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The Crystal Structure of Lower *n*-Paraffins. I. *n*-Octane

N. NORMAN and H. MATHISEN

Central Institute for Industrial Research Blindern - Oslo, Norway

The crystal structure of *n*-octane has been determined by two-dimensional Patterson and Fourier syntheses and refined by two-dimensional difference syntheses 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 $a = 4.16 \pm 0.02$ Å, $b = 4.75 \pm 0.02$ Å, $c = 11.00 \pm 0.02$ Å, $\alpha = 94.8 \pm 0.3°$, $\beta = 84.5 \pm 0.3°$, and $\gamma = 105.1 \pm 0.3°$. The average C–C bond length is 1.53 ± 0.01 Å, the average C– –C repeat distance along the molecular chain is 2.54 ± 0.01 Å and the average <CCC is $112.0 \pm 0.5°$. The intermolecular C– – – –C distances are all normal (*i.e.* about 4.0 Å) except for the head-to-tail $-CH_2- - - - -H_2C-$ contact, which is only 3.62 ± 0.02 Å.

Only a few X-ray investigations of the crystal structures of the lower members of the *n*-paraffin series have been reported in the literature. McLennan and Plummer [1], in their paper dating back to 1926, concluded that *n*-octane crystallizes both in the orthorhombic and the monoclinic systems, the two modifications occurring simultaneously in different proportions depending on the freezing conditions. In 1930 Müller [2] found that crystals of *n*-octane exist in what he called "the second form", the long spacing of this form being somewhat shorter than that of "the first form", which is identical with the usual orthorhombic modification where the molecular chains are normal to the basal plane. Both these investigations were made on powder samples.

In 1948 Müller and Lonsdale [3] published the unit cell parameters for the triclinic modification of *n*-$C_{18}H_{38}$. In their paper it is stated that this low-temperature modification is iso-structural with that of other even *n*-paraffins from *n*-$C_{22}H_{46}$ down to *n*-C_6H_{14}.

It seems that below *n*-$C_{18}H_{38}$ no single crystal X-ray work has been reported. It was therefore decided to study the crystal structures of some of these compounds, the particular range chosen being *n*-octane, *n*-heptane, *n*-hexane, and *n*-pentane. The work reported here forms a part of this programme [4,5].

EXPERIMENTAL

The *n*-octane sample used was supplied by the Chemical Research Laboratory, Teddington, Middlesex, England. Its purity as quoted by the manufacturer was 99.63 ± 0.18 %. The single crystals were grown in sealed capillaries of Lindeman glass mounted on the head of a Nonius Weissenberg camera equipped for low-temperature work. The inner diameter of the capillaries used was approximately 0.2 mm. The desired lowering of the temperature was obtained by passing compressed gaseous nitrogen through copper spiral tubes immersed in liquid nitrogen and further through a Dewar tube mounted along the centre line of the Weissenberg camera.

Oscillation and equi-inclination Weissenberg diagrams of zero, first, second, and third layer lines were obtained with rotation about the *a*-axis. Unfiltered Cu-radiation and multiple film technique were used.

The same cooling arrangements as described above was also used in connection with a 14.38 mm Debye-Scherrer camera. By freezing the liquid *n*-octane rapidly, a sample consisting of partly oriented needles was obtained, giving a Debye-Scherrer diagram which was dominated by coarse arcs of the (0*kl*) powder lines. Much smoother lines were obtained by dividing the total exposure time of 2 h into intervals of about 10 min, the sample being melted and refrozen between each interval. During all exposures the crystals were kept at a temperature of about 20 – 25°C below the melting point of −56.5°C.

The Weissenberg reflections were indexed in the usual way, and the blackening measured by a Jarrel-Ash-Microphotometer and converted to relative intensities. The intensities were corrected for the Lorentz-Polarization factor. The necessary correlation of intensities of reflections on different layer lines was performed by the method described by Hägg [6].

CRYSTAL DATA

The *a*-axis was determined from an oscillation diagram about this axis. The three reciprocal parameters b^*, c^*, and a^* were determined by a least squares adjustment to the observed positions of 19 different (0*kl*) reflections which could be indexed on the above-mentioned Debye-Scherrer diagram. The two remaining parameters, the reciprocal angles β^* and γ^*, were determined by observing the displacements of the (1*kl*), (2*kl*), and (3*kl*) reciprocal nets relative to the (0*kl*) net. All reciprocal parameters was refined by means of the powder method, including now reflections with $h = 0$. The crystal data are the following

$a = 4.16 \pm 0.02$ Å	$\alpha = 94.8 \pm 0.3°$
$b = 4.75 \pm 0.02$ »	$\beta = 84.5 \pm 0.3°$
$c = 11.00 \pm 0.02$ »	$\gamma = 105.1 \pm 0.3°$

Crystal system: Triclinic
Space group: $P\bar{1}$
Volume of the unit cell: 215 Å^3
Measured density (of the liquid at + 20°C) 0.7036 g/cm^3
Calculated density (of the crystal at about −70°C): 0.858 g/cm^3

The (yz)-projection. The (*yz*)-projection of the structure was solved by the two-dimensional Patterson synthesis, $P(v,w)$, shown in Fig. 1. The molecule as such is in a special position, *i.e.* a centre of symmetry. The direction of the molecular axis is determined by the position of the Patterson peak at about 2.5 Å (the $C_1 - - C_3$ repeat distance along the molecular chain), and the correct orientation of the molecule about its axis is determined by the positions and the relative heights of the two peaks at about 1.5 Å. (The multiplicities of the distances $C_1 - C_2$ and $C_2 - C_3$ are 4 and 3, respectively.)

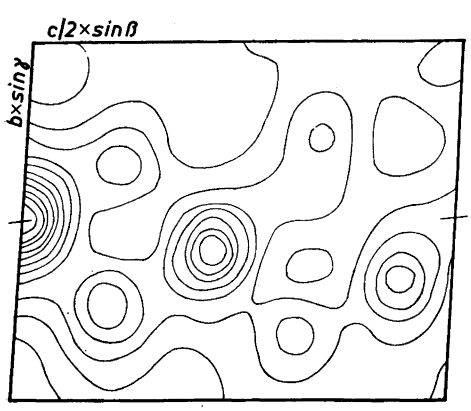

Fig. 1. Patterson projection along the *a*-axis of *n*-octane. Contours are at equal, arbitrary intervals.

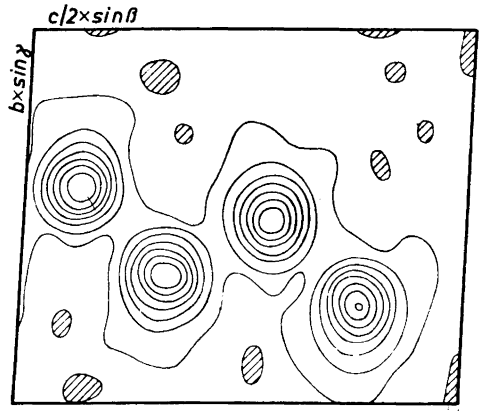

Fig. 2. The final (*yz*) electron density projection of *n*-octane. Contours are at intervals of 1 e/Å², negative areas shaded.

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 Fig. 3 the contributions from the carbon atoms have been subtracted.

As the plane of the molecule is nearly normal to the projection axis, the two hydrogens belonging to the same CH_2-group overlap to a large extent. Such pairs of overlapping hydrogens were therefore in the refinements of this projection treated as one atom with scattering power twice that of hydrogen. In the least squares refinement the carbon atoms were treated as isotropic. The hydrogens were all given a *B*-value of 2.6.

As expected, the final *B*-values for the carbon atoms show a pronounced increase towards the ends of the molecule. The *R*-factor for the 90 observed (0*kl*)-reflections is 0.07. (The total number of theoretically observable (0*kl*)-reflections is 129.)

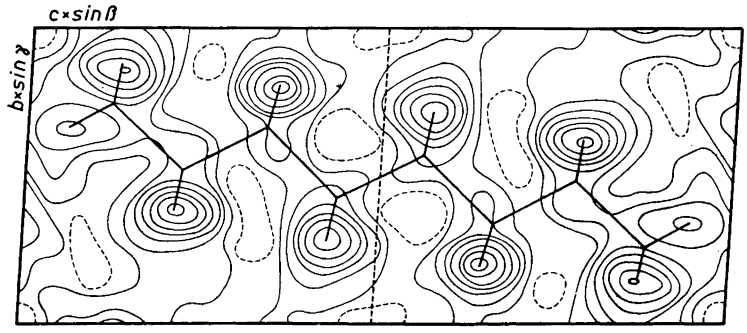

Fig. 3. ($F_o - F_{carbon}$)-map for the (*yz*)-projection of *n*-octane. Contours are at intervals of 0.2 e/Å², zero contour broken.

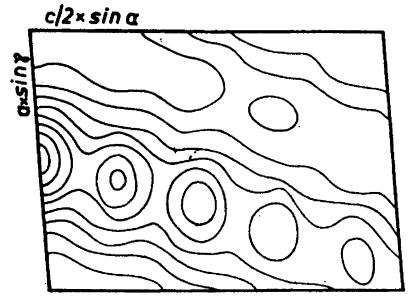

Fig. 4. Patterson projection along the *b*-axis of *n*-octane. Contours are at equal arbitrary intervals.

The two strongest reflections, $(01\bar{1})$ and (010), are considerably weakened by extinction. However, as the amplitudes of those two reflections are rather unsensitive to small changes in the atomic coordinates, their calculated values could quite safely be included in the electron density calculations. The same reflections were throughout excluded from the difference syntheses and the least squares refinements. In the *(xz)*-projection the reflections $(10\bar{1})$ and (100) for similar reasons were treated in the same way.

The (xz)-projection. The (*h*0*l*)-reflections needed for the refinement of this projection were selected from the (0*kl*), (1*kl*), (2*kl*), and (3*kl*) data.

Assuming C—C bond lengths of 1.54 Å and C—C—C bond angles of about 110° preliminary *x*-coordinates of the carbon atoms were evaluated. Practically the same values were obtained from the $P(u,w)$ Patterson projection, Fig. 4. The final electron density projection is shown in Fig. 5. As one would expect the carbon atoms show rather pronounced anisotropy in this projection. This anisotropy obviously had to be taken into account. This was effected by modifying the atomic scattering factor by the exponential factor

$$\exp\ (-u_i h^2 - v_i hl - w_i l^2)$$

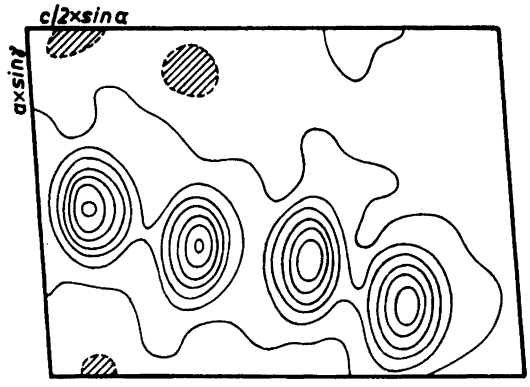

Fig. 5. The final (*xz*) electron density projection of *n*-octane. Contours are at intervals of 1 e/Å², negative areas shaded.

Table 1. Fractional atomic coordinates and temperature factor parameters for *n*-octane.

	x	y	z	$B(yz)$	$B(xz)$ *	u_{xz}	v_{xz}	w_{xz}
C_1	0.3037	0.2447	0.3811	3.22	3.35	0.0982	0.0107	0.0040
C_2	0.1715	0.0161	0.2777	2.82	2.87	0.0937	0.0174	0.0037
C_3	0.1417	0.1585	0.1620	2.78	3.09	0.0834	0.0104	0.0040
C_4	0.0176	−0.0699	0.0576	2.68	2.85	0.0803	0.0104	0.0036
H_1	0.325	0.150	0.449					
H_2	0.550	0.380	0.360					
H_3	0.117	0.379	0.390					
H_4	0.390	−0.126	0.267					
H_5	−0.083	−0.120	0.297					
H_6	0.387	0.293	0.140					
H_7	−0.033	0.295	0.166					
H_8	0.242	−0.223	0.050					
H_9	−0.235	−0.191	0.075					

* A "best fit" isotropic B-values.

The parameters u_i, v_i, and w_i are different for the different carbon atoms. They are included in the least squares refinement programme. The approximate positions of the hydrogens were determined from a difference synthesis where

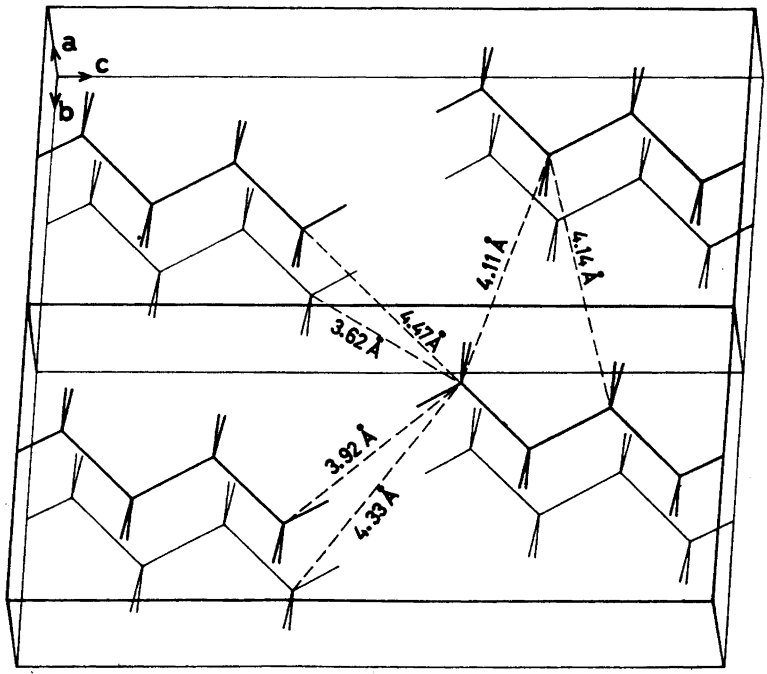

Fig. 6. A schematic drawing showing how the *n*-octane molecules pack in the crystal. Some of the shortest intermolecular carbon-carbon distances are indicated.

Table 2. Comparison of observed and calculated structure factors for the (0*kl*)- and (*h*0*l*)-zones of *n*-octane.

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	3.7	6.8	$02\bar{2}$	1.4	− 1.2	044	—	0.3
002	5.8	− 6.3	$02\bar{1}$	5.2	4.9	045	—	− 0.2
003	5.9	6.1	020	1.3	− 1.3	046	—	− 0.2
004	6.6	− 6.5	021	2.4	2.5	047	1.7	1.8
005	—	0.1	022	3.7	− 3.5	048	2.5	2.3
006	1.7	− 1.7	023	7.3	6.9	049	0.8	− 0.8
007	1.6	1.4	024	15.0	15.2	$05\bar{8}$	—	0.5
008	—	− 0.3	025	1.7	− 1.5	$05\bar{7}$	0.7	− 0.9
009	9.2	− 9.8	026	—	− 0.2	$05\bar{6}$	—	0.1
00,10	2.6	− 2.6	027	1.6	0.8	$05\bar{5}$	—	− 0.5
00,11	1.6	1.4	028	4.6	− 4.1	$05\bar{4}$	0.6	0.6
00,12	1.3	− 1.1	029	1.4	− 1.2	$05\bar{3}$	1.0	− 0.8
00,13	1.4	1.1	02,10	—	− 0.1	$05\bar{2}$	4.4	− 5.3
00,14	0.7	0.6	02,11	—	0.5	$05\bar{1}$	1.1	− 1.1
$01,\bar{1}4$	2.5	2.8	02,12	1.1	− 1.1	050	0.8	1.0
$01,\bar{1}3$	—	0.3	$03,\bar{1}2$	—	0.2	051	0.8	− 0.9
$01,\bar{1}2$	0.8	− 0.7	$03,\bar{1}1$	—	0.2	052	1.6	1.5
$01,\bar{1}1$	1.5	1.4	$03,\bar{1}0$	2.3	2.1	053	1.0	0.9
$01,\bar{1}0$	4.8	− 4.6	$03\bar{9}$	0.7	− 0.7	054	—	0.1
$01\bar{9}$	3.9	− 3.8	$03\bar{8}$	—	0.3	055	—	− 0.2
$01\bar{8}$	—	0.3	$03\bar{7}$	0.7	0.6	056	—	0.1
$01\bar{7}$	0.8	0.6	$03\bar{6}$	7.6	− 7.5	$10,\bar{1}3$	—	− 0.8
$01\bar{6}$	1.6	− 1.4	$03\bar{5}$	3.6	− 3.6	$10,\bar{1}2$	—	0.4
$01\bar{5}$	16.8	−16.1	$03\bar{4}$	1.3	1.4	$10,\bar{1}1$	—	—
$01\bar{4}$	6.0	− 5.7	$03\bar{3}$	—	− 0.7	$10,\bar{1}0$	5.5	− 7.0
$01\bar{3}$	7.4	7.6	$03\bar{2}$	—	0.0	$10\bar{9}$	2.9	− 2.6
$01\bar{2}$	10.6	−10.6	$03\bar{1}$	3.4	− 3.6	$10\bar{8}$	—	1.2
$01\bar{1}$	17.3	22.9	030	—	0.3	$10\bar{7}$	—	− 0.7
010	17.9	24.3	031	1.6	0.9	$10\bar{6}$	—	0.2
011	4.1	− 4.3	032	1.4	− 1.7	$10\bar{5}$	3.4	− 4.3
012	1.3	1.2	033	8.6	8.8	$10\bar{4}$	—	0.6
013	1.2	− 1.2	034	5.1	5.1	$10\bar{3}$	—	1.0
014	16.3	15.6	035	1.7	− 1.8	$10\bar{2}$	3.5	− 4.2
015	5.7	5.4	036	0.9	0.8	$10\bar{1}$	V.V.S.	31.9
016	3.7	− 3.6	037	—	− 0.4	100	V.S.	15.4
017	3.7	3.6	038	0.9	0.7	101	6.6	− 7.3
018	5.5	− 5.5	039	—	0.2	102	3.6	4.0
019	7.4	− 7.3	03,10	—	− 0.5	103	2.5	− 2.9
01,10	0.8	0.5	03,11	0.8	0.6	104	4.5	4.3
01,11	—	0.1	$04,\bar{1}0$	1.9	1.9	105	1.0	− 1.0
01,12	—	− 0.2	$04\bar{9}$	0.9	− 1.2	106	—	− 0.5
01,13	1.0	− 1.1	$04\bar{8}$	1.0	1.1	107	2.8	2.7
$02,\bar{1}3$	0.7	− 0.7	$04\bar{7}$	1.6	− 1.7	108	12.1	−11.6
$02,\bar{1}2$	—	0.6	$04\bar{6}$	3.6	− 4.0	109	7.8	− 7.5
$02,\bar{1}1$	—	− 0.3	$04\bar{5}$	—	− 0.2	10,10	2.9	2.7
$02,\bar{1}0$	1.4	− 1.3	$04\bar{4}$	—	0.2	10,11	1.4	− 1.3
$02\bar{9}$	—	0.1	$04\bar{3}$	—	0.5	10,12	—	0.3
$02\bar{8}$	1.1	− 1.0	$04\bar{2}$	3.3	− 3.6	10,13	0.9	0.6
$02\bar{7}$	2.5	2.2	$04\bar{1}$	3.4	− 3.8	10,14	—	0.1
$02\bar{6}$	7.0	− 6.7	040	1.4	1.7	$20,\bar{1}2$	0.6	0.6
$02\bar{5}$	12.0	−12.0	041	1.1	− 1.2	$20,\bar{1}1$	3.0	− 3.2
$02\bar{4}$	2.0	2.1	042	1.5	1.3	$20,\bar{1}0$	2.8	− 2.7
$02\bar{3}$	—	− 0.4	043	5.1	5.5	$20\bar{9}$	—	0.4

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
$20\bar{8}$	—	− 0.2	207	5.6	− 5.5	$30\bar{2}$	5.7	5.6
$20\bar{7}$	—	0.1	208	8.4	− 8.1	$30\bar{1}$	—	0.4
$20\bar{6}$	2.4	− 2.0	209	1.1	1.1	300	—	0.1
$20\bar{5}$	1.0	− 1.2	20,10	—	0.1	301	—	− 0.1
$20\bar{4}$	1.5	1.3	20,11	—	− 0.5	302	0.9	1.6
$20\bar{3}$	3.1	− 2.5	20,12	—	− 0.2	303	1.7	2.0
$20\bar{2}$	7.9	7.3	20,13	0.6	− 0.4	304	1.2	− 1.3
$20\bar{1}$	7.7	9.1	$30,\bar{1}0$	—	− 0.1	305	1.1	1.2
200	1.9	− 2.0	$30\bar{9}$	—	− 0.1	306	1.2	− 1.5
201	0.9	1.0	$30\bar{8}$	—	0.1	307	4.8	− 5.9
202	0.7	− 0.9	$30\bar{7}$	1.7	− 1.7	308	1.3	− 0.9
203	2.7	2.6	$30\bar{6}$	1.6	− 1.7	309	0.7	0 7
204	1.5	1.2	$30\bar{5}$	1.1	1.1	30,10	0.5	− 0.4
205	2.0	− 1.6	$30\bar{4}$	1.3	− 1.1	30,11	0.7	− 0.7
206	2.7	2.6	$30\bar{3}$	2.3	2.0	30,12	1.1	− 1.0

the carbon atoms had been subtracted. In this projection a uniform isotropic temperature factor of 2.4 was used for the hydrogen atoms.

The final R factor was 0.08 for the 62 ($h0l$)-reflections included in the least squares refinement. (The total number of theoretically observable ($00l$), ($10l$), ($20l$), and ($30l$) reflections is 92.) The final coordinates and temperature factors for the 4 carbon and 9 hydrogen atoms in the asymmetric unit are given in Table 1. In Table 2 are listed the observed and calculated structure factors.

Table 3. Interatomic distances and bond angles of *n*-octane.

Distances

C_1-C_2 = 1.542 Å	C_1-H_1 = 0.93 Å
C_2-C_3 = 1.519 »	C_1-H_2 = 1.07 »
C_3-C_4 = 1.542 »	C_1-H_3 = 1.12 »
C_4-C_5 = 1.514 »	C_2-H_4 = 1.26 »
	C_2-H_5 = 1.10 »
C_1-C_3 = 2.535 »	C_3-H_6 = 1.07 »
C_2-C_4 = 2.536 »	C_3-H_7 = 1.09 »
C_3-C_5 = 2.538 »	C_4-H_8 = 1.32 »
	C_4-H_9 = 1.07 »

Angles

$C_1-C_2-C_3$ = 111.8°	$H_1-C_1-H_2$ = 104°
$C_2-C_3-C_4$ = 111.9°	$H_1-C_1-H_3$ = 118°
$C_3-C_4-C_5$ = 112.3°	$H_2-C_1-H_1$ = 110°
$C_2-C_1\ldots C_1'$ = 173.8°	$H_4-C_3-H_5$ = 113°
	$H_6-C_3-H_7$ = 108°
	$H_8-C_4-H_9$ = 115°

Mean values

The C−C bond length	1.53 ± 0.01 Å
The C−H bond length	1.11 ± 0.10 Å
The C−C−C bond angle	112.0° ± 0.5°
The repeat distance along the molecular chain	2.54 ± 0.01 Å
The H−C−H bond angle	111° ± 5°

DISCUSSION

The interatomic distances and bond angles of the *n*-octane structure are given in Table 3. The standard deviations were calculated by use of Cruickshanks formulæ. Because of the uncertainties in cell dimensions, however, the uncertainties in bond lengths and bond angles are probably somewhat greater than indicated by these formulæ. The deviations given in Table 3 should therefore be regarded as total estimates of the uncertainties in the distances and angles given.

The *n*-octane molecules pack in the extended *trans* configuration, *i.e.* the molecules are planar. The packing is schematically visualized in Fig. 6, where some of the shortest distances between carbon atoms of different molecules are indicated. The order of magnitude of most of these distances shows good agreement with the van der Waals' radius of 2.0 $\pm$ 0.1 Å usually found for CH_2— or CH_3— groups. The rather close approach of 3.62 Å between the terminal CH_3-groups across the center of symmetry at (1/2, 1/2, 1/2) is very surprising in view of the results of Rushworth's [8] NMR investigation of *n*-pentane and *n*-hexane, which seem to indicate that the end methyl groups are freely rotating. A reinvestigation of this point will be undertaken in this laboratory.

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