positions of all the carbon atoms were calculated for the whole molecule. Comparison of the calculated values with those of Table 2 revealed no indication of a bent or a systematically

distorted chain, the deviations being random and within experimental error. The average discrepancy of coordinates of individual atoms was $\pm 0.02 \text{ \AA}$ and the greatest discrepancy 0.04 \AA for C_{18} . One can thus conclude that the chain is periodic within experimental error and that the averaging of the bond lengths and angles over the chain is justified.

From the above data, new more accurate subcell dimensions were obtained:

$$a_s = 5.57 \pm 0.01, \quad b_s = 7.42 \pm 0.01, \quad c_s = 2.546 \pm 0.004 \text{ \AA}, \\ \beta_s = 117^\circ 24' \pm 5',$$

and the average bond lengths

$$C'_1-C_1 = 1.538 \pm 0.007 \text{ \AA} \quad (\text{bond across the centre of symmetry}),$$

$$C_1-C_2 = 1.529 \pm 0.010 \text{ \AA}.$$

The zigzag angle $C'_1-C_1-C_2$ is $112^\circ 1' \pm 21'$.

There is therefore no evidence of alternating bond lengths, both bond lengths being equal within experimental error.

The positions of hydrogens were now recalculated, assuming the same C-H bond lengths and angles as before, and are given in Table 4 referred to the subcell axes and centre. This table is thus comparable with Table 1.

Table 4. *Final co-ordinates of the subcell atoms, referred to the subcell axes and centre*

	X/a_s	Y/b_s	Z/c_s	X	Y	Z
C	0.0649	0.0381	-0.1836	0.361	0.283	-0.467
H ₁	0.049	0.179	-0.200	0.27	1.33	-0.51
H ₂	0.273	0.010	0.026	1.52	0.07	0.07

The arrangement of the subcell atoms in the projections along b_s and a_s axes is shown in Fig. 3. In the

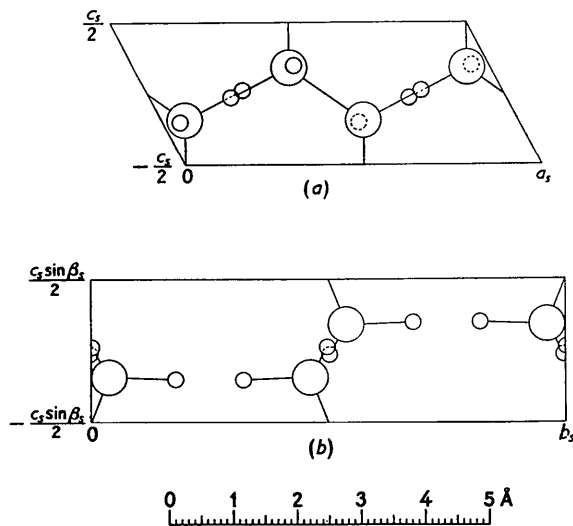


Fig. 3. Arrangement of the atoms in the projections of the subcell (a) along the b_s axis, (b) along the a_s axis. In the latter case, alternate C-C bonds are omitted.

projection along the a_s axis the alternate C-C bonds are omitted for clarity. The two general terms of the transformation matrix s_k^3 were recalculated and the following better values obtained:

$$s_1^3 = 0.015494, \quad s_3^3 = 0.053496.$$

The main cell structure factors were then recalculated and the figure of merit was found to have fallen to 16.7 and 13.8% for the $(h0l)$ and $(0kl)$ reflexions, indicating correctness of the refinement procedure. None of the structure factors (Table 5) was found to

Table 5. *Observed and calculated structure factors*

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	
000	-	580	2,0,17	8	6	4,0,13	23	21	0,2,18	39	-35
200	77	84	2,0,18	9	-7	4,0,18	<6	-12	0,2,19	64	-63
400	<6	0	2,0,19	10	7	4,0,17	<6	8	0,2,20	7	11
600	<4	4	2,0,20	10	-7	*	*	*	0,2,21	<5	-5
			2,0,21	11	8	403	<6	2	0,2,22	<5	2
			2,0,22	11	-8	402	<6	-3	*	*	*
020	324	300	2,0,23	12	9	401	16	-7	0,2,24	<7	2
040	110	104	2,0,24	13	-10	401	<7	0	0,2,25	<7	-4
060	20	0	2,0,25	14	11	*	*	*	0,2,26	7	6
			2,0,26	15	11	*	*	*	0,2,27	7	6
			2,0,27	16	-14	4,0,14	<7	2	0,2,28	31	-27
001	-	21	2,0,28	17	14	4,0,15	<6	-3	0,2,29	20	-17
002	-	22	2,0,29	18	-15	4,0,16	10	-9	0,2,30	8	8
003	-	23	2,0,30	19	16	4,0,17	<6	2	*	*	*
004	18	-22	2,0,31	20	17	4,0,18	22	-28	0,3,12	<5	-5
005	18	21	2,0,32	21	-18	4,0,19	8	9	0,3,13	<5	5
006	17	-21	2,0,33	22	19	*	*	*	0,3,14	6	-6
007	17	21	2,0,34	23	-20	6,0,21	27	22	0,3,15	8	8
008	17	-20	2,0,35	24	21	6,0,20	27	29	0,3,16	12	-10
009	16	20	2,0,36	25	-22	6,0,19	<6	-9	0,3,17	17	15
0,0,10	16	-19	2,0,37	26	23	6,0,18	<6	5	0,3,18	37	-33
0,0,11	16	18	2,0,38	27	-24	*	*	*	0,3,19	77	-68
0,0,12	14	-18	2,0,39	28	25	6,0,17	<5	-3	0,3,20	12	15
0,0,13	15	18	2,0,40	29	-26	6,0,16	<5	3	0,3,21	7	-7
0,0,14	16	-19	2,0,41	30	27	6,0,15	<6	-9	0,3,22	<6	4
0,0,15	18	21	2,0,42	31	-28	6,0,14	8	-10	0,3,23	<6	-3
0,0,16	24	-22	2,0,43	32	29	*	*	*	*	*	*
0,0,17	31	28	2,0,44	33	-30	019	<3	3	0,3,24	<7	4
0,0,18	57	-25	2,0,45	34	31	0,1,10	<3	-4	0,3,25	<7	-7
0,0,19	100	-96	2,0,46	35	-32	0,1,11	4	4	0,3,26	22	24
0,0,20	14	17	2,0,47	36	33	0,1,12	4	-5	0,3,27	15	14
0,0,21	7	-7	2,0,48	37	-34	0,1,13	5	5	0,3,28	9	-5
0,0,22	<5	23	2,0,49	38	35	0,1,14	<6	-6	*	*	*
0,0,23	<5	-2	2,0,50	39	-36	0,1,15	9	7	0,4,15	<5	5
0,0,24	<5	1	2,0,51	40	37	0,1,16	12	-9	0,4,16	<6	-6
0,0,25	<5	0	2,0,52	41	-38	0,1,17	17	12	0,4,17	7	8
0,0,26	<5	0	2,0,53	42	39	0,1,18	34	-28	0,4,18	15	-15
0,0,27	<6	0	2,0,54	43	-40	0,1,19	52	-54	0,4,19	24	-27
0,0,28	<6	0	2,0,55	44	41	0,1,20	11	11	0,4,20	<6	5
0,0,29	<6	0	2,0,56	45	-42	0,1,21	7	-6	0,4,21	<6	-2
0,0,30	<6	1	2,0,57	46	43	0,1,22	5	3	*	*	*
0,0,31	<6	-1	2,0,58	47	-44	0,1,23	<5	-2	0,4,25	<7	-2
0,0,32	<6	1	2,0,59	48	45	0,1,24	<5	1	0,4,26	<7	4
0,0,33	<6	-2	2,0,60	49	-46	*	*	*	0,4,27	14	-16
0,0,34	<6	3	2,0,61	50	47	0,1,25	<7	-2	0,4,28	8	-10
0,0,35	9	-5	2,0,62	51	-48	0,1,26	<7	-3	*	*	*
0,0,36	13	13	2,0,63	52	49	0,1,27	13	11	0,5,14	<6	-5
0,0,37	43	-37	2,0,64	53	-50	0,1,28	11	7	0,5,15	<6	6
0,0,38	25	-24	2,0,65	54	51	0,1,29	9	9	0,5,16	7	-8
0,0,39	10	10	2,0,66	55	-52	021	-	11	0,5,17	11	12
0,0,40	8	-7	2,0,67	56	53	022	-	12	0,5,18	23	-28
			2,0,68	57	-54	023	-	12	0,5,19	9	-9
			2,0,69	58	55	024	8	11	0,5,20	<7	13
			2,0,70	59	-56	025	8	-11	0,5,21	<7	-7
			2,0,71	60	57	026	8	-11	*	*	*
			2,0,72	61	-58	027	7	-11	0,5,25	<6	4
			2,0,73	62	59	028	7	-11	0,5,26	<6	-7
			2,0,74	63	-60	029	7	11	0,5,27	18	25
			2,0,75	64	61	0,2,10	7	-10	0,5,28	12	15
			2,0,76	65	-62	0,2,11	6	-10	0,7,15	<7	4
			2,0,77	66	63	0,2,12	6	-10	0,7,16	<7	-6
			2,0,78	67	-64	0,2,13	7	10	0,7,17	8	9
			2,0,79	68	65	0,2,14	9	-11	0,7,18	12	-19
			2,0,80	69	-66	0,2,15	10	-12	0,7,19	29	-40
			2,0,81	70	66	0,2,16	14	-13	*	*	*
			2,0,82	71	-67	0,2,17	20	-18	*	*	*
			2,0,83	72	68	94					

* Group of non-observed planes. Maximum values of F_o and $|F_c|$ as for adjoining non-observed planes.

change sign, so that the Fourier syntheses shown in Fig. 2 are final. The temperature factor B did not change.

Intermolecular distances

The standard molecule at the origin of the main cell was called A and the reflected molecule at $(\frac{1}{2}, \frac{1}{2}, 0)$ was called B . The shortest distances of approach between non-bonded atoms, assuming the positions calculated for the regular structure, were found to be:

$$C_1(A) \dots C_2(B) = 4.14, C_1(A) \dots C_1(B) = 4.20, \\ C_1(A) \dots C_3(B) = 4.20 \text{ \AA}.$$

The H-H distances were also calculated and found to range between 2.61 and 2.98 Å. The distance between the observed positions of the carbon atoms of the terminal methyl groups across the centre of symmetry at $(0, 0, \frac{1}{2})$ was found to be 3.91 Å.

Comparison with the orthorhombic form

If the a_s axis is displaced in the direction of the c_s axis by an amount corresponding to one zigzag of the chain, a transformed subcell is obtained, which, however, is not a true subcell of the structure, and which has the following dimensions:

$$a_0 = 4.945 \pm 0.01, \quad b_0 = 7.42 \pm 0.01, \quad c_0 = 2.546 \pm 0.004 \text{ \AA}, \\ \beta_0 = 90^\circ 11' \pm 7'.$$

This subcell agrees very closely with that of the orthorhombic form of *n*-paraffins and the angle β_0 does not differ significantly from 90° . The transformed atomic co-ordinates are given in Table 6, the departure from 90° being ignored.

Table 6. Co-ordinates of the subcell atoms, referred to the orthogonal subcell

	X'/a_0	Y'/b_0	Z'/c_0	X'	Y	Z'
C	0.0649	0.0381	-0.2489	0.321	0.283	-0.634
H ₁	0.049	0.179	-0.249	0.24	1.33	-0.63
H ₂	0.273	0.010	-0.249	1.35	0.07	-0.63

These co-ordinates correspond very closely with those derived from polythene by Bunn (1939) and also with those obtained by electron diffraction by Vainshtein & Pinsker (1950, 1951) for the orthorhombic *n*-paraffin. The agreement is close in spite of the fact that Bunn's work was carried out on the high polymer and the Russian work on an ill-defined mixture of *n*-paraffins, neither of which showed any well-defined main cell. The subcells only are compared. Note that Z'/c_0 does not differ significantly from $\frac{1}{4}$, and if the latter value is assumed the space group D_{2h}^{16} -*Pbnm* is obtained in agreement with that found by Bunn. The contention of Schoon (1938) as to the way in which monoclinic cells can be derived from the basic orthorhombic arrangement is thus very nearly true since β_s is very nearly equal to β , but the value of the monoclinic angle depends not only on the length of the zigzag unit but also to some extent on the end packing of the molecules and hence on the length of the hydrocarbon chain.

The plane containing the carbon atoms of the chain passes through the main cell origin, the subcell origin and the point C_1 and its equation referred to the orthogonal axes a' , b and c is given by $X' - 1.1347Y = 0$.

The plane then makes an angle of $41^\circ 23'$ with the b axis.

Discussion

The results of this work are in general agreement with the earlier investigations. The side packing of the molecular chains was found to be very similar to that of the orthorhombic paraffins. Schoon's contention as to the way in which the monoclinic form of the *n*-paraffins is derived from the orthorhombic form is basically correct. The results obtained from two projections suggest that the chains are regular within experimental error: in particular, no alternation in bond lengths can be detected. At most, there may be some slight distortion at the chain ends where the end effects of packing may be greatest, and perhaps an increase in temperature motion towards the ends, but the latter needs more detailed confirmation from study of termination errors. The periodicity of the chain permits substantially more accurate values of the atomic co-ordinates to be obtained. The averaged length of one zigzag of the chain is thus 2.546 ± 0.004 Å and the two C-C bond lengths are alternatively 1.538 ± 0.007 and 1.529 ± 0.010 Å. The combination of these two averages gives for the best value of a single bond in an aliphatic $-\text{CH}_2-\text{CH}_2-$ chain a value 1.534 ± 0.006 Å.

This is slightly shorter than the single carbon bond in diamond, which is 1.5445 Å, but whether the effect is real may be in doubt. The angle of the zigzag is, however, significantly different from the tetrahedral angle, being $112^\circ 1' \pm 21'$, which has been known since Ingold (1921) predicted the discrepancy.

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