

Then the coupling tensors for the internal modes of the molecule have to be calculated from a complete force-constant matrix. We do not see a solution in which the quantum-chemically calculated static densities can correctly be converted to dynamic densities.

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X-ray Diffraction Study of the Structure of 1-Propanol at -25°C

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(Received 16 November 1976; accepted 17 December 1976)

Molybdenum $K\alpha$ X-radiation, monochromated by an NaCl single crystal, was scattered in 1-propanol at -25°C . The angular distribution of the scattered X-ray intensity was determined and used for the calculation of the experimental pair function. On the basis of some models of the structure of liquid 1-propanol, the theoretical curves of pair functions were calculated and then compared to the experimental curve. The most probable model of the liquid is that of statistically distributed chains of 1-propanol molecules. Such chains are created by intermolecular bonds of the $\text{O}-\text{H}\cdots\text{O}$ type, the length of which is 2.65 Å. The angles between the $\text{O}\cdots\text{O}$ bonds have a value between 100 and 110° . In this model the oxygen and equivalent carbon atoms all lie in the same plane, and the carbon atoms of the individual molecules are in parallel planes, inclined at an angle of 80° to the oxygen-containing plane. The inhibited rotation of the $(\text{CH}_2)_2\text{CH}_3$ group around the $\text{O}-\text{C}(1)$ bond and the free rotation of the CH_3 group around the $\text{C}(2)-\text{C}(3)$ bond are possible.

Introduction

The first X-ray structural studies of aliphatic alcohols were carried out by Stewart & Morrow (1927). Methanol was the subject of the structural studies of Zachariasen (1935). According to the structural model proposed by Zachariasen, the methanol molecules conglomerate into associated polymer chains by hydrogen bonding. This model was later confirmed by Harvey (1938). Ethanol at 25°C and -75°C was also studied by Harvey (1939), while Prietzsck (1941) studied it in the super-cooled state at -150°C . Both these authors discovered the tendency of ethanol molecules to associate by the creation the hydrogen bridges of OH groups. The experimental results of Harvey and Prietzsck were confirmed theoretically by Jagodzinski (1947). The structural X-ray analysis of aliphatic alcohols was carried out by Ukrainian scientists (Golik, Skryshevskii & Adamienko, 1967; Golik, Skryshevskii & Ravikovich, 1954). Their studies confirmed the tendency of alcohol molecules to associate at room temperature as well as the increase of coordination number from 3 for amyl alcohol to 5 for decyl alcohol.

This paper shows the results of structural studies of 1-propanol at -25°C . 1-propanol at room temperature was investigated by Golik, Skryshevskii & Ravikovich (1954), but the plane model of the molecule suggested by them is not satisfactory and does not seem to be probable.

For a molecular liquid the interpretation of the maxima of the radial distribution function of electron density is rather difficult because it often happens that several interacting atom pairs with comparable interatomic distances can be attributed to one maximum. This is the reason why it is impossible to evaluate the coordination number only on the basis of the comparison between the surface areas of the distribution curve maxima and the surface areas calculated theoretically. In practice the pair function method, which is precise and approximation-free, is applied.

Experimental procedure

In the X-ray study of 1-propanol Mo $K\alpha$ radiation, monochromatized by a ground crystal monochromator set in the primary beam, was used. Samples of the alcohol at -25°C were put into a liquid holder

with two mica windows limiting the liquid layer to 1 mm. Constant temperature was maintained by placing the liquid holder in a thermostatically controlled chamber. Fluctuation of temperature did not exceed $\pm 0.3^{\circ}\text{C}$.

The angular distributions of the scattered X-ray intensity were measured up to $s_m = 4\pi \sin \theta/\lambda = 11.365 \text{ \AA}^{-1}$. The corrections for the background, polarization, absorption and Compton scattering were made over a mean angular distribution of the scattered X-ray intensity, which was next normalized according to Norman's (1957) method.

In order to obtain the quantitative characteristic of the 1-propanol structure, the pair function distribution was calculated on a basis of equation (10.39) of Warren (1969):

$$\sum_{uc} \sum_i \frac{N_{ij}}{R_{ij}} P_{ij}(R) = 2\pi^2 R \rho_e \sum_{uc} Z_j + \int_0^{s_m} si(s) \exp(-\alpha^2 s^2) \sin(sR) ds, \quad (1)$$

where:

\sum_{uc} stands for summing over unit of composition,
 N_{ij} is the average number of neighbours in the i th shell around atom j at a distance R_{ij} ,
 $P_{ij}(R)$ is the pair function,
 ρ_e is the average electron density,
 Z_j is the number of electrons in the j th atom,
 $s = 4\pi \sin \theta/\lambda$, where 2θ is the angle of scattering and λ is the X-ray wavelength,
 $i(s)$ represents the structural sensitive part of the total coherent intensity I_{eu}/N in electron units per molecule,

$$i(s) = [I_{eu}/N - \sum_{uc} f_j^2] / g^2(s),$$

$g(s)$ is a sharpening factor,
 $\exp(-\alpha^2 s^2)$ is a convergence factor.

The series of pair functions $P_{ij}(R)$ is determined as

$$P_{ij}(R) = \int_0^{s_m} [f_i f_j / g^2(s)] \times \exp(-\alpha^2 s^2) \sin(sR_{ij}) \sin(sR) ds. \quad (2)$$

In practice, the simplified method for the calculation of the $P_{ij}(R)$ function is applied by the use of the auxiliary pair function:

$$Q_{ij}(x) = \frac{1}{2} \int_0^{s_m} [f_i f_j / g^2(s)] \exp(-\alpha^2 s^2) \cos(xs) ds. \quad (3)$$

The auxiliary function $Q_{ij}(x)$ is related to the $P_{ij}(R)$ function by

$$P_{ij}(R) = Q_{ij}(R - R_{ij}) - Q_{ij}(R + R_{ij}). \quad (4)$$

The right-hand side of (1) is calculated on the basis of the experimental data with the suitable selection of the $\exp(-\alpha^2 s^2)$ and $g(s)$ coefficients and then plotted

as the R function. Next, with the use of the same convergence and sharpening factors the auxiliary pair functions $Q_{ij}(x)$ for interatomic interactions existing in the investigated sample are calculated. The left-hand side of (1) is calculated for all such values of R_{ij} and N_{ij} , so as to obtain the best agreement with the right-hand side. The model of the interatomic interactions is correct if the whole curve obtained by summing all pair functions determined from the left-hand side of (1) shows a good agreement with the experimental curve with respect both to the position and to the surface area of the obtained maxima.

The distribution curve of the pair function determined from (1) was calculated for the coefficient $\alpha = 0.03$, $s_m = 11.365$ and $g(s) = \sum_{uc} f_j / Z_j$. The numerical integration was carried out by Simpson's method with integration steps of 0.25° . The parameter R was varied with steps of 0.05 \AA . The maximum experimental

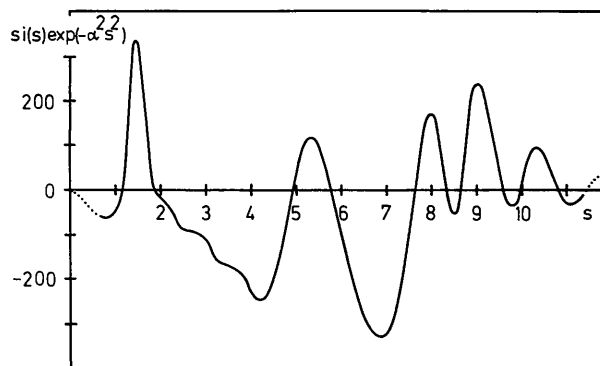


Fig. 1. The experimental curve $si(s) \exp(-\alpha^2 s^2)$ for 1-propanol at -25°C .

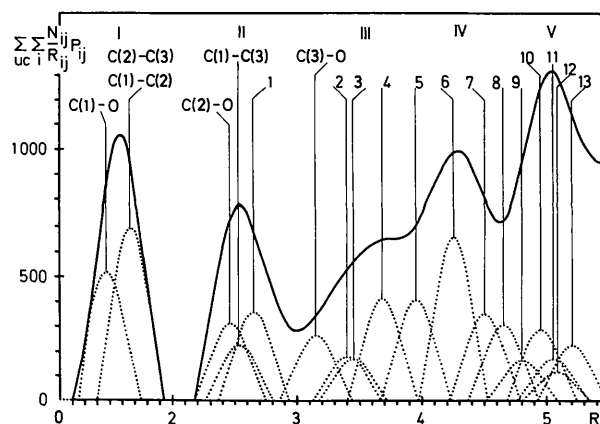


Fig. 2. The pair-function distribution curve for 1-propanol at -25°C . The dotted maxima correspond to the theoretical maxima of the effective pair functions calculated for individual interatomic interactions.

error $\Delta(R)$ of the pair-function distribution curve was estimated to be 5%.

The results and interpretation

Fig. 1 shows the angular distribution of the curve $si(s) \exp(-\alpha^2 s^2)$ obtained for 1-propanol at -25°C . The pair-function distribution curve calculated from the experimental data is shown as the continuous line in Fig. 2. The positions of the successive maxima of the pair function on the R axis are presented in Table 1.

Table 1. Positions of maxima of the pair function

No.	Position (Å)
I	1.54
II	2.54
III	3.60
IV	4.28
V	5.04

At the beginning it was assumed that the first maximum of the experimental pair function, for $R = 1.54 \text{ \AA}$, was the result of the interactions between the neighbouring atoms in the 1-propanol molecule. In order to calculate the theoretical maximum of these interactions the auxiliary pair functions shown in Fig. 3 were calculated. The suitable selection of N_{ij}/R_{ij} values assured good agreement between the first maximum of

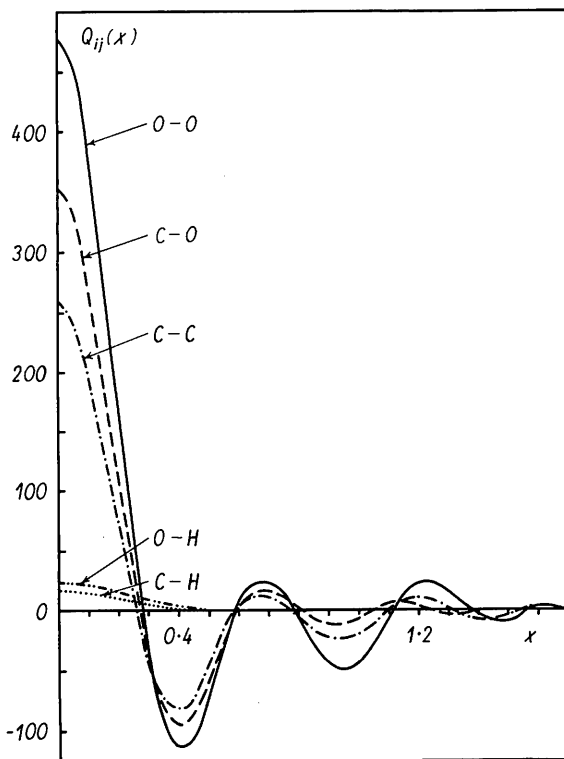


Fig. 3. The pair functions for 1-propanol calculated for $\alpha = 0.03$ and $s_m = 11.365$.

the experimental pair function and the theoretical maximum of the pair function calculated for the interatomic interactions of the C(1)-O and C(1)-C(2), C(2)-C(3) types. The pair functions calculated for the individual interatomic interactions are represented by maxima shown in Fig. 2 by dotted lines. The positions of these maxima (on the R axis) determine the distances R_{ij} assumed between interacting pairs of atoms.

The interpretation of the successive pair-function maxima was carried out for some alternative models of the 1-propanol molecule, as well as for chains of these molecules. Fig. 4(a) shows three possible cases for the molecule model with respect to varying orientation of the plane containing the carbon atoms relative to the C(1)-O bond direction. Cases 1 and 2 correspond to a three-dimensional model of the molecule while the case 3 corresponds to the planar model of the molecule.

The proposed model of the chain, including the molecule model described by case 1 in Fig. 4(a), is shown in Fig. 4(b). Shown schematically, the molecule A is the central molecule bonded by a hydrogen bond to molecules II and III. The length of this bond is 2.65 \AA . The average angle between the directions of the $\text{O} \cdots \text{O}$ bonds is between 100 and 110° . Because of the assumed coordination number ($N = 2$) an open chain is created, like that proposed for methanol by Zachariassen (1935). The cyclic model of the association of 1-propanol molecules, with coordination number $N = 2$, was rejected because of the considerable divergence between the theoretically calculated pair function and that obtained experimentally.

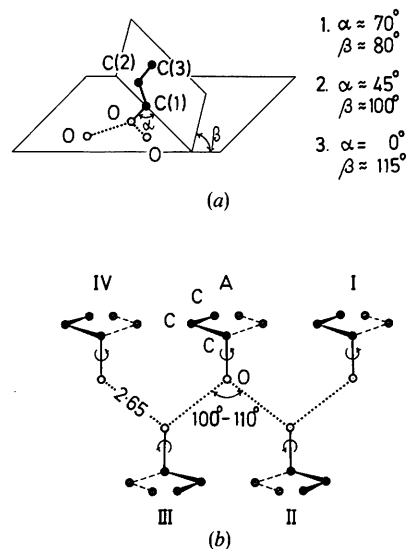


Fig. 4. The 1-propanol structure model. (a) Three cases for the model of the molecule, (b) the chain model. O-oxygen atoms, ●-carbon atoms; bonds between carbon atoms point out of the plane of the figure.

In the chain model assumed for propanol 1 (Fig. 4b), the O and C(1), C(1ⁱ), C(1ⁱⁱ), C(1ⁱⁱⁱ), C(1^{iv}) atoms of different molecules lie in the plane of the figure. The hydrocarbon groups of the individual molecules: A, I, II, III and IV lie in parallel planes at an angle $\beta \approx 80^{\circ}$ with the plane of the figure. The line of intersection of the two planes forms an angle $\alpha \approx 70^{\circ}$ with the O-C(1) bond direction.

The chain model allows the free rotation of the CH₃ group around the C(2)-C(3) bond. There is also the possibility of inhibited rotation of (CH₂)₂CH₃ hydrocarbon groups around the O-C(1) bond, so that these groups have equal probability of being in either the $\alpha \approx 70^{\circ}$ position or the $\alpha \approx 290^{\circ}$ position (Fig. 4a).

Table 2 shows the $\sum_{uc} \sum_i N_{ij}/R_{ij}$ magnitudes for inter- and intramolecular interactions between the pairs of atoms, fixed in accordance with the model. The intramolecular interactions, represented by the corresponding pairs of atoms, are shown in Fig. 2 by the individual maxima of the pair function. The intermolecular interactions are indicated with the arabic numbers 1 to 13 both in Fig. 2 and in Table 2.

Table 2. Types of intra- and intermolecular interactions and the magnitudes of $\sum_{uc} \sum_i N_{ij}/R_{ij}$ for the assumed chain model of 1-propanol

The carbon atoms are numbered successively along the carbon chain starting from the carbon atom next to the oxygen atom. Roman numerals stand for different molecules (Fig. 4).

Type of intramolecular interaction	$\sum_{uc} \sum_i N_{ij}/R_{ij}$
C(1)-O	2/1.47
C(1)-C(2), C(2)-C(3)	4/1.66
C(2)-O	2/2.46
C(1)-C(3)	2/2.53
C(3)-O	2/3.15

Type of intermolecular interaction	Peak No.	$\sum_{uc} \sum_i N_{ij}/R_{ij}$
O-O ⁱⁱ , O-O ⁱⁱⁱ	1	2/2.65
C(1)-C(2 ⁱ), C(2)-C(1 ^{iv})	2	2/3.40
C(3)-C(2 ⁱ), C(2)-C(3 ^{iv})	3	2/3.45
O-C(1 ⁱⁱ), C(1)-O ⁱⁱ , O-C(1 ⁱⁱⁱ), C(1)-O ⁱⁱⁱ	4	4/3.68
O-C(2 ⁱ), C(2)-O ^{iv} , C(2)-O ⁱⁱⁱ , O-C(2 ⁱⁱⁱ)	5	4/3.95
O-O ⁱ , O-O ^{iv}	6	2/4.25
C(1)-C(1 ⁱ), C(1)-C(1 ^{iv}), C(2)-C(2 ⁱ), C(2)-C(2 ^{iv})	6	4/4.25
C(3)-C(3 ⁱ), C(3)-C(3 ^{iv})	6	4/4.25
O-C(1 ⁱ), C(1)-O ⁱ , O-C(1 ^{iv}), C(1)-O ^{iv}	7	4/4.50
O-C(3 ⁱⁱⁱ), C(3)-O ⁱⁱⁱ	8	2/4.65
C(1)-C(3 ⁱ), C(3)-C(1 ^{iv})	8	2/4.65
O-C(2 ⁱⁱ), C(2)-O ⁱⁱ	9	2/4.80
O-C(3 ⁱⁱ), C(3)-O ⁱⁱ	10	2/4.95
C(1)-C(1 ⁱⁱ), C(1)-C(1 ⁱⁱⁱ)	10	2/4.95
O-C(3 ⁱ), C(3)-O ^{iv}	11	2/5.05
C(1)-C(2 ⁱⁱⁱ), C(2)-C(1 ⁱⁱⁱ)	12	2/5.08
C(1)-C(3 ^{iv}), C(3)-C(1 ⁱ), C(2)-C(3 ⁱ), C(3)-C(2 ^{iv})	13	4/5.20

Fig. 5 shows the comparison of the experimental curve of the pair function with the theoretical curves of the pair functions calculated for three different models of 1-propanol. Curve 1 in Fig. 5 was calculated for the model described above with the molecule corresponding to case 1 in Fig. 4(a). Curve 2 in Fig. 5

was calculated for the model with the O...O bond length equal to 2.80 Å and the molecule described by case 2 in Fig. 4(a). Curve 3 corresponds to the model with the plane 1-propanol molecule, case 3 in Fig. 4(a), with the O...O bond length equal to 2.65 Å.

The agreement between the calculated and model 1 experimental pair functions is very satisfactory for the first two maxima (Fig. 5, curve 1), with regard both to the position and to the surface area. The positions of successive maxima also show a good agreement with the experimental maxima. The fluctuations of the theoretical curve relative to the experimental one for increasing R values are caused by the interacting atom pairs not included in Table 2. The reason for this is that the distribution curve, being the sum of the effective pair functions for interacting atom pairs, does not include the whole surroundings but only part of the range of the considered model.

The calculated pair functions presented as curves 2 and 3 in Fig. 5 show a good agreement with the experimental curve for maximum I only, the interpretation of which is not related to any structure model, while maximum II for both theoretical curves 2 and 3 does not conform with the corresponding experimental curve maximum with regard either to the position or to the surface area. The reason for this disagreement is the assumptions given in Fig. 4(a) for cases 2 and 3. It is not therefore necessary to explain any further disagreement between theoretical and experimental pair function curves.

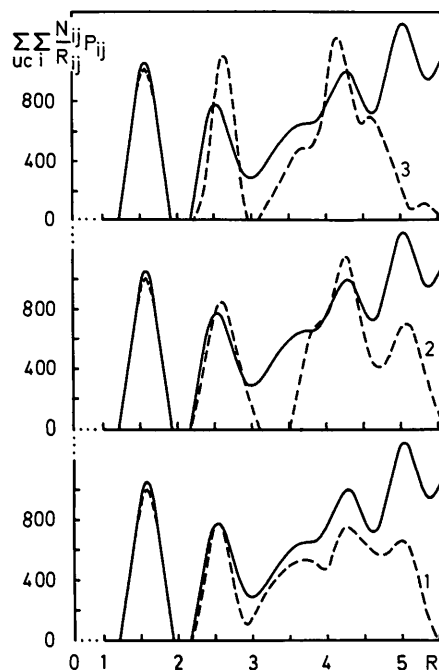


Fig. 5. Comparison between the experimental pair-function curve and the theoretically calculated pair function for three models of the 1-propanol chains.

The best explanation for the shape of the curve is the assumption of case 1 in Fig. 4(a) for the 1-propanol molecule model together with the chain model shown in Fig. 4(b).

Discussion

The structural analysis carried out above shows that the 1-propanol molecule has a three-dimensional structure. Data shown in Fig. 6 and given by Vyrodov, Budko & Dierkach (1964) concerning the radius of the 1-propanol molecule lead us to conclude that the 1-propanol molecule has a spherical shape in the liquid. These molecules create so-called open chains by the intermolecular bond of the $O \cdots O$ type. The mean distance between the oxygen atoms of the neighbouring molecules in the $O \cdots O$ bond was found to

be 2.65 Å. The chain model of 1-propanol (Fig. 4) has a parallel arrangement of hydrocarbon groups $(CH_2)_2CH_3$, which leads to the conclusion about the existence of domain structures. Eyring & Jhon (1969) and Stewart & Morrow (1927) noticed the same phenomenon, the associated polymer chain called a 'domain' should exhibit directional electric polarization. Associated chains are labile entities exhibiting the possibility of breaking and molecule exchange between neighbouring chains. This conclusion is derived from the broadening of the second maximum of the pair function as well as from the weak limiting of this maximum on the side of the increasing R in comparison with the theoretical maximum.

The author wishes to express her indebtedness to Professor Dr S. Kielich and Associate Professor Dr M. Surma for their helpful discussions.

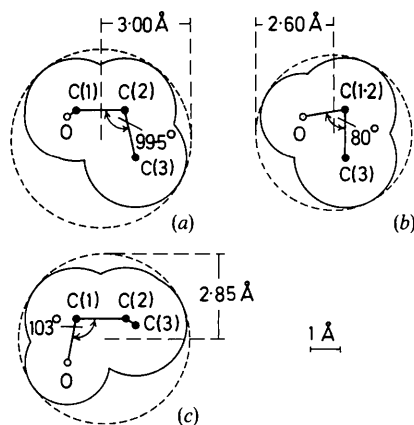


Fig. 6. The molecule of 1-propanol. (a) Projection of the molecule onto the plane in which carbon atoms lie. (b) Projection of the molecule onto the plane perpendicular to the plane in which carbon atoms lie. (c) Projection of the molecule onto the plane in which oxygen and carbon atoms C(1) and C(2) lie. The projection plane is the plane of the figure.

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