

The Crystal Structure of Lower *n*-Paraffins. II. *n*-Hexane

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The crystal structure of *n*-hexane has been determined by two-dimensional ordinary and generalized Patterson syntheses and refined by ordinary and generalized Fourier projections and the method of least squares. The crystals are triclinic, space group $P\bar{1}$, with one molecule in the unit cell. The unit cell dimensions are $a = 4.17 \pm 0.02$ Å, $b = 4.70 \pm 0.02$ Å, $c = 8.57 \pm 0.02$ Å, $\alpha = 96.6 \pm 0.3^\circ$, $\beta = 87.2 \pm 0.3^\circ$, and $\gamma = 105.0 \pm 0.3^\circ$. The average C—C bond length is 1.53 ± 0.01 Å, the average C—C repeat distance along the chain of the molecule is 2.56 ± 0.01 Å, and the average $\langle CCC \rangle$ is $113.9 \pm 0.5^\circ$. The intermolecular C— — — C distances are all normal (*i.e.* about 4.0 Å) except for the head-to-tail $-\text{CH}_2-\text{ — — — }-\text{H}_2\text{C}-$ contact, which is only 3.62 ± 0.02 Å.

The work reported herein forms the second part of a series of papers concerning the crystal structures of lower *n*-paraffins, the first part being our paper on *n*-octane¹.

EXPERIMENTAL

The experimental techniques used for the study of *n*-hexane were the same as described earlier¹. In this case equi-inclination Weissenberg diagrams of zero and second layer lines were obtained with rotation about the *a*-axis.

CRYSTAL DATA

The unit cell dimensions were determined in the same way as described in the previous article¹. The crystal data are the following

$$\begin{array}{ll} a = 4.17 \pm 0.02 \text{ \AA} & \alpha = 96.6 \pm 0.3^\circ \\ b = 4.70 \pm 0.02 \text{ \AA} & \beta = 87.2 \pm 0.3^\circ \\ c = 8.57 \pm 0.02 \text{ \AA} & \gamma = 105.0 \pm 0.3^\circ \end{array}$$

Crystal system: Triclinic

Space group: $P\bar{1}$ Volume of the unit cell: 161 Å³Measured density (of the liquid at +20°C) = 0.6603 g/cm³Calculated density (of the crystal at about -115°C) = 0.888 g/cm³

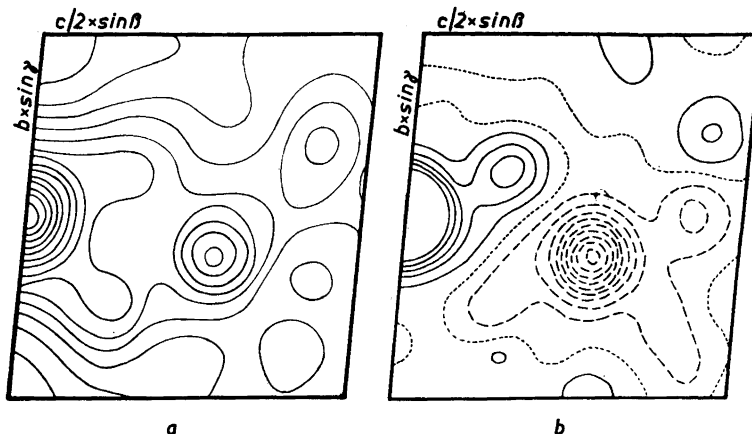


Fig. 1a. The $P_0(vw)$ ordinary Patterson projection along the a -axis of n -hexane. Contours are at equal arbitrary intervals.

Fig. 1b. The real part, $C_1(vw)$, of the $P_2(vw)$ generalized Patterson projection along the a -axis of n -hexane. Contours are at equal, arbitrary intervals zero contour dotted, negative contours broken.

The (yz)-projection. The structure was solved in this projection by means of the Patterson synthesis shown in Fig. 1a. The projection was refined through several Fourier and difference syntheses and finally by the method of least squares. The final projection of the electron density is shown in Fig. 2.

In the least squares refinements of this projection, the three pairs of overlapping hydrogens were treated as single atoms with scattering power twice that of hydrogen. Initial hydrogen coordinates were obtained from a Fourier synthesis from which the carbon atoms had been subtracted. The hydrogens were assigned a uniform, isotropic temperature factor, B , of 2.4, in accordance with the overall value as determined by Wilson's method. The carbon atoms were treated as isotropic. Three of the strongest reflections, (001), (01 $\bar{1}$) and

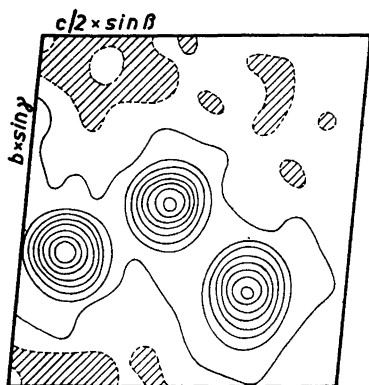


Fig. 2. The final (yz) electron density projection of n -hexane. Contours are at intervals of $1 \text{ e}/\text{\AA}^2$ negative areas shaded.

Table 1. Comparison of observed and calculated (*Ok**l*) structure factors for *n*-hexane.

<i>Ok</i> <i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>Ok</i> <i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>Ok</i> <i>l</i>	<i>F</i> _o	<i>F</i> _c
001	4.6	6.0	015	3.7	3.7	03— 1	2.9	— 2.9
2	5.9	6.4	6	5.4	— 5.3	1	1.2	1.4
3	6.3	6.7	7	5.7	— 5.9	2	7.5	— 7.3
4	0.8	— 0.9	10	0.6	0.8	3	4.4	— 4.1
5	1.6	1.7	02—10	0.8	0.5	4	1.4	1.2
6	1.1	— 1.2	— 9	1.0	— 0.3	8	1.1	— 0.4
7	7.2	— 7.9	— 8	1.0	— 0.9	04— 8	1.7	1.8
8	2.2	— 2.4	— 6	1.7	— 1.5	— 7	1.0	— 1.1
9	1.5	1.2	— 5	16.0	5.4	— 6	1.6	1.6
10	1.3	— 1.3	— 4	10.0	9.5	— 5	3.3	3.1
01—11	1.9	— 2.5	— 3	1.0	— 1.2	— 2	2.7	— 2.7
—10	1.1	— 0.7	— 2	0.9	— 0.7	— 1	3.1	— 3.2
— 9	1.2	1.0	— 1	4.4	4.6	0	1.3	1.5
— 8	3.9	— 3.8	0	1.6	— 1.4	1	1.7	— 1.5
— 7	3.0	— 2.8	1	3.1	3.1	2	4.3	— 4.3
— 5	1.4	1.4	2	6.4	— 5.9	3	0.7	— 0.5
— 4	11.9	12.3	3	12.2	—12.1	5	1.3	1.3
— 3	6.4	6.2	4	0.9	0.9	6	1.8	1.9
— 2	8.7	— 9.1	6	4.0	— 3.6	05— 6	0.6	1.0
— 1	11.0	17.3	7	1.0	— 0.9	— 3	1.1	— 0.9
0	10.0	18.6	9	1.1	1.0	— 2	3.8	— 4.1
1	2.8	— 2.8	03— 8	1.9	1.8	— 1	1.1	— 1.1
2	1.0	0.9	— 5	6.1	5.9	0	0.8	0.8
3	11.8	—11.9	— 4	3.2	3.0	1	1.5	— 1.6
4	5.0	— 4.8	— 3	0.8	— 0.8	2	0.8	— 0.7

(010), were left out because they were obviously strongly influenced by extinction.

The observed and calculated structure factors are compared in Table 1. The final agreement factor for the 75 observed (*Ok**l*)-reflections included in the least squares refinements is 0.064. (The total number of theoretically observable (*Ok**l*)-reflections is 104.)

The x-coordinates. Because the crystals always grew along the shortest axis, the *a*-axis, one was restricted to one single rotation axis for the exposures. In this case it was decided to use the method of generalized projections. This method has been developed and described by several authors, notably by Clews and Cochran², Dyer³, and Cochran and Dyer⁴, and later by Rumanova⁵. For details of calculation and interpretation reference should be made to one or more of these papers. The generalized Patterson projection along the *a*-axis may be expressed as

$$P_H(vw) = C_H(vw) + iS_H(vw) \quad (1)$$

where

$$C_H(vw) = \frac{a}{V} \sum_k \sum_l |F(Hkl)|^2 \cos 2\pi(kv + lw) \quad (2)$$

and

$$S_H(vw) = \frac{a}{V} \sum_k \sum_l |F(Hkl)|^2 \sin 2\pi(kv + lw) \quad (3)$$

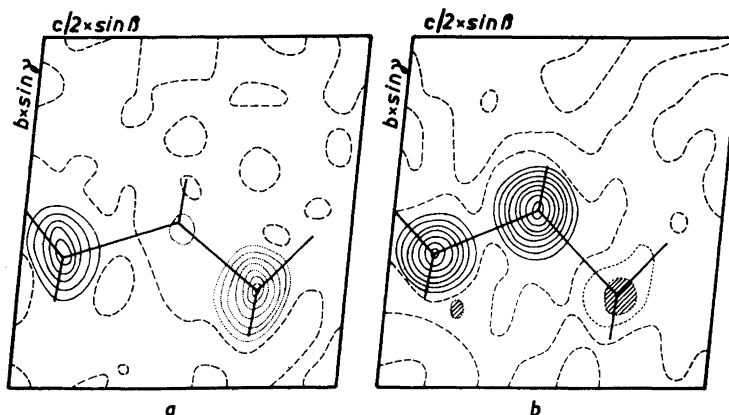


Fig. 3. a) The imaginary part, $S_2(yz)$, of the $\rho_2(yz)$ generalized electron density projection along the a -axis of n -hexane. Contours are at equal, arbitrary intervals.
 b) The real part, $C_2(yz)$, of the $\rho_2(yz)$ generalized electron density projection along the a -axis of n -hexane. Contours are at the same intervals as in a).

where H is a whole, positive number. In the present case it was 2. Corresponding expressions apply for the generalized electron density projection of centrosymmetrical structures. By eqn. (2) a map can be calculated from which the u -coordinates of the Patterson peaks can be determined by comparing the peak heights of this map to the corresponding peak heights of the ordinary Patterson projection, provided that the two sets of data which are involved, the $|F(0kl)|^2$'s and $|F(2kl)|^2$'s, are on the same scale. Another method is to compare the heights of corresponding peaks on maps calculated according to eqns. (2) and (3). In this case no scaling is involved.

In the present case the first method was employed. The $C_2(vw)$ -synthesis for n -hexane is shown in Fig. 1b. From this map and that of Fig. 1a approximate x -coordinates could be evaluated for the three carbon atoms in the asymmetric unit. Based on these coordinates generalized electron density projections were calculated. From these projections refined values for the x -coordinates were obtained, changing the signs of a few of the weak $(2kl)$ -reflections. The refined generalized electron density projections are shown in Fig. 3.

Table 2. Fractional atomic coordinates and temperature parameters for n -hexane.

	x	y	z	$B(yz)$
C_1	0.2795	0.2322	0.3482	2.95
C_2	0.1366	-0.0065	0.2153	2.62
C_3	0.0723	0.1180	0.0664	2.35
H_1		0.146	0.428	
(H_2, H_3)		0.356	0.335	
(H_4, H_5)		-0.131	0.223	
(H_6, H_7)		0.248	0.057	

Table 3. Relative $F_o(2kl)$ -values with calculated signs.

$2kl$	F_o	Sign	$2kl$	F_o	Sign
201	5.7	-	209	14.6	-
253	8.1	-	208	14.0	-
250	10.2	-	205	13.7	+
251	9.8	-	204	7.9	+
254	5.8	+	203	16.1	-
257	5.1	+	202	46.4	+
244	10.3	-	201	45.8	+
243	15.6	-	200	8.6	-
240	9.3	-	201	3.5	+
243	9.2	+	202	11.8	-
244	17.8	+	203	8.3	-
247	8.3	+	204	10.3	+
237	7.3	-	205	21.1	-
234	22.9	-	206	28.9	-
233	10.7	-	219	9.6	-
232	3.9	+	216	15.1	+
230	15.3	+	215	27.9	+
233	29.4	+	214	12.2	-
234	16.8	+	212	44.9	+
235	5.7	-	211	13.3	+
239	3.9	+	211	13.0	-
228	12.8	-	212	37.7	-
227	11.2	-	213	5.8	+
226	8.7	+	215	28.5	-
225	10.5	-	216	7.4	-
224	16.6	-	219	13.3	+
222	3.2	-	226	27.7	+
221	32.5	+	225	16.1	+
220	28.8	+	224	8.1	-
221	14.9	-	223	10.1	+
222	14.3	+	222	8.6	+
223	32.2	+	220	4.4	+
224	4.1	+	221	36.5	-
225	4.5	-	222	24.2	-
226	6.9	-	223	10.1	+
227	10.6	-	224	8.2	-
228	5.0	+	228	15.3	+
229	3.5	-	238	4.7	-
2210	13.0	-	237	8.4	+
219	6.1	-	236	18.1	+
218	21.2	-	233	9.1	-
215	9.4	-	232	12.6	-
213	8.9	-	231	8.4	+
212	11.0	+	230	9.7	-
211	55.0	+	231	28.7	-
211	6.7	-	235	9.3	+
212	20.0	+	237	4.0	+
213	19.7	+	244	5.7	-
214	3.0	+	243	19.9	-
215	3.5	-	242	6.9	-
216	26.5	-	241	3.6	+
217	8.4	-	240	12.2	-
218	6.9	+	241	8.8	-
219	10.3	-	244	14.5	+
2110	6.9	-			

Table 4. Interatomic distances and bond angles of *n*-hexane.

<i>C—C distances</i>	<i>C—H distances in the (yz-)plane</i>
$C_1-C_2 = 1.530 \text{ \AA}$	$C_1-H_1 = 0.82 \text{ \AA}$
$C_2-C_3 = 1.526 \text{ \AA}$	$C_1-(H_4, H_5) = 0.58 \text{ \AA}$
$C_3-C_4 = 1.524 \text{ \AA}$	$C_2-(H_4, H_5) = 0.58 \text{ \AA}$
$C_1-C_3 = 2.557 \text{ \AA}$	$C_3-(H_4, H_7) = 0.60 \text{ \AA}$
$C_2-C_4 = 2.559 \text{ \AA}$	
$C_1 \cdots \cdots C_1' = 3.62 \text{ \AA}$ (across the centre of symmetry at $(1/2, 1/2, 1/2)$)	
<i>Angles</i>	
$C_1-C_2-C_3 = 113.6^\circ$	
$C_2-C_3-C_4 = 114.1^\circ$	
$C_2-C_1 \cdots \cdots C_1' = 172^\circ$	
<i>Mean values</i>	
The C—C bond length	$1.53 \pm 0.01 \text{ \AA}$
The C—C—C bond angle	$114 \pm 1^\circ$
The repeat distance along the molecular chain	$2.56 \pm 0.01 \text{ \AA}$

The final fractional atomic coordinates are given in Table 2. The observed $F(2kl)$ -values and their calculated signs are listed in Table 3.

DISCUSSION

The calculated interatomic distances and bond angles are given in Table 4. The deviations quoted in the table is to be regarded as total estimates of the uncertainties in the distances and bond angles given. The *n*-hexane molecules pack in the extended *trans* configuration, *i.e.* the molecules are planar. The order of magnitude of most of the intermolecular C—C distances shows good agreement with the van der Waals' radius of $2.0 \pm 0.1 \text{ \AA}$ usually found for CH_2 - or CH_3 -groups. The only exception is the rather close approach of $3.62 \pm 0.02 \text{ \AA}$ between the terminal CH_3 -groups across the centre of symmetry at $(1/2, 1/2, 1/2)$. This is, however, in excellent agreement with what was found for *n*-octane¹. The agreement in bond lengths and bond angles is also fairly good.

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