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The Crystal Structure of Lower Paraffins

V. Cell Dimensions of Nonane, Decane, Undecane, Dodecane, Tridecane, Tetradecane, and Hexadecane

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The unit cell dimensions of the n-paraffins nonane, decane, undecane, dodecane, tridecane, tetradecane, and hexadecane have been determined from Debye-Scherrer diagrams. All paraffins with an even number of carbon atoms in the molecule are triclinic with one molecule in the unit cell, in accordance with what has been found for both the higher and the lower members of this series. Nonane has the same structure as heptane, *i.e.* a triclinic cell containing two molecules. Both undecane and tridecane are orthorhombic with four molecules in the unit cell, in agreement with the results of previous work carried out in other laboratories.

The structural properties of the lower members of the n-paraffin series from pentane to octane were studied at the Central Institute for Industrial Research, Oslo, some years ago, and their crystal structures have been solved and refined by ordinary single crystal techniques.[1–4] Previously the crystal structures of those n-paraffins which are solids at room temperature, *i.e.* those with 18 or more carbon atoms in the molecule, had been investigated by several investigators in different laboratories. In order to fill in the gap in our knowledge about the n-paraffin series seven out of the nine different n-paraffins between octane and octadecane were studied by X-ray powder methods. Our aim was to determine the unit cell dimensions and the crystal systems of these paraffins in order to establish the packing of the molecules and to see how the structures are interrelated.

EXPERIMENTAL

The n-paraffin samples used were obtained from different manufacturers. They were all of high purity. Their specifications are listed below.

Substance	Specifications	Manufacturer
$n\text{-}C_9H_{20}$	Research Grade, 99.69 mol %	Phillips Petroleum Co.
$n\text{-}C_{10}H_{22}$	"Olefinfrei", 99 %, *purum*	Fluka AG
$n\text{-}C_{11}H_{24}$	Research Grade, 99.33 mol %	Phillips Petroleum Co.
$n\text{-}C_{12}H_{26}$	"Olefinfrei", *purum*	Fluka AG
$n\text{-}C_{13}H_{28}$	Pure Grade, 99 mol % minimum	Phillips Petroleum Co.
$n\text{-}C_{14}H_{30}$	*Purum*	Fluka AG
$n\text{-}C_{16}H_{34}$	*Purum*	Fluka AG

An ordinary 14.38 mm General Electric Debye-Scherrer camera and Ni-filtered Cu-radiation were used in the measurements. The sample was frozen in a sealed tube of Lindeman glass of inner diameter 0.3 mm. In order to obtain smooth diffraction lines the total exposure time of 2 to 3 h was divided into intervals of about 10 min, the sample being melted and refrozen each time. Experimental d-values were obtained from micro-photometer curves of the Debye-Scherrer diagrams.

RESULTS

As most of the substances crystallize in the triclinic system, the diagrams were rather complex, so indexing them was not always a straightforward matter. It could only be done on the basis of what already was known about the unit cell parameters and molecular packing of other n-paraffins, both above $n\text{-}C_{16}H_{34}$ and below $n\text{-}C_9H_{20}$. The small and only slightly varying values of the a and b axes were of great help in the indexing of the lines, of which the innermost ones always were of the type $(00l)$. When a unit cell that would give a satisfactory explanation of all the observed d-values had been found, the parameters were adjusted to give the best possible agreement between observed and calculated spacings. Due to the large number of theoretically possible reflections, the number of unequivocally indexable reflections in most cases were too few to justify more elaborate refinements of the parameters by for instance the method of least squares.

The observed and calculated d-values are listed in Table 1. The crystal data are given in Table 2. For comparison this table also contains our results for pentane,[4] hexane,[2] heptane,[5] and octane.[4]

DISCUSSION

The data in Table 2 indicate that all the even-numbered n-paraffins are isostructural, as already stated by Müller and Lonsdale in 1948.[6] The polymorphism of the higher homologues has been reported by many investigators.[6–8] Ohlberg [9] has shown that at 37.5°C the stable modification of $n\text{-}C_{20}H_{42}$, $n\text{-}C_{24}H_{50}$, and $n\text{-}C_{26}H_{54}$ are all triclinic. Smith [10] has found that all odd-numbered n-paraffins down to $n\text{-}C_{21}H_{44}$ are orthorhombic with space group *Pbcm*. The variation in the length of the c-axis shows that the molecules pack with their chain axes normal to the ab-plane of the unit cell. This is the "normal" orthorhombic mode of packing for n-paraffins. From Table 2 it is seen that the n-paraffins with 11 and 13 carbon atoms in the molecule are

Table 1. Comparison of calculated and observed d-values for nonane, decane, undecane, dodecane, tridecane, tetradecane, and hexadecane.

Nonane			Decane			Undecane			Dodecane		
hkl	d_c(Å)	d_o(Å)	*hkl*	d_c(Å)	d_o(Å)	*hkl*	d_c(Å)	d_o(Å)	*hkl*	d_c(Å)	d_o(Å)
002	12.425	12.413	001	13.43	13.51	002	15.77	15.81	001	15.86	15.87
004	6.213	6.207	002	6.711	6.716	004	7.883	7.882	002	7.931	7.917
010	4.526	4.547	010	4.575	4.575	006	5.256	5.242	003	5.288	5.288
011	4.405	4.424	01$\bar{1}$	4.361	4.370	110	4.047	4.047	010	4.610	4.610
006	4.142	4.163	100	4.010	4.010	017	3.821	3.803	01$\bar{1}$	4.436	4.436
01$\bar{3}$	4.079	4.105	01$\bar{2}$	3.821	3.833	020	3.608	3.608	100	4.043	4.032
100	3.981	3.982	10$\bar{1}$	3.710	3.709	023	3.413	3.429	10$\bar{1}$	3.770	3.770
013	3.872	3.880	1$\bar{1}$0	3.507	3.506	117	3.011	3.019	1$\bar{1}$0	3.577	3.577
10$\bar{3}$	3.658	3.658	004	3.356	3.347	120	2.903	2.915	01$\bar{3}$	3.488	3.484
007	3.550	3.546	10$\bar{2}$	3.258	3.245	01.12	2.469	2.460	10$\bar{2}$	3.381	3.381
1$\bar{1}$0	3.478	3.478	01$\bar{3}$	3.236		200	2.444		1$\bar{1}$1	3.380	
1$\bar{1}$2	3.345	3.345	014	2.736	2.736	210	2.315	2.314	005	3.173	3.175
016	3.154	3.150	014	2.677	2.670	10.12	2.315		1$\bar{1}$2	3.088	3.085
008	3.107	3.097	111	2.672					01$\bar{4}$	3.018	3.005
016	2.966	2.986	1$\bar{1}$3	2.597	2.596				014	2.995	
01$\bar{7}$	2.881	2.888	11$\bar{1}$	2.596					11$\bar{1}$	2.606	2.604
017	2.713	2.727	01$\bar{5}$	2.339	2.338				015	2.604	
107	2.588	2.596	1$\bar{1}$4	2.278	2.274				1$\bar{2}$0	2.299	2.291
11$\bar{3}$	2.586		016	2.028	2.028				016	2.286	
11$\bar{4}$	2.510	2.524							115	2.168	2.161
10$\bar{8}$	2.509								1$\bar{2}$2	2.150	
019	2.425	2.425									
019	2.295	2.295									

Tridecane			Tetradecane			Hexadecane			
hkl	d_c(Å)	d_o(Å)	*hkl*	d_c(Å)	d_o(Å)	*hkl*	d_c(Å)	d_o(Å)	
002	18.29	18.39	001	18.24	18.20	002	10.29	10.31	
004	9.15	9.13	002	9.113	9.127	010	4.598	4.598	
006	6.10	6.12	003	6.076	6.077	01$\bar{1}$	4.473	4.481	
008	4.57	4.54	010	4.612	4.612	01$\bar{2}$	4.175	4.144	(poorly defined)
110	4.09	4.08	01$\bar{1}$	4.468	4.468	005	4.117		
018	3.88	3.88	100	4.032	4.032	102	3.998	3.998	
020	3.65	3.65	10$\bar{1}$	3.790	3.790	01$\bar{3}$	3.793	3.793	
01.10	3.27	3.25	1$\bar{1}$0	3.588	3.588	10$\bar{2}$	3.577	3.577	
025	3.26		1$\bar{1}$1	3.416	3.424	006	3.431	3.431	
17	3.22		007	2.604	2.598				
0.10	2.94	2.94	11$\bar{1}$	2.603					
20	2.93								

also orthorhombic. Their unit cell dimensions suggest the same space group for these compounds as for the higher odd-numbered homologues. The difference in the length of the c-axes [10] for n-$C_{29}H_{60}$ and n-$C_{11}H_{24}$ is 46.2 Å, or about 5.1 Å for every second carbon atom, which agrees very well with the expected value of $2 \times 2.54 = 5.08$.

Table 2. Crystal data of n-paraffins in the range from n-C_5H_{12} to n-$C_{16}H_{34}$. N is number of carbon atoms in the molecule, V the volume of the unit cell, and n the number of molecules in the unit cell.

N	Sym.	a	b	c	α	β	γ	V	n
5	*Pbcn*	4.10	9.076	14.859	90	90	90	545	4
7	$P\bar{1}$	4.18	4.78	20.17	93.9	95.0	105.4	385	2
9	Triclinic	4.13	4.70	24.92	92.9	91.9	105.2	465	2
11	Ortho-rhombic	4.89	7.22	31.53	90	90	90	1113	4
13	»	4.94	7.29	36.59	90	90	90	1318	4
6	$P\bar{1}$	4.17	4.70	8.57	96.6	87.2	105.0	161	1
8	»	4.22	4.79	11.02	94.7	84.3	105.8	215	1
10	Triclinic	4.20	4.75	13.57	93.4	81.8	105.6	258	1
12	»	4.28	4.81	16.12	93.3	79.9	106.6	313	1
14	»	4.29	4.82	18.58	93.1	78.8	107.0	361	1
16	»	4.29	4.81	20.87	91.9	80.5	106.9	406	1

From n-$C_{11}H_{24}$ to n-C_9H_{20}, however, this difference is 6.6 Å, showing that the nonane molecule forms an angle of about 20 degrees with the normal to the *ab*-plane. The unit cell dimensions indicate that this angle has about the same value in the heptane structure. This is confirmed by the results of our single crystal investigation of heptane,[5] so there are good reasons for believing that the space group and mode of packing for the nonane structure are the same as for heptane.

The particular mode of packing in the pentane structure is quite distinct from any other paraffin structure that has been published so far. The chain axes of the pentane molecules are neither parallel to the *c*-axis nor to each other. The pentane molecules are evidently too short to show the characteristics of typical long-chain molecules.

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