Physical Chemistry

Structural properties of liquid formamide

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Computer simulations of liquid formamide were carried out by the Monte Carlo method at 298 and 348 K. The atom-atom spatial distribution functions, the concentrations of closed H-bonded ring, the radial distributions functions of the geometric centers of the rings, and a number of other characteristics of hydrogen-bonded systems were calculated. It was found that the open chains dominate over cyclic structures, which are prone to association and formation of structural heterogeneities. Characteristic types of molecular associates were determined.

Key words: organic solvents, formamide, liquid structure, intermolecular interactions, hydrogen bonds; computer simulation of liquids; Monte Carlo method.

Theoretical and experimental studies of formamide are of great interest because of its rather simple molecular structure and the ability to be involved in intermolecular hydrogen bonding as a proton donor and acceptor. Strong specific molecular interactions lead to self-association of pure formamide in the liquid phase and in solutions due to which formamide bears similarities to liquid water. Analysis of the data available in the Cambridge Structural Database (CSD) demonstrated[1] that 601 compounds are characterized by the presence of intermolecular hydrogen bonds topologically similar to bonds with the participation of the *cis* and *trans* protons of formamide. Most of these compounds play an important role in biological processes. Therefore, formamide is the simplest model system for studying properties and interactions of biological macromolecules.

Only the contradictory data on the structure and intermolecular interactions in liquid formamide are available in the literature.[2–6] All authors stated that formamide exists as a strongly associated liquid. However, opinions differ as to the composition and forms of associates, the topology of the system of hydrogen bonds, and the structures of molecular associates. For example, it was assumed[7] that liquid formamide contains cyclic dimers along with linearly bonded molecules that form planar networks. Other authors[5] believed that the system of H bonds is characterized by a three-dimensional structure containing both H-bonded chains and cyclic structures among which dimers dominate. In alternative works,[8,9] it was stated that chain associates dominate over cyclic dimers. In a number of works,[6,10] it was suggested that cyclic dimers are the major structural elements. The interpretation of the results of measurements of relaxation times by NMR spectroscopy holds a special place. It was also believed[3] that 95% of molecules in liquid formamide are associated to form six-membered rings in which H bonds are formed only through *trans* H atoms.

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Recently, many theoretical works[3,11–16] were devoted to elucidation of molecular structures and characteristic features of intermolecular interactions in amides. Liquid formamide was studied in a number of works[2,15–18] by computer simulation methods. Conclusions about the spatial arrangement, orientations of the molecules, the character of their self-association, and the characteristic features of motions were made based on a comparison of the calculated and experimental data. However, the data on the supermolecular structure of formamide are scarce.

The aim of this work was to determine the modes of association of molecules in liquid formamide, to elucidate the regularities of their mutual arrangement, and to establish typical intermolecular fragments and structural elements of the system of H bonds. Previously,[19–22] we have studied models of liquid water, methanol, and DMF and demonstrated that calculations of the topological properties of the system constructed from H bonds or lines that link the centers of adjacent molecules provide important data on supermolecular structures of liquids. In this work, we used this procedure for analyzing the structure of formamide.

Calculation procedure

Systems of potential functions, which allow one to calculate the energy of intermolecular interactions, were developed for simulations of liquids. The OPLS potentials[16,17] have found wide use. These potentials were involved in standard programs used in computational chemistry and were used in a number of works for simulating formamide.[2,16,17] These works demonstrated that, although many properties of formamide determined experimentally were confirmed by calculations, a number of calculated characteristics depend substantially on the model used.[2,15,16] This refers primarily to functions determined by the mutual arrangement of the molecules. Previously, it has been demonstrated that the more complex T model[18] is in better agreement with the experimental data on the rotational motion of formamide molecules than the model involving the OPLS potential although the structural results obtained with the use of the above two models are qualitatively similar. It was found[16] that the methodological characteristics of the computer experiment are substantially reflected in the behavior of the dipole-dipole correlation function as well as in the value of the dielectric constant. A comparison of the results of calculations of the functions characterizing the spatial structure of formamide and, in particular, the atom-atom radial distribution functions demonstrated that their behavior depends only slightly on the model used and on the calculation procedure.[2,15–18]

With the aim of studying the regularities of the supermolecular structure in more detail, in this work we used a simpler and more commonly used system of OPLS functions for describing intermolecular interactions. Calculations were carried out using the *NVT* ensemble by the Monte Carlo method with the use of original programs. The cubic unit cell taken with periodic boundary conditions contains 125 formamide molecules. The conditions of the computer experiment corresponded to the density of 1.129 and 1.08 g cm^{-3} at 298 K and 348 K, respectively. The spherical restriction of the scope of the potential was applied. Markovian chains with a length of ~30 million configurations were generated. The energy-geometric criterion for bonds was used for constructing the system of H bonds in configurations. It was assumed[17] that two molecules form an H bond if the O...H distance is shorter than 280 pm and the energy of the cleavage of the bond is higher than 18.8 kJ mol^{-1}. The similarity of the calculated values of the energy and the structural characteristics of liquid formamide to the published data[2,15–17] is indicative of the correctness of the computer experiment performed.

Results and Discussion

It is common practice to determine the spatial arrangement of atoms in liquids from the behavior of atom-atom radial distribution functions (RDF), some of which are shown in Fig. 1. For liquid formamide, these functions were calculated by computer simulation methods. The results of calculations were described in the literature in detail.[2,15–18] Note that RDFs change only slightly as the temperature increases by 50 K. This can be due to the fact that under atmospheric pressure, the liquid phase exists in the temperature range of ~208 K.

When RDFs were calculated, averaging was carried out over the ensemble of configurations in spherical layers surrounding each atom. Therefore, it is impossible to imagine the pattern of the most probable arrangement and mutual orientations of molecules in most molecular liquids based only on a knowledge of these functions.[20] More detailed information can be obtained with the use of generalized functions of spatial distribution of atoms by determining them as the ratio between the numerical density of atoms in the volume unit of arbitrary shape and the mean value of ρ

$$g_{ab}(x, y, z) = [dN_{ab}(x, y, z)/dxdydz]/\rho.$$

Here, dN_{ab} is the number of particles of the type b in the volume unit $dxdydz$ at the distance $r(x, y, z)$ from

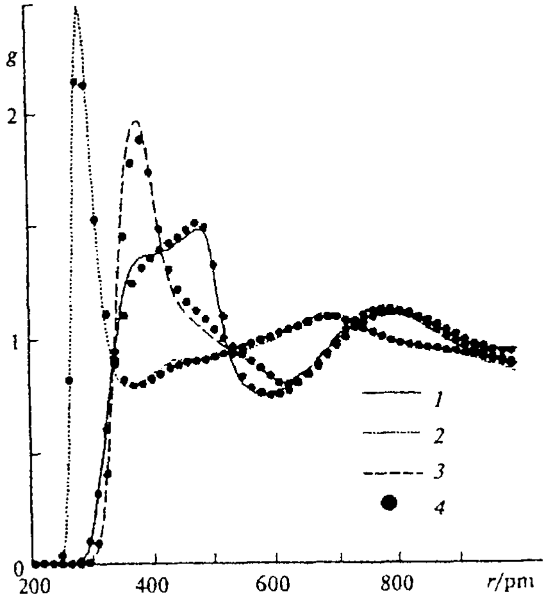

Fig. 1. Radial distribution functions of atoms in liquid formamide, $g(r)$; *1*, NN; *2*, NO; *3*, NC (T = 298 K); *4*, the same functions at 348 K.

the particle of the type *a*. By fixing one coordinate, we obtain the function of two variables, which can be represented in a plane. In our calculations, a rectangular parallelepiped with the length of the side of the square base of 15 pm and with the height of 400 pm was taken as the volume unit. We studied the distribution of atoms

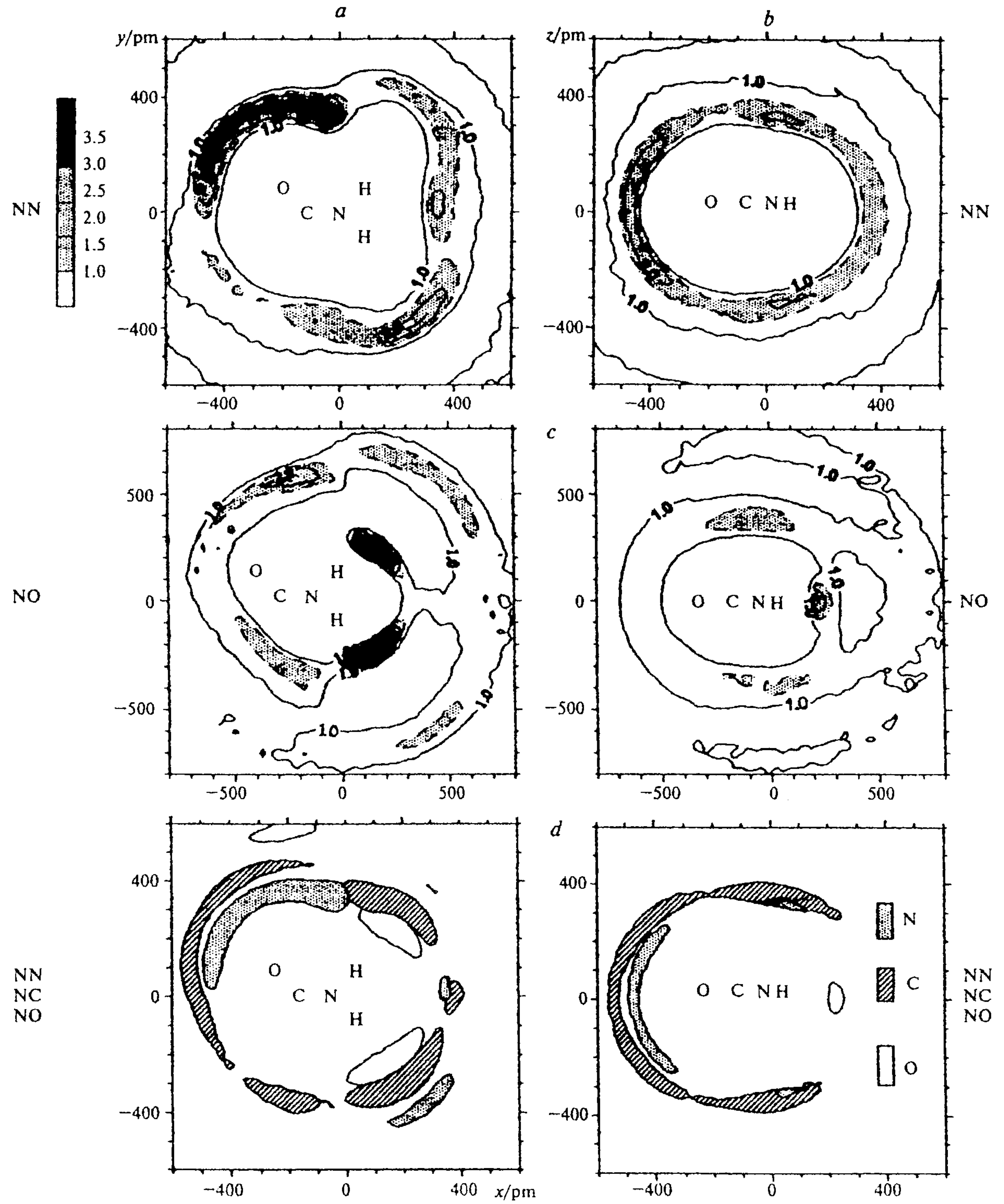

Fig. 2. Generalized spatial distribution functions of atoms of the type *i,j* of formamide molecules, $g_{ij}(x, y, 0)$ (*a*) and $g_{ij}(x, 0, z)$ (*b*); *c*, *d*, the lower plots were obtained as a result of the mutual superposition of the regions in which the local densities of the N, C, and O atoms are more than twice as large as the average value.

in two layers, namely, in the layers parallel and perpendicular to the plane of the molecule under consideration. In both cases, the N atom of the molecule is located at the origin of coordinates and the N—C bond is located at the midpoint between the cutting planes.

The plots of the generalized functions of spatial distribution of the atom density are shown in Fig. 2. Compared to the atom-atom RDFs, the generalized functions carry substantially more detailed information on the mutual arrangement of molecules. Within the first coordination shell of the central molecule, the areas of the highest probability of location of atoms have complex shapes. The anisotropy of the distribution is determined both by electrostatic interactions and the shape of the molecule. The maximum density of the N atoms is observed in the vicinity of the O and H atoms of the central molecule. The formation of intermolecular H bonds is most clearly seen in the plots of the g_{NO} functions. The H atoms in the *cis* and *trans* positions are involved in interactions with adjacent molecules to different degrees. A large distance between the *trans* H atom and the O atom and the absence of steric hindrances are more favorable for the formation of an H bond. When atoms are located at distances larger than 600 pm, the contour lines are more symmetrical and are primarily determined by the shape of the molecule. Outside the first coordination shell, the packing factors have the major effect on the spatial structure.

Two possible modes of molecular association, which correspond to the positions of the regions of the highest probability of location of atoms in the layer parallel to the plane of the central molecule (see Fig. 2, *a*), are shown in Fig. 3. In the first configuration, two adjacent chains are linked in a ribbon through the *cis* H atoms to form cyclic dimers (see Fig. 3, *a*). In the second case, the association of the molecules is favorable for the formation of open spatial structures, namely, chains, branched associates, and networks. The topological properties of the system of H bonds are determined by the predominance of one mode of molecular association over the second one. A change in the environmental conditions may lead to a shift of the dynamic equilibrium and to a structural rearrangement.

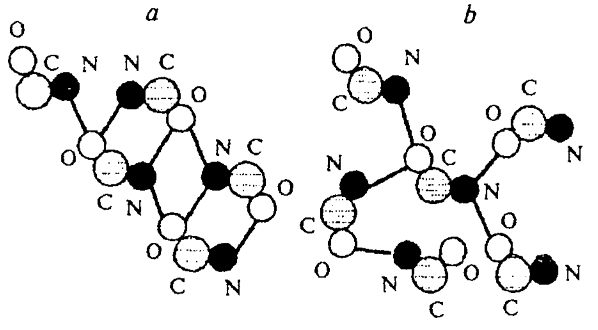

Fig. 3. Two possible modes of association of formamide molecules: *a*, cyclic dimers; *b*, open spatial structures. The atomic coordinates correspond to the positions of the regions of the increased density of the functions $g_{ij}(x, y, 0)$ (see Fig. 2, *a*).

The anisotropy of distribution of atoms in the layer perpendicular to the plane of the central molecule is less pronounced (see Fig. 2, *b*). The large regions of increased density of the N and C atoms in the vicinity of the O atom of the central molecule indicate that the angles between the molecules vary over a wide range and that the H bonds are highly flexible. The overlap of the contours in the plots of the g_{NN}, g_{NO}, and g_{NC} functions in the supermolecular region indicates that the liquid contains molecules, which are characterized by the parallel arrangement of the planes and by a broad spectrum of possible orientations of the C—N bonds. In this case, it is difficult to separate the most typical fragments of the vibrationally averaged V structure of the liquid.

Therefore, information on the short-range order can be obtained based only on the analysis of the spatial correlation functions. However, it is difficult to make conclusions about the modes of molecular association in liquid formamide, namely, of the structure formed from elements consisting of several molecules.

It is common practice to interpret experimental results within the framework of intuitive ideas of the intermolecular V structure of the liquid. The data on the V structure can be obtained by computer simulation methods, which allow one to determine statistical distributions and correlation functions for objects consisting of several molecules. For example, molecules associated in cyclic species through H bonds can serve as elements of the intermolecular structure. The ratios between the concentrations of the rings with different numbers of vertices are very important topological characteristics of the system of H bonds. If the geometric centers of the rings are determined from the coordinates of the N atoms, the effect of vibrational motions of the molecules decreases as the correlation between these motions decreases and the number of molecules involved in the ring increases because of the averaging over time (molecular dynamics) or over the ensemble (Monte Carlo method). In this case, the correlation functions calculated from the coordinates of the centers of the rings characterize the intermolecular V structure of the liquid.

There are, on the average, 129.5 bonds per 100 molecules in the molecular configurations of liquid formamide determined by simulation at 298 K. Most of these bonds (78.8) are formed with the participation of the *trans* H atoms. The connectivity parameter equals 2.59 bonds per molecule. Calculation of the concentrations of the cyclic species demonstrated that there are 10.3 cyclic dimers, 0.69 trimers, 3.6 tetramers, 1.8 pentamers, 3.0 hexamers, and 2.9 heptamers per 100 molecules. Two *cis* bonds are involved in each dimer. If H bonds in dimers are ignored, the system of H bonds contains 30.1 *cis* bonds and 78.8 *trans* bonds. Taking into account the relatively small number of the rings formed and the fact that each bond links two molecules, it can be concluded that fragments of chains and branched structures dominate over cyclic structures.

In the system consisting of 100 molecules, 6.4 *cis* bonds and 4.1 *trans* bonds are, on the average, broken as the temperature increases by 50 K. The increased thermal stability of the *trans* bonds is attributable to the larger average energy of the cleavage of these bonds compared to the *cis* bonds (at 298 K, 26.1 kJ mol^{-1} and 23.9 kJ mol^{-1}, respectively). The connectivity parameter decreases to 2.38 bonds per molecule as a result of which the concentration of the ring structures also decreases. In going from the dimer to the heptamer, the number of rings per 100 molecules are 7.4, 0.65, 2.3, 1.4, 2.0, and 2.5, respectively. The rings with the odd number of vertices are less prone to thermal decomposition. This behavior of the bond system is indicative of a particular regularity of the spatial arrangement of the rings. The association of predominating fragments, namely, dimers, results in the appearance of ribbon structures consisting of four- and six-membered rings.

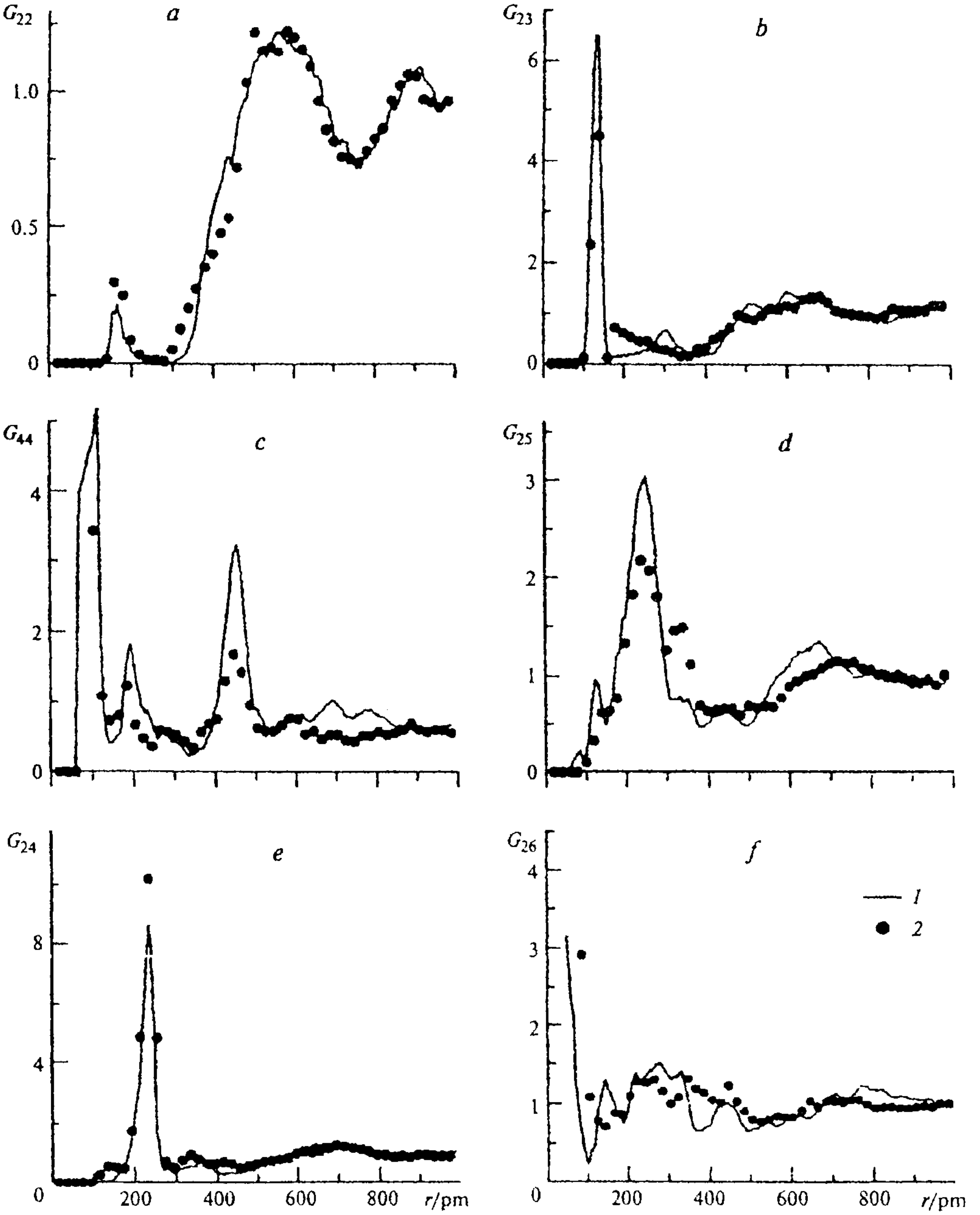

Fig. 4. Functions of the radial distribution of the geometric centers of the rings of H bonds, $G_{ij}(r)$ (i,j is the number of vertices in the ring); ij = 22 (*a*), 23 (*b*), 44 (*c*), 25 (*d*), 24 (*e*), and 26 (*f*): *1*, 298 K; *2*, 348 K.

In the crystal of formamide, each molecule has two *cis* bonds involved in formation of the cyclic dimer and two *trans* bonds, which lead to formation of chains.[12–13] It is reasonable to suggest that upon melting, chains in the crystal dissociate into individual fragments containing dimers as a result of cleavage of some *trans* bonds. Some dimers are incorporated into tetramers, hexamers, and more complex structures. When weaker *cis* bonds are broken, branched and chain associates are formed simultaneously, and their amount becomes larger than the amount of associated rings. The fact that the angles between the planes of the molecules (see Fig. 2, *b*) vary in a wide range is indicative of high flexibility of the chains. A small number of rings containing odd numbers of molecules is indicative of a weak tendency to self-closure.

The mutual spatial arrangement of the rings is characterized by the functions of radial distribution of their geometric centers $G_{ij}(r)$[19–22] (Fig. 4). The center of each ring of the type *i* (where *i* is the number of formamide molecules involved in the ring) was calculated as the arithmetical mean value of the coordinates of the N atoms. For the system of points obtained in this manner, we calculated RDFs, which are equal to the ratio of the local numerical density in the spherical layer with the radius *r* to its average value. The positions of the peaks of the functions correspond to the distances with the maximum probability of location of the rings.

To make structural interpretation of the behavior of the $G_{ij}(r)$ functions in the initial molecular configurations, it is necessary to choose rings with the distances between their centers corresponding to the positions of the maxima. Some of these rings are shown in Fig. 5.

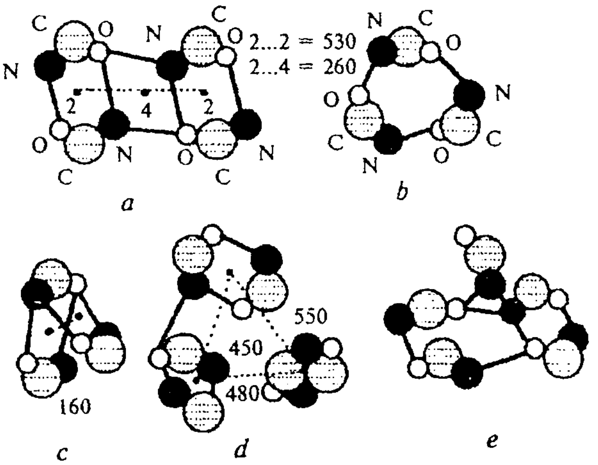

Fig. 5. A set of associates of the molecules, which were found in the molecular conformations of liquid formamide. The average values of the interring distances (pm) are given: *a*, the associate consisting of two dimers with an inter-ring distance of ~530 pm and the tetramer; *b*, the cyclic trimer; *c*, the associate consisting of three formamide molecules; *d* the associate consisting of three dimers; *e*, the associate consisting of three four-membered rings.

The first fragment (see Fig. 5, *a*) is analogous to the fragment resulting from the analysis of the behavior of the generalized correlation functions (see Fig. 3, *a*). Two dimers with an inter-ring distance of ~530 pm and the tetramer, whose center is at a distance of approximately 260 pm from the centers of the dimers, can be separated in this fragment. The cyclic trimer is shown in Fig. 5, *b*. As mentioned above, the concentration of rings of this type is rather small. The sharp first peak of the G_{23} function (see Fig. 4, *b*) indicates that trimers tend to form associates with dimers.

The position of the first peak of G_{22} corresponds to an associate consisting of three formamide molecules (see Fig. 5, *c*). The central molecule donates the *cis* proton to two O atoms to form a bifurcated H bond. The fragment consisting of three dimers is shown in Fig. 5, *d*. The configurations with the mutually perpendicular arrangement of the planes of the dimers are often observed in liquid formamide. Here, all three inter-ring distances correspond to the region of the maximum values of the G_{22} function. Vibrational and rotational motions of the dimers that occur due to high flexibility of chain bonds lead to changes in the distances and to broadening of the maxima of the functions.

As the number of molecules incorporated in the associate increases, visualization of the associate in a plane becomes more difficult. Thus, Fig. 5, *e* shows the associate in which three four-membered rings can be separated. The molecule that acts as a proton donor links two opposite angles of the tetragonal base. Changes in the numbers of molecules in the linking bridge and in the base lead to the appearance of a multitude of typical fragments of the system of H bonds, whose compositions and geometric parameters vary over wide ranges.

If molecules are represented by circles and H bonds are indicated by lines, the representation of molecular associates is simplified. The graphs corresponding to the most probable modes of arrangement of rings in liquid formamide are shown in Fig. 6. According to the accepted notation, the associate *c* (see Fig. 5) is represented by the graph *1* (see Fig. 6). The associate *e* is represented by the graph *10*.

The typical inter-ring distances shown in Fig. 6 coincide with the positions of the maxima of the G_{ij} functions. It should be mentioned that the real pattern of the supermolecular structure of the liquid differs substantially from that obtained as a result of analysis of the atom-atom RDFs and the generalized functions of spatial distribution of the atom density, which provide information on the local order.

The results of this study confirm the concepts of the structure of liquid formamide that assume no distinct predominance of one mode of association of molecules over alternative modes. Unlike the suggestions made previously, the computer simulation demonstrated that the system of H bonds is characterized by a broad spectrum of molecular associates, which have complex topological structures. Formamide is characterized by

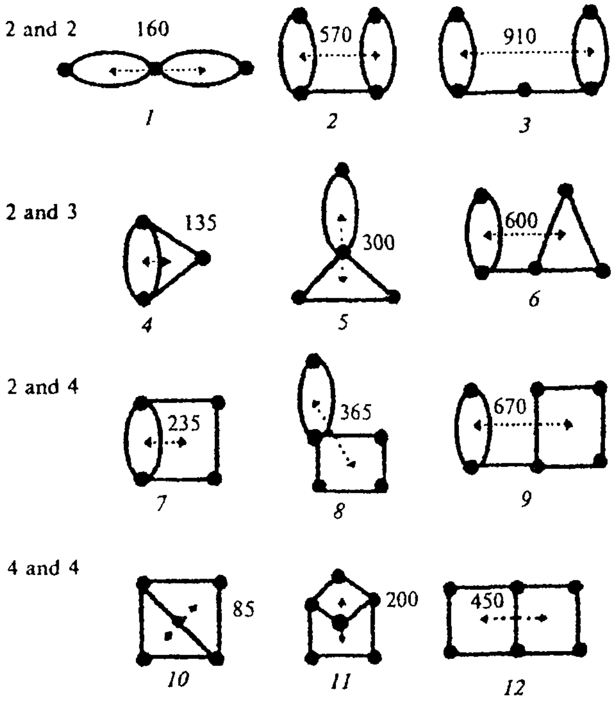

Fig. 6. Graphs (*1—12*) corresponding to the typical associates of formamide molecules. Molecules are represented by circles, H bonds are indicated by lines, and H bonds in dimers are indicated by arcs. The average values of the interring distances (pm) are given.

chain association of molecules and a relatively small number of cyclic fragments of bonds among which dimers dominate. The rings exhibit a pronounced tendency to self-association. The formation of the typical molecular constructions results in the structural heterogeneity of the system of H bonds, which is also observed in water and in a number of polymers.[19] As the temperature increases, weaker *cis* bonds are cleaved first. This leads to a shift of the dynamic equilibrium toward the formation of chain structures and to weakening of self-association of the rings.

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