THE STRUCTURE OF 2-METHYL-1-PROPANOL AT 20°C

By A. Mikusińska-Planner

Optics Laboratory, Institute of Physics, A. Mickiewicz University, Poznań*

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The structure of 2-methyl-1-propanol at 20°C was investigated using the X-ray diffraction method. Monochromatic radiation Cu$K\alpha$ an Mo$K\alpha$ enabled one to determine the scattered radiation intensity between $s_0 = 4\pi \sin\vartheta_0/\lambda = 0.617$ Å^{-1} and $s_{max} = 11.831$ Å^{-1}. The interpretation of the results was carried out using the method of pair functions. For the proposed model of short-range order in liquid 2-methyl-1-propanol, the theoretical curve of the pair function was calculated and compared to the experimental one. The theoretical and experimental curves were in good agreement thus confirming the proposed structure of an open chain of hydrogen bonds of a length of 2.65 Å. The mean angle between O...O bonds is 120°. The intermolecular and intramolecular bonds (O...O and C–O, respectively) lie in the same plane. The $CH(CH_3)_2$ groups of neighbouring molecules, hydrogen bonded to the molecule on the opposite side of the chain, are inclined in opposite directions with respect to this plane. This is the reason why these groups can librate about the C–O bond, with free rotation of the CH_3 groups.

1. Introduction

X-ray structural studies of aliphatic alcohols were carried out by Stewart and Morrow [1] and then continued by Warren [2], Zachariasen [3], Harvey [4], Prietzschke [5] and Jagodziński [6]. The aliphatic alcohols were also the subject of X-ray investigation by research workers in the RSR [7, 8].

The present article deals with the structural study of 2-methyl-1-propanol at 20°C. The most probable model of the structure of short-range order was obtained using the method of exact analysis of the distribution curve in terms of pair functions. The application of the pair functions has been described by Warren [9]. Lately, pair functions have been applied for the determination of the structure of 1-propanol at −25°C [10].

The basic equation, describing the curve of the pair function distribution, has the following form:

$$\sum_{uc}\sum_{i}\frac{N_{ij}}{R_{ij}}P_{ij}(R) = 2\pi R^2 \varrho_e \sum_{uc} Z_j + \int_0^{s_{max}} si(s)\exp(-\alpha^2 s^2)\sin(Rs)ds. \qquad (1)$$

* Address: Instytut Fizyki UAM, Grunwaldzka 6, 60-780 Poznań, Poland.

The right-hand side of equation (1) is evaluated on the basis of experimental data, and ϱ_e is the average electron density, Z_j — the atomic number, $i(s) = [I_{eu}/N - \sum_{uc} f_i^2]/g^2(s)$, I_{eu}/N is the coherent radiation intensity per component unit (uc), $g(s) = \sum_{uc} f_j / \sum_{uc} Z_j$, and $\exp(-\alpha^2 s^2)$ is a convergence factor.

In the exact method, one has to find such a set of pair functions described by the left-hand side of equation (1) that gives, as a result, the right-hand side of this equation. The pair functions $P_{ij}(R)$ are calculated for chosen interactions of pairs of atoms on the basis of the following equation:

$$P_{ij}(R) = \int_0^{s_{max}} [f_i f_j / g^2(s)] \exp(-\alpha^2 s^2) \sin(sR_{ij}) \sin(sR) ds, \tag{2}$$

where $g(s)$ and $\exp(-\alpha^2 s^2)$ stand for the same factors as in equation (1).

Previous structural investigations of the aliphatic alcohols [4–8] are based on an approximation assuming the same shape of various atomic scattering functions:

$$f_m = K_m f_e, \tag{3}$$

where K_m is the effective electron number and

$$f_e(s) = \sum_{uc} f_m(s) / \sum_{uc} Z_m.$$

According to the approximate method [11, 12], the surface area of the maximum of the electron density distribution curve is calculated from the dependence:

$$A_T = 2K_i K_j n, \tag{4}$$

where n is the number of pairs of atoms with the same distance between each other. The position of this maximum corresponds to the distance between an interacting pair of atoms "i" and "j" in the molecule.

If this maximum is the superposition of two or more discrete peaks which are the result of interactions between pairs of atoms "i" and "j" with different distances between each other, the total maximum area is:

$$A_T^t = \sum_{i \neq j}^{m} K_i K_j n_{ij}, \tag{5}$$

where m is the number of atoms in the molecule, and n_{ij} the number of pairs of atoms interacting at different distances. Although the surface area of the maximum A_T^t can be calculated with high accuracy for samples containing light atoms, it is impossible to determine the position of the discrete maxima. The traditional method of analysis of the distribution curves for molecular liquids [13] is illustrated in diagrams A, B and C in Fig. 1. These diagrams show 3 different ways of drawing the discrete maxima, corresponding to intermolecular interactions in 2-methyl-1-propanol. The positions of the discrete maxima *1*, *2*, *3* and *4* and corresponding to interactions between the pairs of atoms are shown in Table I.

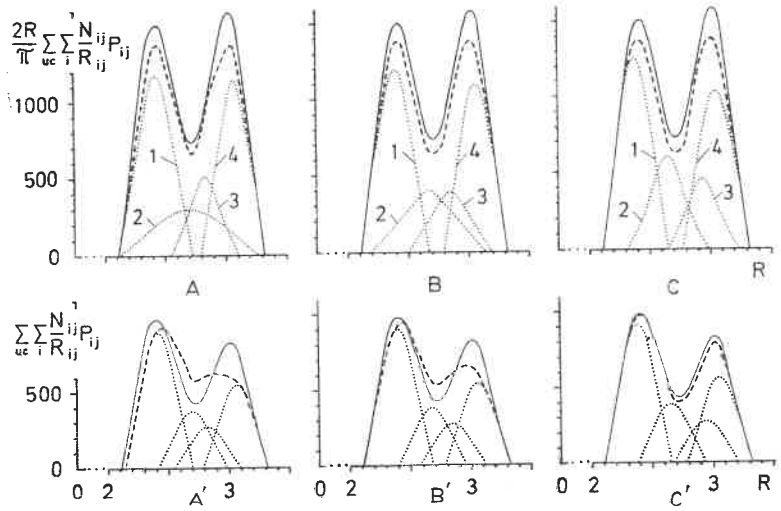

Fig. 1. Three ways of interpreting the maxima of the radial distribution function for 2-methyl-1-propanol

Fig. 1 illustrates also the interpretation of the distribution function in terms of pair functions. From this figure A′, B′, C′ it can be concluded that the best agreement of the theoretical curve (broken line) and experimental one (continuous line) is obtained in the case of C′ (Table I). The arbitrary shape of the discrete maxima (dotted line in Fig. 1) and consequent divergences between the corresponding structural parameters (Table I) admit

TABLE I

Position of discrete maxima and corresponding interactions between pairs of atoms in 2-methyl-1-propanol

Discrete maxima	Interacting pairs of atoms, assigned to discrete maxima	Position of discrete maxima [Å]		
		Method		
		A	B	C
1	C(1)–C(3), C(1)–C(4), C(3)–C(4)	2.42	2.40	2.38
2	O–O^{II}, O–O^{III}	2.70	2.68	2.65
3	C(2)–O	2.82	2.85	2.94
4	C(3)–O, C(4)–O	3.06	3.06	3.05

of the simultaneous existence of some probable structural models. An unambiguous interpretation, leading to one structural model, can be made only if both the shape and surface area of the maxima are available for the pairs of interacting atoms. The best result in structural studies of molecular liquids can be obtained by the method of "ideal peaks" [14–16] or the more practical method of "pair functions" [9, 17], the latter being used in this work.

2. Experimental

Monochromatic X-ray radiation Cu$K\alpha$ and Mo$K\alpha$ was scattered through a thin layer of 2-methyl-1-propanol, thermostatically controlled at 20°C±0.2°C. A photographic method of recording of the scattered radiation with the use of Agfa-Gevaert X-ray films of the D7 type was applied. The mean angular distribution of the scattered X-ray intensity was obtained from photometric curves of the diffractograms. The corrections for background, polarization, absorption and Compton scattering were applied over a mean angular distribution of the scattered X-ray intensity which was next normalized according to the Krogh-Moe [18] and Norman [19] method.

The accuracy of reading the ϑ angle from the recording paper was $\pm 0.1°$. The systematic errors originating in the shrinking of the film during processing of the photographs and caused by the thickness of the layer of the sample ($d = 1$ mm) are linear functions of the ϑ angle. In the range of experimentally accessible values of the ϑ angle ($2° \leqslant \vartheta \leqslant 42°$), the total maximum error $\Delta\vartheta$ does not exceed $\pm 0.3°$. Taking into account the applied method, causing both systematic and random errors in the experimental data, the accuracy of the pair function obtained is estimated to be about 6%.

3. Results and discussion

On the basis of the experimental mean angular distribution of the scattered X-ray intensity the integrand of the equation (1) [$si(s) \exp(-\alpha^2 s^2)$] was calculated. This integrand, evaluated for $\alpha = 0.045$ and $s_{max} = 11.831$, is shown in Fig. 2. The pair function distribution curve, determined by the right-hand side of equation (1), is shown as the full line in Fig. 3, where the broken line represents the left-hand side of equation (1). The discrete maxima (dotted lines in Fig. 3) illustrate the pair functions calculated from equation (2).

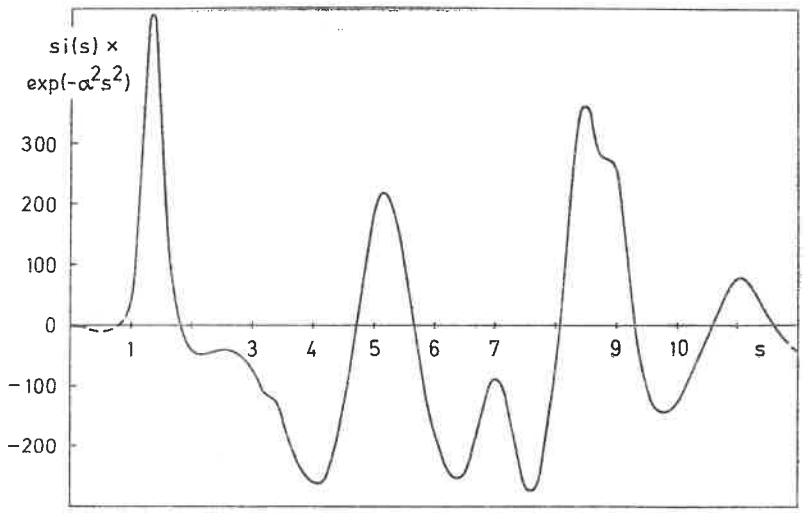

Fig. 2. Curve of $si(s)\exp(-\alpha^2 s^2)$ for 2-methyl-1-propanol ($\alpha = 0.045$, $s_{max} = 11.831$ Å^{-1})

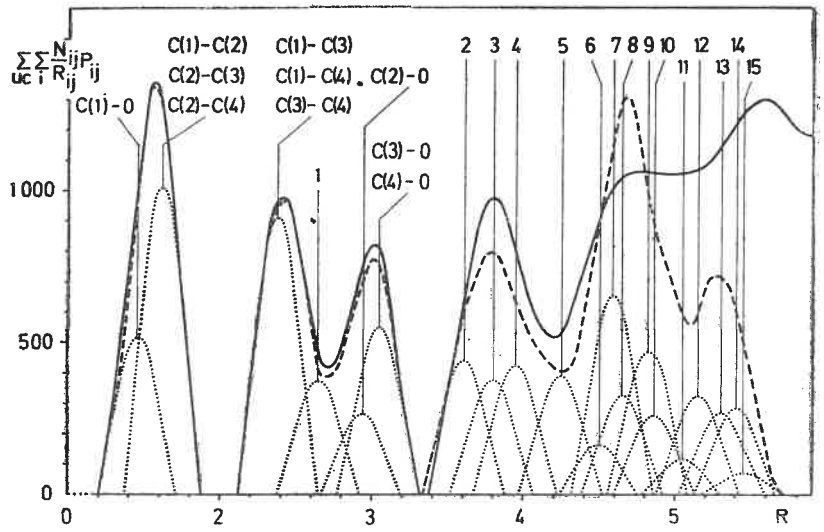

Fig. 3. The pair function distribution curve for 2-methyl-1-propanol. The broken line represents the theoretical curve which is the sum of discrete maxima (dotted line)

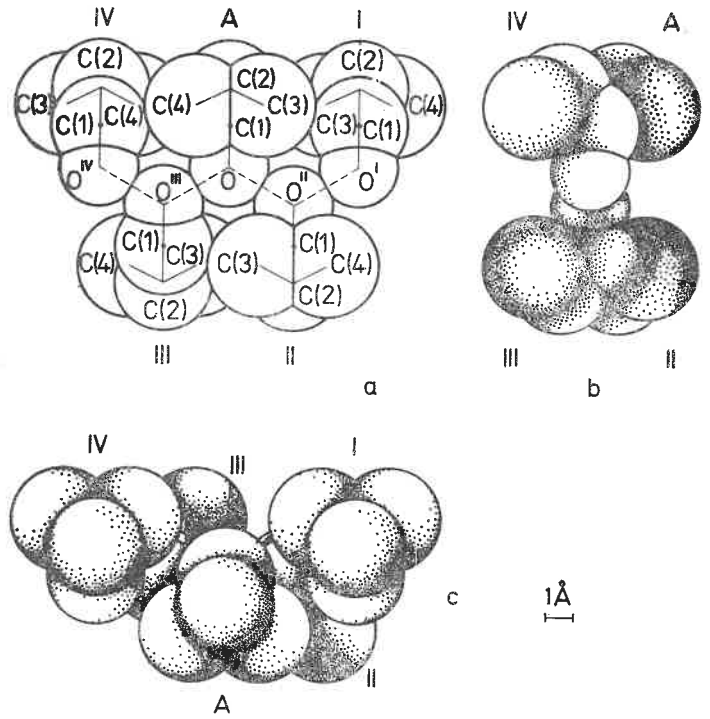

Fig. 4. Model of 2-methyl-1-propanol structure: a) orthogonal projection of the model structure onto the plane in which the O and C(1) atoms lie; b) orthogonal projection of the model structure onto the plane of the O−C(1) and C(1)−C(2) bonds; c) orthogonal projection of the model structure onto the plane perpendicular to the directions of the O−C(1) bonds

The values of $\sum_{uc}\sum_{ij} N_{ij}/R_{ij}$, attributed to the corresponding interatomic interactions for the proposed structural model of 2-methyl-1-propanol shown in Fig. 4, are given in Table II.

The intramolecular interactions, represented by corresponding pairs of atoms, are indicated in Fig. 3. The intermolecular interactions are indicated with Arabic numbers from *1* to *15*, both in Fig. 3 and in Table II.

TABLE II

Type of intra- and intermolecular interactions and the $\sum_{uc}\sum_{i} N_{ij}/R_{ij}$ magnitudes for the assumed 2-methyl-1-propanol structure model

Type of intramolecular interactions		N_{ij}/R_{ij}
C(1)–O		2/1.46
C(1)–C(2), C(2)–C(3), C(2–C(4)		6/1.62
C(1)–C(3), C(1)–C(4), C(3)–C(4)		6/2.38
C(2)–O		2/2.94
C(3)–O, C(4)–O		4/3.05
Type of intermolecular interactions	**Peak No**	
$O-O^{II}$, $O-O^{III}$	1	2/2.65
$C(1)-O^{II}$, $C(1)-O^{III}$, $O-C(1^{II})$, $O-C(1^{III})$,	2	4/3.61
$C(1)-C(3^{I})$, $C(3)-C(1)^{I}$), $C(1)-C(4^{IV})$, $C(4)-C(1^{VI})$	3	4/3.80
$O-C(3^{II})$, $O-C(3^{III})$, $C(3)-O^{II}$, $C(4)-O^{III}$	4	4/3.95
$O-C(3^{I})$, $O-C(4^{IV})$, $O^{I}-C(3)$, $O^{IV}-C(4)$	5	4/4.25
$C(3)-C(3^{I})$, $C(4)-C(4^{IV})$	6	2/4.50
$O-O^{I}$, $O-O^{IV}$	7	2/4.59
$C(1)-C(1^{I})$, $C(1)-C(1^{IV})$	7	2/4.59
$C(2)-C(3^{I})$, $C(2)-C(4^{IV})$, $C(3)-C(2^{I})$, $C(4)-C(2^{IV})$	7	4/4.59
$O-C(2^{II})$, $O-C(2^{III})$, $C(3)-O^{II}$, $C(2)-O^{III}$	8	4/4.65
$C(1)-O^{I}$, $C(1)-O^{IV}$, $O-C(1^{I})$, $O-C(1^{IV})$	9	4/4.82
$C(1)-C(1^{II})$, $C(1)-C(1^{III})$	9	2/4.82
$C(2)-C(1^{I})$, $C(2)-C(1^{IV})$, $C(1)-C(2^{I})$, $C(1)-C(2^{IV})$	10	4/4.86
$C(2)-C(2^{I})$, $C(2)-C(2^{IV})$	11	2/5.05
$O-C(4^{II})$, $O-C(4^{III})$, $C(4)-O^{II}$, $C(3)-O^{III}$	12	4/5.15
$C(1)-C(3^{II})$, $C(1)-C(3^{III})$, $C(3)-C(1^{II})$, $C(4)-C(1^{III})$	13	4/5.30
$O-C(2^{I})$, $O-C(2^{IV})$, $C(2)-O^{I}$, $C(2)-O^{IV}$	14	4/5.40
$C(3)-C(3^{II})$	15	1/5.45

The central molecule *A* (Fig. 4) is connected by a hydrogen bond of a length of 2.65 Å with the molecules II and III. The molecules *A*, I, II, III and IV form an open chain with a mean angle of 120° between the O...O bonds. As it is concluded from Fig. 5, the angle 120° gives the best agreement of the experimental and theoretical pair functions.

According to the suggested model, shown in Fig. 4, the molecules I and IV have $CH(CH_3)_2$ groups inclined to the plane containing the atoms O and C(1) in a direction opposite to the *A* molecule. The C(1)–C(2) bonds of the individual molecules in the chain

form an angle of about 35° with the plane. Figs 4a and 4b clearly show the possibility of free rotation of the CH_3 groups and Fig. 4c show the possibility of inhibited rotation of the $CH(CH_3)_2$ groups about the C(1)–O bond.

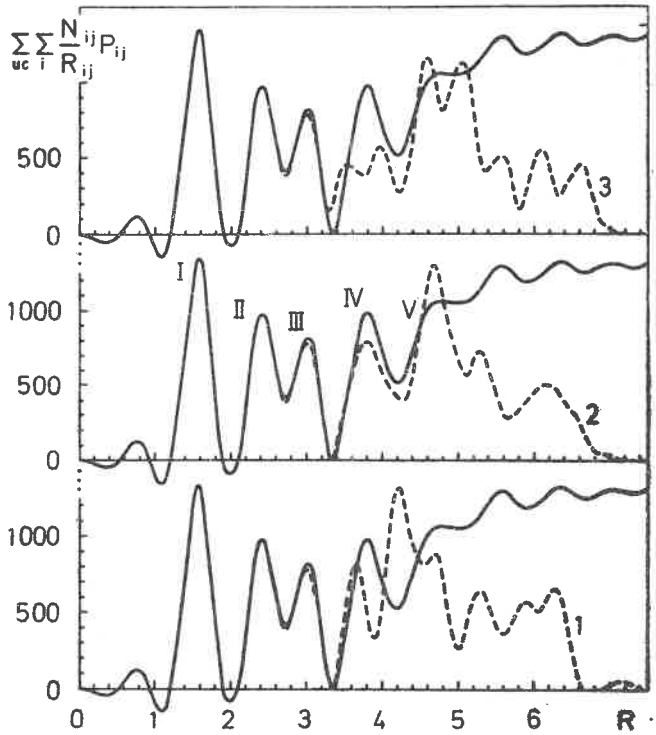

Fig. 5. Comparison of the theoretically calculated pair functions (broken lines) and experimental curve (continuous line) obtained for 2-methyl-1-propanol. Pair function calculated for the model structure with the angles: 1) 110°, 2) 120°, 3) 130°

4. Conclusions

The pair function, calculated on the basis of the model shown in Fig. 4, is in good agreement with the experimental curve for the maxima I, II and III (Fig. 5). The positions of these maxima are shown in Table III.

TABLE III

Positions of pair function maxima

Maximum No	Position of maximum
I	1.57 Å
II	2.41 Å
III	3.02 Å
IV	3.80 Å
V	4.68 Å

The positions of the maxima IV and V show good agreement with the experimental maxima. The considerable widening of the maximum V for $R = 4.68$ Å in comparison with the calculated maximum is a result of the rigidity of the model proposed. According to Table III, the greatest contribution to the maximum V is given by the interactions $O–O^{I}$, $O–O^{IV}$, $C(1)–C(1^{I})$ and $C(1)–C(1^{IV})$ at the distance $R = 4.59$ Å and $C(1)–O^{I}$, $C(1)–O^{IV}$, $O–C(1^{I})$ and $O–C(1^{IV})$ at the distance $R = 4.82$ Å. These distances are the most sensitive to changes in the angle between the O...O bonds. Slight fluctuations of this angle around the mean value of 120° were observed. The theoretical curve is different in comparison with the experimental one for $R > 5$ Å as a result of interactions of pairs of atoms, not included in Table II and Fig. 5.

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