

STRUCTURE AND MOLECULAR CORRELATION OF LIQUID ALKANES

Z. BOCHYŃSKI AND H. DROZDOWSKI

Non-Crystalline Materials Division, Institute of Physics
A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań 2, Poland

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The paper reports structural investigations of a series of liquid alkanes, from $n\text{-C}_6\text{H}_{14}$ (n -hexane) to $n\text{-C}_{16}\text{H}_{34}$ (n -hexadecane), differing by two methyl groups $(\text{CH}_2)_2$, $n\text{-C}_{20}\text{H}_{42}$ (n -eicosane) and $n\text{-C}_{30}\text{H}_{62}$ (n -triacontane) performed in temperatures from 20°C to 70°C . The average angular distribution of intensity was determined by diffraction of monochromatic X-ray radiation $\text{Mo } K_\alpha$, $\lambda = 0.7107 \text{ \AA}$ and the functions of radial distribution of electron density were calculated for the studied compounds. Mean structural parameters including distances between molecules and atoms, coordination numbers as well as correlation parameters were obtained. The suitability of the method for structural studies of n -alkanes with the number of carbon atoms from 6 to 30 is discussed.

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Introduction

Hexane was the first aliphatic liquid studied by X-ray methods [1]. In its X-ray diffraction [2, 3] and electron diffraction [4] studies it was established that the mean distance between carbon atoms in the chain was $\text{C}(1)\text{-C}(2) = 1.53 \pm 0.01 \text{ \AA}$ and the distance $\text{C}(1)\text{-H}(11) = 1.12 \text{ \AA}$. So far X-ray diffraction studies of liquid n -alkanes have been reported by Hewlett [5], Sogani [6], Stewart [7, 8], Wilson and Ott [9], Pierce [10], Golik, Skryshevskii, Adamenko [11] and Habenschuss and Narten [3].

This paper presents results of X-ray structural investigations of eight n -alkanes (Tables I and II) with an even number of carbon atoms. Such n -alkanes as n -tetradecane, n -hexadecane and n -triacontane have not been studied by X-ray diffraction yet [12]. Alkanes have practically zero dipole moment ($\mu = 0$) [13] and their centre of symmetry is between the middle carbon atoms.

TABLE I

Physical parameters of the studied liquid *n*-alkanes.

Liquid	<i>M</i> [g/mol]	Temperature [°C]			<i>d</i> [g/cm ³]
		Melting point	Boiling point	Measured point	
<i>n</i> -hexane	86.18	-95	69	20	0.661
<i>n</i> -octane	114.23	-57	126	20	0.703
<i>n</i> -decane	142.28	-30	174	20	0.730
<i>n</i> -dodecane	170.34	-10	216	20	0.749
<i>n</i> -tetradecane	198.40	6	253	20	0.763
<i>n</i> -hexadecane	226.44	20	288	20	0.773
<i>n</i> -eicosane	282.55	37	343	40	0.778
<i>n</i> -triacontane	422.82	66	446	70	0.810

TABLE II

Structural parameters of the studied liquid *n*-alkanes.

Liquid	\bar{K}_H	\bar{K}_C	$\sum \bar{K}_m$	$\sum Z_m$	ρ_0 [el/Å ³]
<i>n</i> -hexane	0.352	7.536	50.144	50	0.232
<i>n</i> -octane	0.351	7.484	66.190	66	0.245
<i>n</i> -decane	0.350	7.453	82.252	82	0.253
<i>n</i> -dodecane	0.349	7.432	98.284	98	0.260
<i>n</i> -tetradecane	0.347	7.418	114.352	114	0.264
<i>n</i> -hexadecane	0.345	7.406	130.396	130	0.267
<i>n</i> -eicosane	0.343	7.391	162.478	162	0.269
<i>n</i> -triacontane	0.338	7.370	242.138	242	0.279

2. Experimental

The studies were performed using an X-ray apparatus TUR M-62 equipped with a horizontal counter goniometer HZG-3. The characteristic Mo K_α radiation generated in an X-ray tube working at the voltage $U = 40$ kV and the current intensity $I = 30$ mA. The radiation was monochromatized by reflection from a graphite crystal [14] in a very efficient system [15].

Measurements were performed for the angles $3^\circ \leq \vartheta \leq 60^\circ$ at every 0.2° (where 2ϑ is the scattering angle) by the transmission method with the directions of the incident and diffracted beams symmetric with respect to the surface of the flat preparation. The intensity of diffracted radiation was measured by a proportional VA-G-120.

A triply thermostated cuvette for liquids, designed and constructed especially for this experiment with replaceable inserts (from 1.8 to 4.1 mm) and thin foil win-

dows of 0.01 mm in thickness, was connected to a flow-through ultrathermostat equipped with a double pump U-10 ($-60 \div +300 \pm 0.02$)°C. The measurements were carried out in the temperature range ($20.0 \div 70.0 \pm 0.1$)°C and the temperature was controlled by a copper-constantan thermocouple and a very sensitive mirror galvanometer GL-1. The studied liquids were purchased at Aldrich-Chemie Germany, Janssen Chimica, Belgium and Reachim, Russia.

3. The calculations

The radial distribution function of electron density $\rho(r)$ for a given liquid was determined from the modified Warren-Krutter-Morningstar equation [16, 17] in the following form:

$$\sum \bar{K}_m 4\pi r^2 \rho(r) = \sum \bar{K}_m 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{S_0} S i(S) \sin(Sr) dS, \quad (1)$$

where $K_m = f_m/f_e$ is the effective number of diffracting electrons in the atom m , and $f_e = \sum f_m / \sum Z_m$ is the mean value of the atomic factor for a molecule per a single electron, f_m is the atomic factor of the m -th atom and Z_m is the number of electrons in the atom, see Table II.

The mean effective number of diffracting electrons was found from the integral average

$$\bar{K}_m = \frac{1}{S_0} \int_0^{S_0} K_m dS,$$

where $S = 4\pi \sin \vartheta / \lambda$ and the value of $i(S)$ is given by

$$i(S) = [\bar{I}(S) - \sum (f_m^2 + I_m^{\text{INC}})] / f_e^2, \quad (2)$$

where I_m^{INC} is the incoherent radiation intensity. The corrections for absorption [17, 18] and polarization [19, 20] were taken into account in the averaged angular distributions of the scattered radiation intensity $\bar{I}(S)$ which were afterwards normalized [21-23]. The integral in Eq. (1) was calculated numerically by the Simpson method in the range $0 \leq r \leq 20 \text{ \AA}$ at a step of $\Delta r = 0.05 \text{ \AA}$.

The mean number of electrons in a unit volume (1 \AA^3) is given by the following formula [24]:

$$\rho_0 = (dN10^{-24} \sum \bar{K}_m) / M, \quad (3)$$

where d is the macroscopic density of the liquid, N — the Avogadro number and M — molecular mass (Table I).

4. Results and discussion

The normalized angular distribution functions $\bar{I}(S)$ for all n -alkanes studied (Fig. 1) have one main and a few smaller diffuse maxima. The main maximum at $S = 1.36 \text{ \AA}^{-1}$ corresponds to the mean intermolecular distance in liquid n -alkanes of $\bar{d} = 4.63 \text{ \AA}$ which was determined directly from the Bragg equation [17, 25].

The least mean intermolecular distance is calculated to be 5.38 \AA and is the same for all n -alkanes studied.

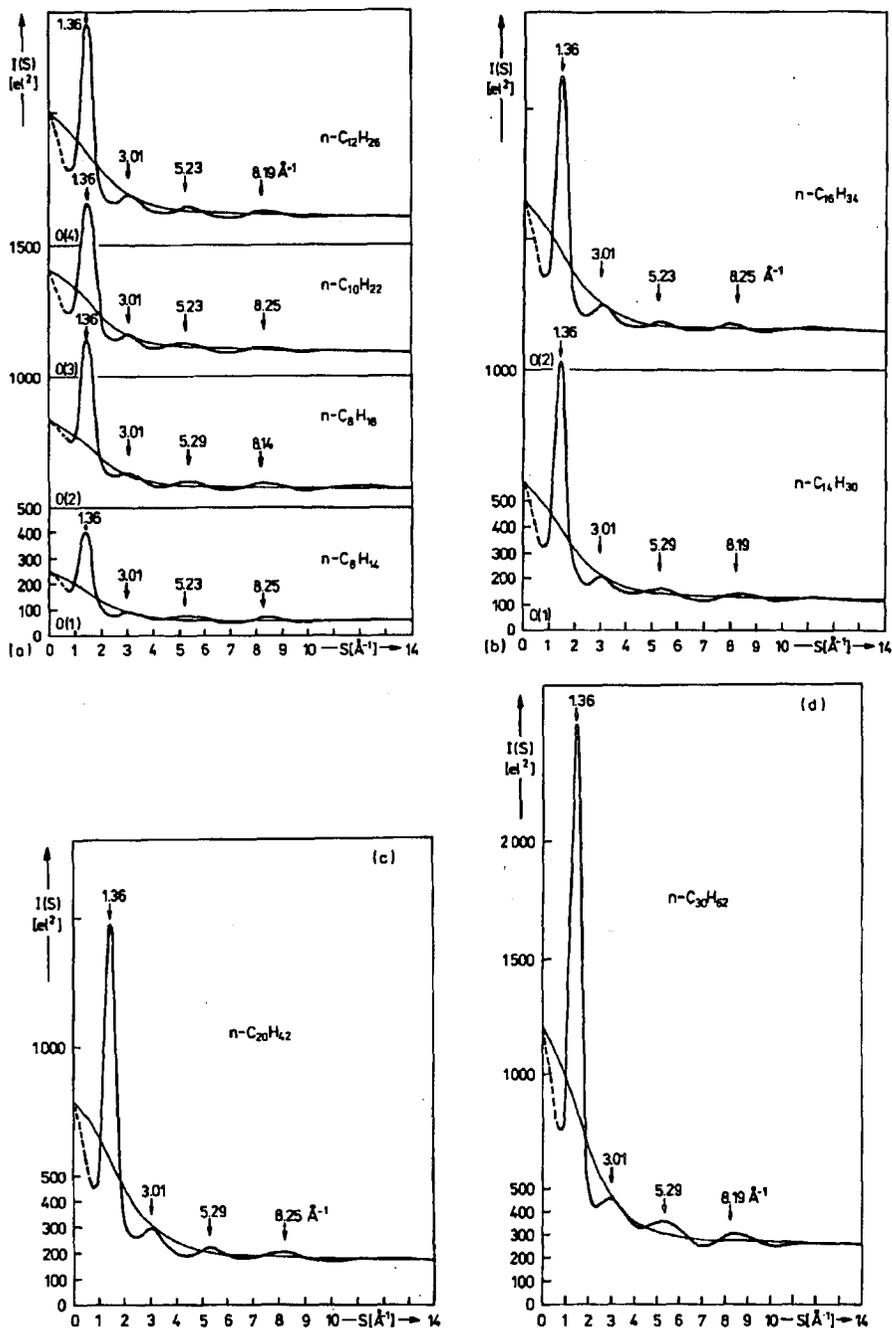


Fig. 1. The normalized functions of angular distribution of intensity obtained for (a) *n*-hexane, *n*-octane, *n*-decane, *n*-dodecane, (b) *n*-tetradecane and *n*-hexadecane, (c) *n*-eicosane and (d) *n*-triacontane, using a K_{α} -Mo radiation source ($\lambda = 0.7107 \text{\AA}$).

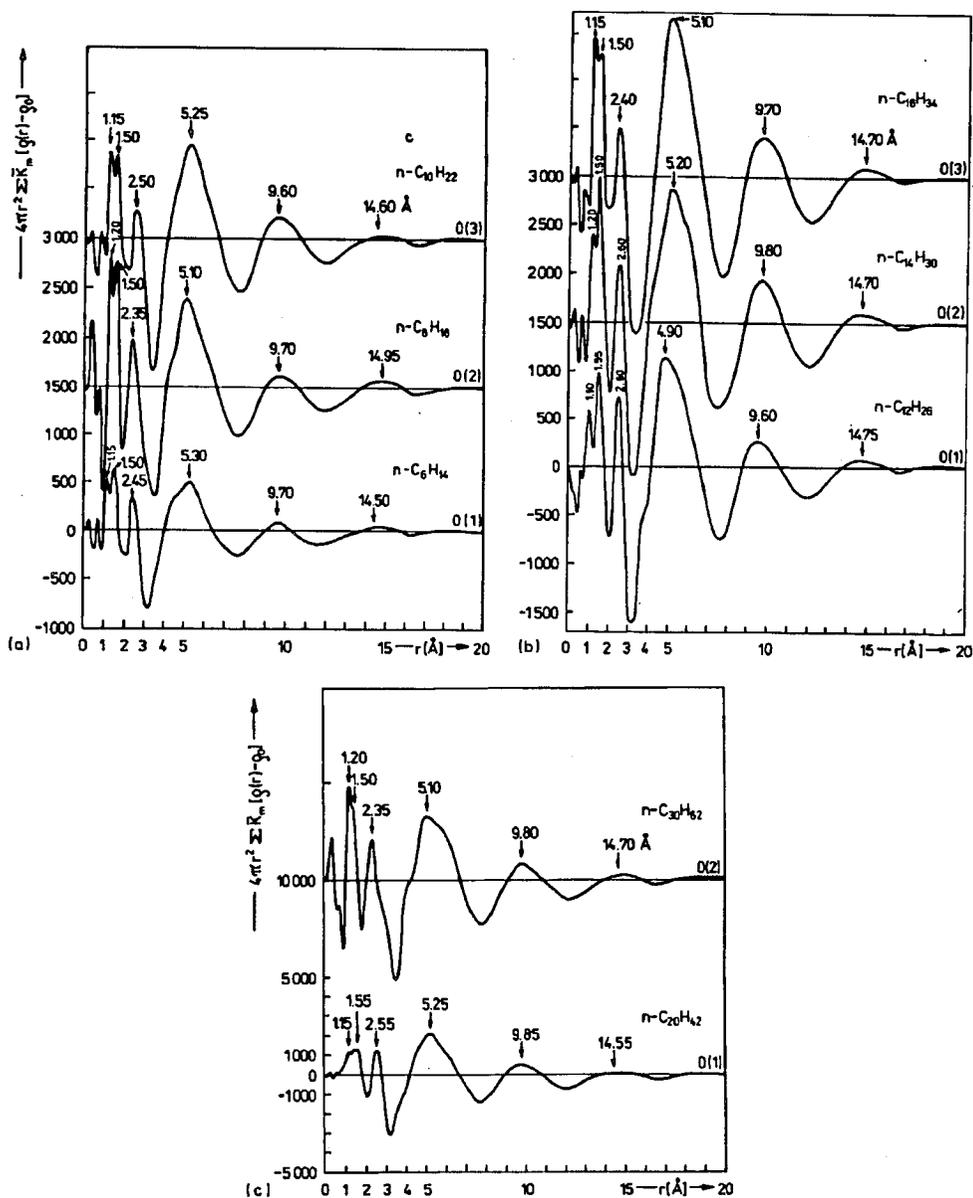


Fig. 2. Differential radial distribution functions for (a) n -hexane, n -octane, n -decane; (b) n -dodecane, n -tetradecane, n -hexadecane and (c) n -eicosane and n -triacontane.

The differential functions of radial distribution of electron density

$$4\pi r^2 \sum \bar{K}_m [\rho(r) - \rho_0] = \frac{2r}{\pi} \int_0^{S_0} S i(S) \sin(Sr) dS \quad (4)$$

are shown in Fig. 2. In all studied n -alkanes the presence of the coordination

spheres of intermolecular ordering was established. Subsequently, the ranges of the spheres and coordination numbers (Table III) were determined.

TABLE III
The range of coordination spheres and the number of molecules in each sphere for the studied *n*-alkanes.

Liquid	Range [Å]		
	(Number of molecules)		
	Sphere I	Sphere II	Sphere III
<i>n</i> -hexane	3.15–7.70 (8.4)	7.70–11.60 (21.4)	11.60–16.20 (52.3)
<i>n</i> -octane	3.45–7.60 (6.0)	7.60–11.95 (19.7)	11.95–16.45 (42.7)
<i>n</i> -decane	3.30–7.70 (5.5)	7.70–11.90 (15.9)	11.90–16.60 (37.3)
<i>n</i> -dodecane	3.20–7.70 (4.8)	7.70–12.00 (14.1)	12.00–16.60 (31.6)
<i>n</i> -tetradecane	3.30–7.50 (3.8)	7.50–12.10 (13.1)	12.10–16.65 (27.6)
<i>n</i> -hexadecane	3.30–7.65 (3.6)	7.65–12.05 (11.2)	12.05–16.70 (25.0)
<i>n</i> -eicosane	3.20–7.70 (3.0)	7.70–12.00 (8.8)	12.00–16.60 (19.5)
<i>n</i> -triacontane	3.45–7.75 (2.1)	7.75–12.20 (6.5)	12.20–16.75 (13.9)

The mean coordination numbers diminish with increasing length of the aliphatic chain. The macroscopic densities of *n*-alkanes vary from 0.661 (*n*-C₆H₁₄) to 0.810 g/cm³ (*n*-C₃₀H₆₂), their molecular mass increases along the homologous series from 86.18 (*n*-C₆H₁₄) to 422.82 g/mol (*n*-C₃₀H₆₂). This means that in the same volume there is a greater number of lighter molecules than heavier ones. It also explains a decreasing mean number of neighbours when moving along the homologous series of *n*-alkanes. The same regularity was observed for the three coordination spheres considered, Table III.

The electron densities of the studied *n*-alkanes are not much different and take values from 0.232 (*n*-C₆H₁₄) to 0.279 el/Å³ (*n*-C₃₀H₆₂). The value of electron density has no essential effect on the radial distribution functions of electron density.

The analysis of the radial distribution functions in the first coordination sphere (usually from 3.30 to 7.70 Å) indicated the possibility of such intermolecular configuration in which the chains of neighbouring molecules are not only arranged

in parallel and shifted relative to one another by about 2.5 Å but also rotated relative to one another by the right angle.

5. Conclusions

The appearance of clear maxima on all functions of angular distribution of intensity of the scattered X-ray radiation as well as on all functions of radial distribution of electron density indicates the existence of a short-range ordering. The shapes of the radial distribution functions are similar for all studied liquids which confirms their structural similarity.

The applied X-ray diffraction method combined with analytical calculations permits determination of the least mean interatomic and intermolecular distances up to 20 Å. The maxima for $1 \text{ \AA} < \bar{r} \leq 3 \text{ \AA}$ are interpreted as a result of intramolecular diffraction. The maximum for $\bar{r} \approx 5.30 \text{ \AA}$ should be ascribed to intermolecular diffraction.

A decrease in the mean coordination numbers (in all three coordination spheres considered) along the homologous series has been explained on the basis of an analysis of the macroscopic parameters of the liquids studied.

On the basis of the obtained radial and angular distribution functions one can conclude about the presence of the dominant parallel intermolecular configurations (for $\bar{r} \approx 4.2 \div 5.4 \text{ \AA}$) in which the chains of the molecules are not only shifted relative to one another but also rotated by the right angle.

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References

- [1] P. Debye, P. Scherrer, *Phys. Zeit.* **17**, 277 (1916).
- [2] H. Mathisen, N. Norman, B.F. Pedersen, *Acta Chem. Scand.* **21**, 127 (1967).
- [3] A. Habenschuss, A.H. Narten, *J. Chem. Phys.* **9**, 92 (1990).
- [4] R.A. Bonham, L.S. Bartell, D.A. Kohl, *J. Am. Chem. Soc.* **81**, 4765 (1959).
- [5] C.W. Hewlett, *Phys. Rev.* **2**, 688 (1922).
- [6] C.H. Sogani, *Indian J. Phys.* **2**, 97 (1928).
- [7] G.W. Stewart, *Phys. Rev.* **31**, 174 (1928).
- [8] G.W. Stewart, *Phys. Rev.* **32**, 153 (1928).
- [9] D.A. Wilson, E. Ott, *J. Chem. Phys.* **2**, 231 (1934).
- [10] W.C. Pierce, *J. Chem. Phys.* **3**, 252 (1935).
- [11] A.Z. Golik, A.F. Skryshevskii, I.I. Adamenko, *Zh. Strukt. Khim.* **8**, 1015 (1967).
- [12] H. Drozdowski, PhD. Thesis, UAM, Poznań 1994.
- [13] A. Kirrmann, J. Cantacuzene, P. Duhamel, *Chimie Organique*, Librairie Armand Colin, Paris 1971.
- [14] L.J. Mirkin, *Rentgenostrukturnyj analiz*, Nauka, Moskwa 1976 (in Russian).
- [15] Z. Bochyński, *Progress Report for the Physics Committee of the Polish Academy of Sciences*, Patent Protection Centre at the Polish Academy of Sciences, Warszawa 1974.

- [16] B.E. Warren, H. Krutter, O. Morningstar, *J. Am. Ceram. Soc.* **19**, 202 (1936).
- [17] H.P. Klug, L.E. Alexander, *X-Ray, Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley, New York 1966.
- [18] P. Schwager, K. Bartels, R. Hubner, *Acta Crystallogr. A* **29**, 291 (1973).
- [19] K. Sagel, *Tabellen zur Röntgenstrukturanalyse*, Springer Verlag, Berlin, Göttingen, Heidelberg 1958.
- [20] W. Grinten van der, *Phys. Zeit.* **34**, 609 (1933).
- [21] J. Krogh-Moe, *Acta Crystallogr.* **9**, 951 (1956).
- [22] N. Norman, *Acta Crystallogr.* **10**, 370 (1957).
- [23] R. Kaplov, S.L. Stroug, B.L. Averbach, *Phys. Rev. A* **138**, 1336 (1965).
- [24] W. Kast, *Kolloidn. Zh.* **120**, 40 (1952).
- [25] J.T. Randall, *The Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids and Gases*, Chapman and Hall, London 1934.