

The Crystal Structure of Lower Paraffins

III. Pentane

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The crystal structure of pentane has been determined by two-dimensional Patterson and Fourier syntheses and refined by the method of least squares. The crystals are orthorhombic, space group *Pbcn* with four molecules in the unit cell. The unit cell dimensions are $a = 4.10 \pm 0.02 \text{ \AA}$, $b = 9.04 \pm 0.02 \text{ \AA}$, $c = 14.70 \pm 0.02 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. The average C—C bond length is $1.525 \pm 0.010 \text{ \AA}$, the average C—C repeat distance along the molecular chain is $2.535 \pm 0.010 \text{ \AA}$, and the average $\angle \text{CCC}$ is $112 \pm 0.50^\circ$. The shortest intermolecular C—C distances are all about 3.9 \AA .

The work reported herein forms the third part of a series of papers concerning the crystal structures of lower paraffins, the first and second parts being our papers on octane¹ and hexane.²

EXPERIMENTAL

The experimental techniques used for the study of pentane were the same as described earlier.¹ The purity of the sample was $99.95 \pm 0.03 \%$. The melting point of pentane is -131.5°C . During the exposures the temperature on the sample was kept at about -140 to -150°C .

Equi-inclination Weissenberg photographs were taken of zero, first, second, and third layer lines with rotation about the *a*-axis.

DETERMINATION OF SPACE GROUP AND UNIT CELL DIMENSIONS

The *b* and *c* axes were determined from a Debye-Scherrer diagram, which, because of orientation effects, showed the (*0kl*) reflections only. The *a*-axis was determined from rotation diagrams about this axis.

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The systematic extinctions were the following,

$$\begin{aligned} hkl & \text{ none} \\ 0kl & k = 2n + 1 \\ h0l & l = 2n + 1 \\ hk0 & h + k = 2n + 1 \end{aligned}$$

This leads to the space group $Pbcn$. However, since rather few ($hk0$) reflections are actually observable because of the short a - and b -axes and the experimental technique, the space groups $Pbc2_1$ and $Pbcm$ must also be regarded as possible ones.

The space group $Pbcm$ has an 8-fold general position and mirror planes at $z = 1/4$ and $3/4$ as the only point symmetry element. The pentane molecule is expected to have symmetry planes. Since there are 4 pentane molecules in the unit cell (see below), the space group, $Pbcm$, would require that the central carbon atom C_3 lies in a mirror plane, and that the molecular chain is parallel to the c -axis. It is, however, evident from the $P(uw)$ Patterson projection that the pentane molecules do not have their chain axes parallel to the c -axis of the unit cell. Consequently the space group $Pbcm$ could be excluded.

The centro-symmetric space group $Pbcn$ also has an 8-fold general position. Since the pentane molecule has no centre of symmetry, this point symmetry element in the space group must combine different molecules. The central carbon atom C_3 must lie on an n -glide plane. If the pentane molecule is planar and linear, the molecular plane would have to be normal to the ac -plane and the molecular axis parallel to this plane. The Patterson projections $P(uw)$ and $P(vw)$ indicate that both these requirements are fulfilled. Small deviations in the positions of the molecules would lead to the space group $Pbc2_1$ with a 4-fold general position of the atoms. The space group $Pbc2_1$ could therefore not be excluded. In fact refinements were performed on the basis of both space groups. When this had been done the correctness of $Pbcn$ was finally established.

CRYSTAL DATA

$$a = 4.10 \pm 0.02 \text{ \AA}$$

$$b = 9.04 \pm 0.02 \text{ \AA}$$

$$c = 14.70 \pm 0.02 \text{ \AA}$$

$$\alpha = \beta = \gamma = 90^\circ$$

Crystal system: Orthorhombic

Space group: $Pbcn$

Volume of unit cell: 545 \AA^3

Measured density (of the liquid at $+20^\circ\text{C}$) = 0.626 g/cm^3

Calculated density (of the crystals at about -145°C) = 0.880 g/cm^3

Number of molecules in the unit cell: 4

The (yz)-projection

The structure was solved in this projection by means of the $P(vw)$ Patterson projection shown in Fig. 1. The first set of calculated structure factors gave an R -value of 0.25 for the 63 observed reflections. (The total number of observable ($0kl$)-reflections are 89).

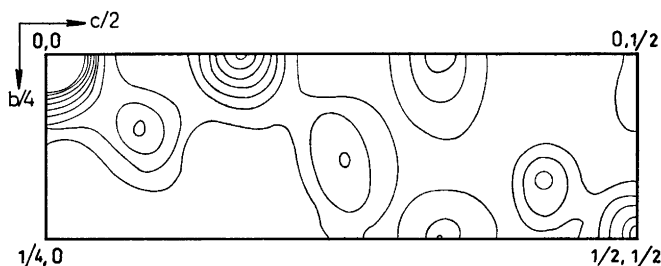


Fig. 1. Patterson projection along the a -axis of pentane. Contours are at equal, arbitrary intervals.

Least squares refinements were then undertaken, at first on the basis of the space group $Pbc2_1$, which in the (yz) -projection has the symmetry $pg1$. The hydrogens were included in the calculations. Pairs of overlapping hydrogens were treated as one atom with scattering power twice that of a single hydrogen atom. The parameters being refined were the (yz) -coordinates and the individual isotropic temperature factors of the carbon atoms and the (yz) -coordinates of the hydrogens. The latter were assigned a constant B -value of 2.4. After 15 cycles of refinements the R -factor had dropped to 0.049. In the projection the molecular axis formed an angle of about 1° with the c -axis.

The projection was then refined on the assumption of space group $Pbcn$ (*i.e.* plane group pgm). The number of symmetrically independent atoms is here only 8.5 (*i.e.* 2.5 carbons and 6 hydrogens). The results of the calculations based on plane group $pg1$ were utilized to some extent as a starting point for the least squares calculations in this case. The parameters to be refined in the first three cycles were the y -coordinates and isotropic temperature factors of C_1 , C_2 , and C_3 , the z -coordinates of C_1 and C_2 , and the scale factor. This brought the R -factor down from 0.074 to 0.067. Then the (yz) -coordinates of the hydrogens were refined in two cycles, the final R being 0.056. In view of the much lower number of parameters in this case, this result seems to indicate that $Pbcn$ is just as likely to be the correct space group for the structure as $Pbc2_1$. The (yz) -coordinates of the hydrogens are given in Table 4.

The (xz) -projection

The 36 observed $(h0l)$ intensities were obtained from the $(0kl)$, $(1kl)$, $(2kl)$, and $(3kl)$ equi-inclination diagrams. They were brought on the same relative scale by a simple method described earlier¹ and the $P(uv)$ Patterson projection shown in Fig. 2 was calculated. From this map together with the known (yz) -coordinates fairly good relative x -coordinates for the atoms within the molecule could be established. The displacement of the molecules with respect to each other still had to be determined. The $(h0l)$ -structure factors were calculated for intervals in X_3 of 0.05, where X_3 is the relative x -coordinate of the central carbon atoms in two molecules. The best correlation with the observed structure factors were obtained for $X_3 = 0.50$ ($R = 0.27$). Least squares refinement were then undertaken, including now the hydrogen atoms. Although the

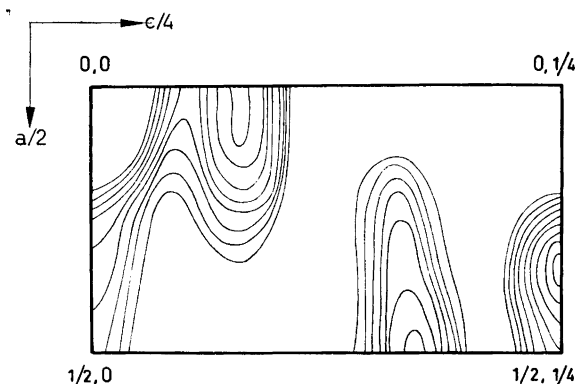


Fig. 2. Patterson projection along the b -axis of pentane. Contours are at the same intervals as in Fig. 1.

thermal vibrations are no doubt definitely anisotropic in this projection, the available data were not sufficient to justify those vibrations to be taken into account. At the beginning of the calculations all atoms were therefore assigned the same, overall B -value of 2.6, as indicated by Wilson's method. Only the (xz) -coordinates and the B -values of the carbons were refined.

After 13 cycles of refinements the R -factor had dropped to 0.073. During these refinements the relative displacement of the molecular central carbon atoms had changed from $X_3 = 0.50$ to $X_3 = 0.4914$. Consideration of the

Table 1. Fractional atomic coordinates and temperature parameters for the three alternative solutions of the pentane structure.

Alternative A: Space group $Pbcn$					
	x	y	z	$B(yz)$	$B(xz)$
C_1	-0.1993	0.1313	0.0870	2.90	2.85
C_2	-0.1003	0.0376	0.1683	2.68	3.10
C_3	0.0000	0.1319	0.2500	2.45	3.05
Alternative B: Space group $Pbc2_1$ relative $X_3 = 0.4914$					
	x	y	z	$B(yz)$	$B(xz)$
C_1	-0.1730	0.1242	0.0852	2.55	0.63
C_2	-0.0794	0.0373	0.1684	3.11	1.38
C_3	0.0043	0.1317	0.2500	2.40	3.62
C_4	0.1205	0.0371	0.3318	2.46	4.16
C_5	0.2370	0.1398	0.4111	3.08	3.98
Alternative C: Space group $Pbc2_1$ relative $X_3 = 0.6036$					
	x	y	z	$B(yz)$	$B(xz)$
C_1	-0.2370	0.1242	0.0852	2.55	4.15
C_2	-0.1459	0.0373	0.1684	3.11	3.60
C_3	-0.0518	0.1317	0.2500	2.40	3.18
C_4	0.0543	0.0371	0.3318	2.46	1.98
C_5	0.1730	0.1398	0.4111	3.08	1.04

Table 2. Interatomic distances in pentane resulting from three different possible refinement schemes.

Space group:	<i>Pbcn</i>	<i>Pbc2₁</i>	
		$X_3 = 0.4914$	$X_3 = 0.6036$
Distances			
C ₁ —C ₂	1.520	1.504	1.501
C ₂ —C ₃	1.529	1.511	1.522
C ₃ —C ₄		1.551	1.539
C ₄ —C ₅		1.565	1.568
C ₁ —C ₃	2.531	2.530	2.539
C ₂ —C ₄	2.538	2.538	2.538
C ₃ —C ₅		2.555	2.543

Table 3. Comparison of observed and calculated (*Ok*l) and (*h*0l) structure factors for pentane.

<i>hkl</i>	<i>F_o</i>	<i>F_c</i>	<i>hkl</i>	<i>F_o</i>	<i>F_c</i>	<i>hkl</i>	<i>F_o</i>	<i>F_c</i>
002	24.8	-26.2	040	14.2	-14.6	086	12.0	-11.8
004	19.4	-20.4	041	4.6	-4.2	087	3.2	-3.0
006	15.4	-14.8	042	8.2	-8.2	088	2.6	2.4
008	9.0	-9.2	043	2.8	2.6	0811	5.4	5.2
0010	4.4	-4.4	044	6.8	-6.4	0812	4.2	4.8
0012	26.2	27.2	045	15.6	14.6	0813	4.6	-5.2
0014	9.2	-8.6	046	33.2	33.2	0.10.0	6.2	-7.0
0016	4.6	-3.8	047	15.6	-15.4	0.10.1	7.6	-8.6
0018	2.6	-2.0	048	8.8	-7.8	0.10.2	2.4	2.4
020	29.4	30.6	049	2.2	-1.6	0.10.4	2.0	1.6
021	V.S		0410	4.6	-4.0	104	10.8	9.6
022	18.8	-19.2	0211	3.6	3.0	108	6.2	-6.0
023	20.8	-20.6	0412	6.6	-5.8	1010	14.2	-15.0
024	14.0	-13.2	0413	3.2	-3.0	1012	5.8	5.2
025	21.6	-21.2	0417	3.4	3.4	1014	9.8	9.4
026	31.4	34.6	060	8.0	8.8	1018	1.8	-1.0
027	17.2	16.0	062	4.0	-3.6	202	14.8	-17.2
028	11.8	-10.8	063	4.2	4.4	204	10.0	10.0
029	6.8	6.2	065	16.4	16.6	206	7.2	6.4
0210	6.6	-5.8	066	3.0	-2.4	208	5.0	5.8
0211	12.0	12.2	067	18.4	-17.6	2010	11.0	-11.2
0212	7.0	6.6	069	2.4	-2.6	2014	3.6	-4.6
0213	15.2	-14.4	0612	4.2	4.0	2016	4.4	4.6
0214	4.6	-4.4	0615	1.8	2.0	302	3.0	3.0
0215	2.8	-2.0	080	7.8	8.2	304	11.4	12.6
0218	5.0	4.8	081	8.4	-8.8	308	7.4	9.2
			085	4.2	3.8	3010	3.0	-2.6

intermolecular C—C distances suggested, however, that a movement of the molecule in the opposite direction might be slightly more favourable. When this was tried least squares refinements brought the molecule further out in this direction, giving $X_3 = 0.6036$ and $R = 0.064$, *i.e.* the correlation was very good in both cases although the coordinates were substantially different.

Table 4. Fractional (yz)-coordinates of the hydrogen atoms of pentane.

	Bonded to	y	z
H_1	C_1	0.074	0.033
$(H_2 + H_3)$	C_1	0.200	0.086
$(H_4 + H_5)$	C_2	-0.025	0.170
$(H_6 + H_7)$	C_3	0.192	0.250

Finally the (xz)-projection was refined on the basis of space group $Pbcn$ (*i.e.* plane group pmg). The hydrogens were included in the calculated structure factors, but their parameters were kept constant during the least squares refinements. The final R -value was 0.105 for the 26 observed ($h0l$)-reflections. The final B -values of the carbon atoms were all reasonable in this case ($B_1 = 2.85$, $B_2 = 3.10$, $B_3 = 3.05$), whereas after the refinements based on plane group $pm1$ they varied within wide limits, namely from 0.63 to 4.16 in the first case and from 1.04 to 4.15 in the second.

DISCUSSION

The fractional atomic coordinates and temperature parameters for the three alternative solutions of the pentane structure are listed in Table 1. The corresponding interatomic distances are given in Table 2.

It is clearly seen from these tables that refinements based on the assumption of space group $Pbcn$ leads to the most reasonable B -values and interatomic distances. It is therefore concluded that $Pbcn$ is the correct space group for the structure. The ($0kl$) and ($h0l$) structure factors calculated on this basis are compared to the observed ones in Table 3.

The bond angles are

$$\angle C_1C_2C_3 = 112.2^\circ, \quad \angle C_2C_3C_4 = 112.2^\circ$$

with an estimated accuracy of $\pm 0.5^\circ$.

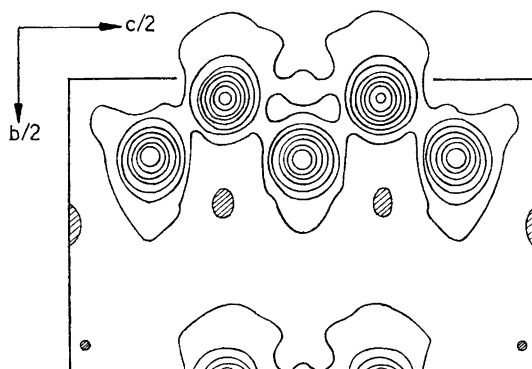


Fig. 3. The final (yz) electron density projection of pentane. Contours are at intervals of $1 \text{ e}/\text{\AA}^2$, negative areas shaded.

The (yz)- and (xz)-projections of the electron density is shown in Figs. 3 and 4, and the packing of the molecules is illustrated in Fig. 5, where also the shortest intermolecular C—C distances are indicated. These are all

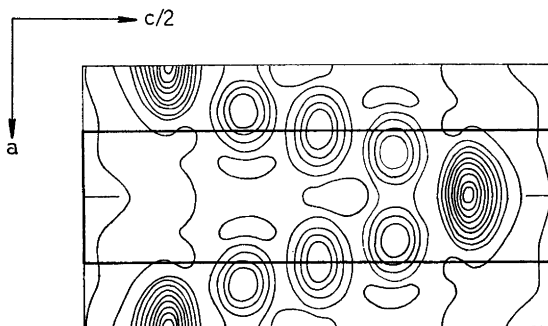


Fig. 4. The final (xz) electron density projection of pentane. Contours are at intervals of $1 \text{ e}/\text{\AA}^2$, first contour at $1 \text{ e}/\text{\AA}^2$.

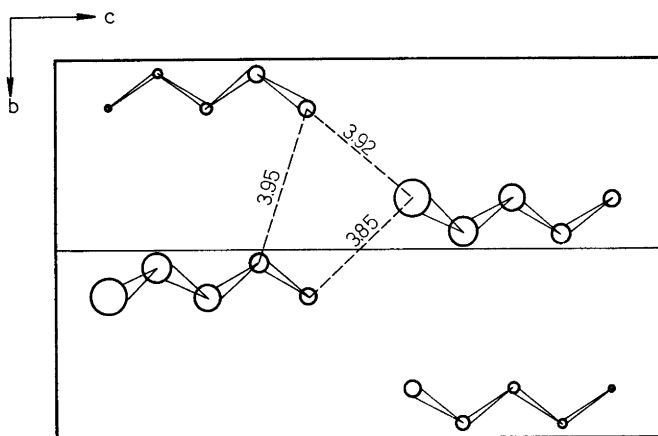


Fig. 5. A schematic drawing showing how the pentane molecules pack in the crystal. Some of the shortest intermolecular carbon-carbon distances are given.

"normal" van der Waal's contacts of about 3.9 \AA (3.85 , 3.92 , and 3.95 \AA). The particular mode of packing in this structure is quite distinct from any other paraffin structure that has been published so far. In all other orthorhombic crystals of paraffins the molecules are mutually parallel with their chain axes normal to the basal plane. The chain axes of the pentane molecules are neither parallel to the c -axis nor to each other. In other words, the pentane molecules are evidently too short to show the characteristics of typical long-chain molecules. In fact the "normal" orthorhombic paraffin structure has

been found for tridecane and undecane, but not for nonane and heptane, which are both triclinic with two molecules in the unit cell.^{3,4}

Acknowledgement. The research reported in this document has been made possible through the support and sponsorship of the *U.S. Department of Army*, through its European Research Office. Our thanks are also due to Mrs. L. Bryn and Mrs. T. L. Rolfsen for their help in carrying out the intensity measurements and some of the calculations, and to other members of the staff for many valuable discussions.

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Received December 2, 1963.