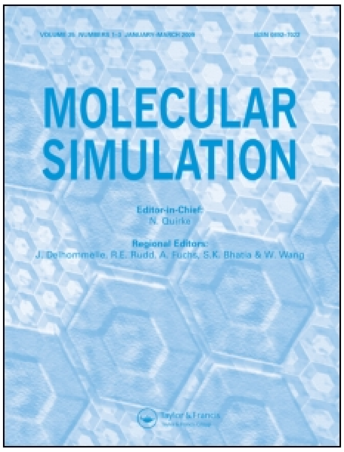

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Radnai, T. , Bakó, I. , Jedlovszky, P. and Pálinkás, G.(1996) 'Local Order in Some Aprotic Dipolar Liquids', Molecular Simulation, 16: 4, 345 — 358

To link to this Article: DOI: 10.1080/08927029608024084

URL: http://dx.doi.org/10.1080/08927029608024084

Molecular Simulation, 1996, Vol. 16, pp. 345–358
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LOCAL ORDER IN SOME APROTIC DIPOLAR LIQUIDS

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(Received March 1995, accepted June 1995)

Analysis of the local order in four aprotic, dipolar liquids (acetonitrile, acetone, *N,N*- dimethylformamide, and pyridine) has been carried out by computer simulation methods. The effect of the dipole-dipole- as well as of the Lennard-Jones interactions on the pair distribution functions and some orientational characteristics are discussed. A general observation for this group of liquids is that the local order is accompanied by a favorable orientation of the nearest neighbor molecules with dipole vectors antiparallel to the central one. This orientation decays rapidly and extends to slightly more than to the first neighbor molecules only. Differences in local order due to the differences in shapes and symmetries of the molecules are discussed.

The present study partly employs the recently developed Reverse Monte Carlo method, special features of which in contrast to the traditional simulation methods are also discussed.

KEY WORDS: Reverse Monte Carlo simulation, aprotic liquids, dipolar liquids, local order in liquids, acetonitrile, acetone, *N,N*-dimethylformamide, pyridine.

1 INTRODUCTION

The structure of H-bonded liquids is mainly formed by the strong attractive interactions between the H-bonded sites of the molecules. Electrostatic and van der Waals type interactions add significant contributions to the interaction energies and exert a remarkable effect on the local order around the molecules. The competitive role of the above three types of interactions has been often described. It was briefly discussed earlier, *e.g.* for formamide and its homologues [1, 2]. In the aprotic dipolar liquids the H-bonds are absent and therefore the number of competitive interactions is reduced to two. The electrostatic interactions are predominated by the interactions between the dipole- and higher multipole moments of the molecules, while the structure forming role of the van der Waals-type interactions depends on the size and shape of the molecules. The competition between these two factors leads to observable differences in macroscopic properties of the liquids, too. Table 1 lists a set of some physicochemical properties of four liquids which are the targets of our present study: acetonitrile (AN), *N,N*-dimethylformamide (DMF), acetone (AC) and pyridine (PY). One of the most important characteristics of these liquids is that all have large dipole moments. Their melting and boiling points, viscosities and even

Table 1 Physicochemical properties[a] of acetonitrile (AN), N, N_1-dimethylformamide (DMF), acetone (AC), and pyridine (PY).

liquid	mw	bp	mp	η	ε	μ	$D_N{}^b$	$A_N{}^b$
AN	41.05	81.6	−43.8	0.341	35.94	3.53	14.1	18.9
AC	58.08	56.3	−95.4	0.327	20.70	2.88	17.0	12.5
DMF	73.09	153.0	−60.4	0.802	36.71	3.86	26.6	16.0
PY	79.10	115.3	−41.6	0.884	12.91	2.37	33.1	14.2

[a] Ref. [3], [b] Ref. [4]

mw: molecular weight, bp: boiling point/°C, mp: melting point/°C, η: viscosity/10^{-2}g cm s^{-1}, ε: relative dielectric constant (25 °C), μ: dipole moment/D at 25 °C, D_N: donor number, A_N: acceptor number.

the dielectric constants exhibit large variations. It is difficult to correlate the changes in the melting- and boiling points to the molecular weights, as it could be done for *e.g.* the liquid alkanes, and even more difficult is the analysis of the interdependence of other parameters with the dipole moment values. Even the dielectric constants do not follow strictly the variations in the dipole moments what is a typical consequence of differences in structure.

The effect might be explained partly by the variations in the locations and directions of the dipole vectors, as it is drawn in Figure 1. We will show that these variations and thus the electrostatic interactions depend on the sizes, symmetries and shapes of the molecules. The latter ones are usually attributed to the other obvious factor, the van der Waals interactions, and they are referred to as "steric effects" in the local order.

The different charge distributions as well as the shapes of the molecules are also reflected by the empirical (electron) donor and acceptor properties of the liquids, as defined by Gutman and Mayer [4]. Although these properties are usually used to explain the different solvation abilities of the molecules in their solutions, some correlations between the magnitude of these parameters and the local structure in liquid mixtures was also reported [1, 5]. It is remarkable that the donor and acceptor properties vary significantly along the series of the four liquids, pointing to the possible influence of these properties on the formation of the local order.

In our recent studies indications to some differences in the local order of the four liquids were found [2, 5–9]. In the present work computer simulation results are presented and some structural results are compared in order to describe the local order around the molecules in the liquid state. The analysis is performed on the level of total pair distribution functions (pdf), partial pair distribution functions, and angular correlation functions. Related experimental results are also reviewed. Since the applied simulation techniques are commonly used and they are more or less irrelevant for the question, they are only briefly summarized, with the exception of the relatively new Reverse Monte Carlo technique, which deserves a little more attention.

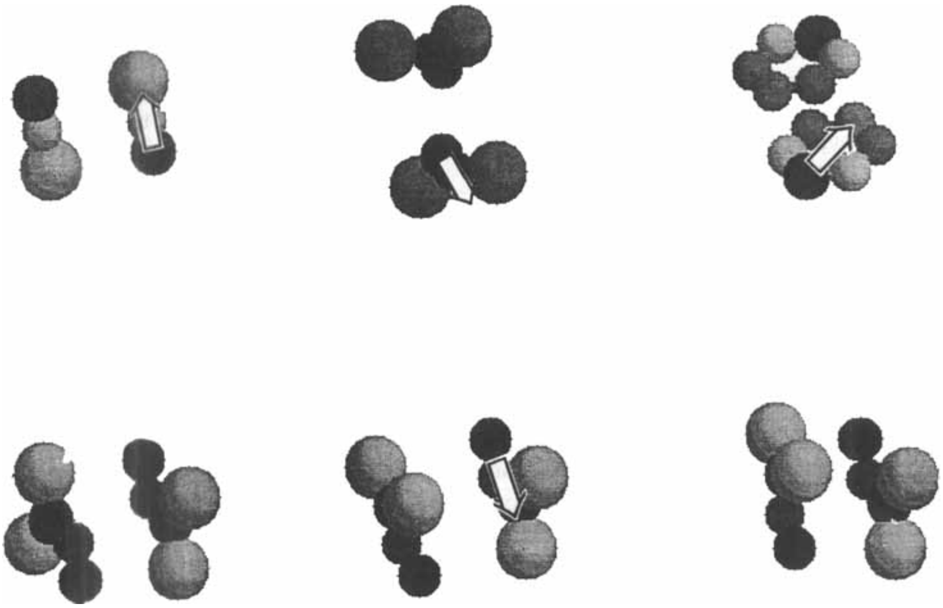

Figure 1 Schematic view of the molecules and their dimer configurations as found from energy minimization process. Top row: AN, AC, PY. Bottom row: DMF. The dark atoms represents the location of the most negative charge. The size of the methyl groups is larger than the other atoms or atomic groups for a better distinction. The arrows indicate the directions of the dipole moment vectors.

2 SIMULATION DETAILS

2.1 *Reverse Monte Carlo Simulation of liquid Acetonitrile and N,N-Dimethylformamide*

In spite of the great success of traditional molecular dynamics (MD) and Monte Carlo (MC) computer simulation methods in the determination of the microscopic properties of the liquids, their accuracy is always limited by the choice of the suitable potential functions to describe the interatomic interactions. The potentials can be checked only indirectly, by comparison of the structural properties calculated from the simulation with those determined experimentally, *after* the simulation had been completed. The Reverse Monte Carlo (RMC) method [10] generates a large set of atomic configurations on the condition that the difference between the experimental and calculated structure functions (or pair-distribution functions) should be minimum. This condition is checked *simultaneously with the simulation run.* Thus there is no need for any potential: in fact, the energetic information is lost. Nevertheless, the same structural properties can be calculated and analyzed as from any traditional simulation. The RMC method has been frequently applied to atomic liquids and amorphous materials or two-component melts. More recently RMC simulations of H-bonded liquids such as liquid water [11] and formic acid [12–13] have been successfully performed. The first RMC study on a heteroatomic, linear, molecular liquid was performed on liquid acetonitrile [6]. The molecule was described by three sites and deviation from linearity was also allowed. Intramolecular structure, partial pair correlation functions, angular distributions and the orientation of the molecules together with density profiles characteristic to spatial distributions of the neighboring molecules were discussed.

The RMC simulation was performed by fitting the calculated X-ray structure function to the experimental result [5]. Technical details of the simulation was reported earlier [6] including the explanation of the representation of "flexible" molecules and the concept of *coordination constraints*. The intermolecular part of the total pdf, calculated from the X-ray structure function of the best fit by Fourier transform is shown in Figure 2, together with the experimental curve.

A similar RMC study of liquid DMF has been completed recently. Detailed description of the method and a complete analysis of the structure of liquid DMF will be reported soon [8]. Here we confine ourselves to some preliminary results relevant to the problem of short-range order. Technical details of the RMC

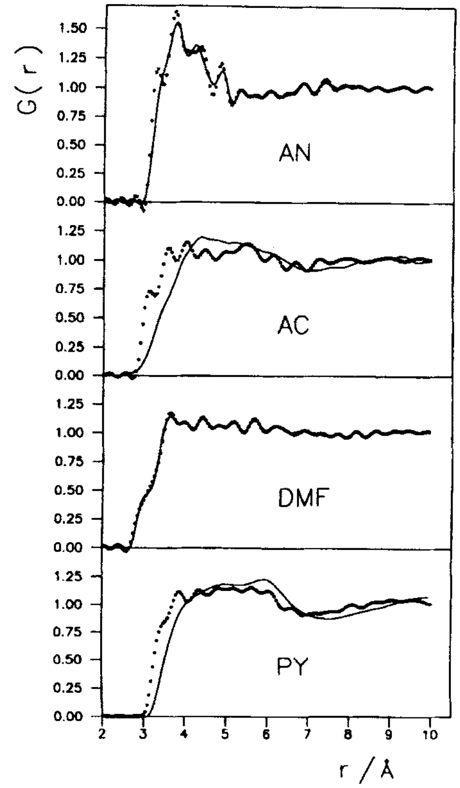

Figure 2 Intermolecular part of the total pair distribution functions $G(r)$ for the studied liquids: X-ray scattering results (asterisks) and simulation studies (full lines).

simulations were similar to those applied for acetonitrile. The simulation was performed again by minimization of the difference between the calculated and experimental X-ray structure functions [5]. The simulation box contained 512 molecules. Since the X-ray diffraction method is not sensitive enough for the hydrogen atoms positions, each molecule was represented by 5 sites: the O and N atoms, the CH group denoted by C for brevity and the two methyl groups, denoted by Me. More than 3 million moves were generated, with an acceptance ratio of 1:12. Finally, 400 configurations, each separated by other 2560 accepted ones, were collected for the sake of evaluation of the liquid structure. The intermolecular contributions to the $G(r)$ functions, calculated from the simulation and from the X-ray experiment, are shown in Figure 2.

2.2 *Monte Carlo Simulation of Acetone*

A traditional MC simulation was performed for liquid acetone. A polarizable potential model was applied for the molecules in order to take the dielectric polarizability of the molecules explicitly into account. The method of simulation, the model of the molecules and the details of the simulation are reported in a separate paper [7]. Here we mention only that all 256 acetone molecules in the simulation box were represented by 4 sites; the methyl groups were considered as sites. The distribution curves were calculated on the basis of 200 collected configurations, separated by 2560 accepted moves. For demonstration of the goodness of reproduction of the liquid structure by the applied potential model, the calculated inter-molecular contribution to the pdf is compared to the corresponding X-ray diffraction result in Figure 2. The experiment was performed in our laboratory.

2.3 *Molecular Dynamics Simulation of Pyridine*

Preliminary results for the local structure in liquid pyridine are reported here on the basis of a more recent molecular dynamics simulation [9]. The 256 pyridine molecules in the simulation box were represented by six sites each and their interactions were described by OPLS potentials. Parameters for Lennard-Jones term and the charge distribution on the molecules were taken from the literature [14]. The total elapsed time of the simulation was 20 ps. For the evaluation of the static structure, 2000 distant configurations were collected. An X-ray diffraction experiment has been carried out as well; the experimental result is compared with the simulated one in Figure 2 in form of the intermolecular pdf.

3 RESULTS AND DISCUSSIONS

3.1 *Dimer Structures*

Prior to the simulations, the equilibrium dimer configurations, belonging to the minimum interaction energy of two isolated molecules were determined. We had two purposes with this calculation. At first, we wanted to get a hint for the optimum orientation of two molecules, which can be, with high probability, characteristic of the predominant orientation of the nearest neighbor molecules in the liquid state as well. In addition, we wanted to have an estimate for the differences in the minimum energies among the pairs of the four types of molecules and for the ratio between the Lennard-Jones and electrostatic interaction for each system. Since RMC simulations were performed for acetonitrile and DMF, they did not provide the energy terms, which assigned to the preliminary calculations a greater importance.

Literature values were used for the Lennard-Jones parameters and the charge distributions of the molecular sites for AN [15] and DMF [16]. A simple program code of fast convergence was used for the determination of the minimum energy configuration [17]. The absolute minima were found for the dimers of each four molecular pairs, while two additional local minimum values were also determined for DMF. The schematic view of the dimers belonging to each minimum are shown in Figure 1. The total pair-interaction energy values together with the separated electrostatic and Lennard-Jones terms are listed in Table 2. Distance values between the molecular centres and the forms of minimum energy configuration of the molecular pairs are also indicated in the table.

According to the results, the deepest energy for dimers of all four types of molecules is obtained with the "anti-dipole" configuration, i.e., when the dipoles of the two molecules are aligned parallel to each other, but their positive ends point to opposite directions. The anti-dipole configuration was previously reported as the predominant one for the nearest neighbors in the liquid state as well, either from X-ray diffraction experimental or from computer simulation studies for AN [5, 6, 15], and DMF [2, 5, 16, 18]. Surprisingly enough, the only available experimental work on the structure of liquid AC [19] concluded in a perpendicular orientation as being predominant between neighboring molecules in the liquid state. This result contradicts to the energy minimum conformation of the dimers, but if it is true, it points to eventual differences between the isolated dimers and the local order in the liquid state. Similar comment holds for the proposed structure of liquid PY [20].

Beyond the general statement of the anti-parallel alignment as the deepest energy configuration, there are some differences between the dimer structures of the four pairs of molecules. At first, the centre-centre distances of the molecules show a

Table 2 Minimum energies, the corresponding centre-centre distances and configurations of molecular dimers.

liquid	*total energy*	*LJ term*	*electrost. term*	r_{cc}	*orientation*
AN	−5.248	−2.320	−2.928	3.39	anti-dipole
AC	−4.797	−1.983	−2.814	3.69	anti-dipole
DMF	−5.351	−2.920	−2.431	3.94	anti-dipole
DMF	−5.261	−2.848	−2.413	4.01	not parallel, T
DMF	−5.206	−2.840	−2.366	3.98	parallel, T
PY	−4.186	−3.500	−0.686	3.94	anti-dipole

All energies are given in kcal/mole. The centre-centre distances of the molecules in minimum energy configurations r_{cc} are in Å.

variation as it is indicated by the r_{cc} values in Table 2. As a matter of fact there is a slight inconsistency in the measurement of the centre-centre distances: they are represented by the intermolecular distances between the carbon atoms for AN and AC, by those between the nitrogen atoms for DMF, and between the centres of mass for PY. However, the actual variations for the distances of minimum configuration can not be related to this slight inconsistency in the definition. It is worth observing that the r_{cc} distances show an increasing tendency in the order AN < AC < DMF ~ PY. This trend correlates qualitatively with the decreasing negative values of the electrostatic contribution to the total interaction energy. The latter one shows a similar tendency. Therefore we should state that the weaker is the electrostatic interaction, the larger is the distance in the minimum energy configuration. The situation is, however, further complicated by the fact that while a significant change can be observed in the electrostatic terms of energy between DMF and PY (from −2.366 to −0.686 kcal/mole), the distances in the minimum energy configurations result in the same value. On the other hand, the Lennard-Jones term of the energy deepens when going from DMF to PY (from −2.840 to −3.500 kcal/mole) which seemingly is able to compensate for the effect of the electrostatic interaction on the distances, inspite of the resulted increase in the total energy. Moreover, since the total energy values themselves do not correlate unambigously with the above order in the distances, we have to conclude that the distances in the minimum energy configurations are determined by several factors and not simply by the electrostatic (*i.e.*, mainly dipole-dipole) interactions alone.

From a phenomenological point of view, factors such as size, shape and symmetry of the molecules also have to be considered. The size of the molecules is not precisely defined. Since the molecules in question contain C, N, and O atoms of roughly similar size, the sizes of the molecules can simply be represented by the number of sites included: 3 for AN, 4 for AC, 5 for DMF and 6 for PY. The molecules include also sites of larger diameter, *i.e.*, CH, CH_2 and CH_3, but their number increases also in the same trend. The other factor to be considered is that while AN is linear, the other three molecules have a planar molecular geometry. Within this concept, acetone is still close to the linearity in the sense that only the two methyl groups span the plane from the main axis of the molecule; while DMF has a "more extended" two-dimensional structure and PY is the "most extended" one, with a close to sixfold symmetry. Summarizing, the size and the "extension in plane" is increasing while the distance of energy minimum configuration decreases, therefore the distances itself could serve as a measure of the size of the molecules, too.

Beside the absolute minimum value for the DMF, two local minima were also found during the optimization process, values of which are also given in Table 2. These local minima show a transition from the most favorable anti-dipole configuration of dimers to a nearly T-shaped alignment. The difference between the latter two configurations is that in one of them (with energy minimum value in between the two other ones) the molecules are not completely parallel to each other. The appearance of these local minima can probably be explained by the symmetry of the DMF molecules. While all the other three molecules exhibit C_{2v} symmetries, the DMF does not, moreover, it is the only one in the series in which the dipole moment vector deviates from the main symmetry axis of the molecule.

It is worth noting that the minimum energy dimer configurations show a fair agreement with the results reported earlier. Thus, a detailed examination of the rotational barriers in DMF dimers [21] confirm that the deepest energy is reached with the anti-dipole, parallel alignment. The minimum value of r_{cc} was found to be 3.7Å. The lower value can be explained by the application of a slightly different charge distribution. Two rotational barriers were found when one of the molecules was systematically rotated around its C—N axis which confirms qualitatively our observations about the local minima.

3.2 *Total Pair Distribution Functions*

The total X-ray pdf's of the four liquids were calculated from the simulation data and they are compared in Figure 2 with those obtained from X-ray diffraction experiments. The pdf's include the intermolecular or "distinct" contributions only, the intramolecular contributions were removed from the Figure.

A good overall agreement can be seen between the experimental and simulated pdf functions which suggests qualitatively that the simulated liquid structure is close to the "real", i.e., the experimentally observable one. This fact is inherent in the concept of the RMC simulations as it was emphasized above and it is proved by the excellent agreement of the experimental and simulated curves for AN and DMF. The agreement between the two curves for the DMF is especially remarkable. For AN, however, some discrepancies can be observed in the range of smaller distances (between 3 and 4Å), which in turn are still much smaller than for AC or PY. This is due to the method of removal of the intramolecular contributions which was performed after the completion of the RMC simulation, and such as it is, an artifact introduced by the required Fourier-transformation process.

The shapes of the total pdf's exhibit the typical features of the aprotic dipolar liquids: there are broad maxima followed by slight and broad minima on the curves. There are no high peaks and the secondary maxima can be only hardly distinguished from the spurious ripples of high frequency. The seemingly most structured liquid is AN. The width and position of the maxima and minima well correlate with the sizes of the molecules. For AC and even more for DMF, the first maxima are so low that they are hardly distinguishable from the random distribution. This is why the experimentalists usually claim that DMF is a "practically disordered" liquid [5, 18]. Previous simulation studies, however, pointed out that it is a simplification since at least the partial pdf's show significant structural features [2, 16]. The fact that the total pdf's are not strongly structured and the fact that the visible structuring does not extend significantly over the first coordination shell suggest that the local order must decay soon after the first several neighboring molecules.

3.3 *Partial Pair Distribution Functions*

In order to better visualize the variations in the local order around molecules in the studied liquids, selected partial pair-distribution functions are shown in Figure 3, together with the contributions of the first 4 neighboring molecules. The *ij* pairs for the partial pdf's $g_{ij}(r)$ were selected by the two atoms distance vectors of which are closest to the dipole moment vector: N—Me for AN, N—C for AC, C—O for DMF, and N—C_{para} for PY. Although this criterion set on *intramolecular* feature does not necessitate that the *intermolecular* part of the partial pdf is a good representative of the local order, our experience is that the distributions of the *j* atom around the *i* atom of the molecule in the origin selected in this way shows the most important structural features of the local order.

Some characteristic features of the selected pdf's are listed in Table 3.

Since there is some arbitrariness in the selection of the *ij* pairs for the present analysis, it is of little physical meaning to compare the location of their extrema in detail. We note that the general observation made on total $G(r)$ functions holds for the partials, too (AN is the most structured, PY has its broadest first peak etc.). This is reflected by the parameters in Table 3, especially as far as the r_{max} positions are

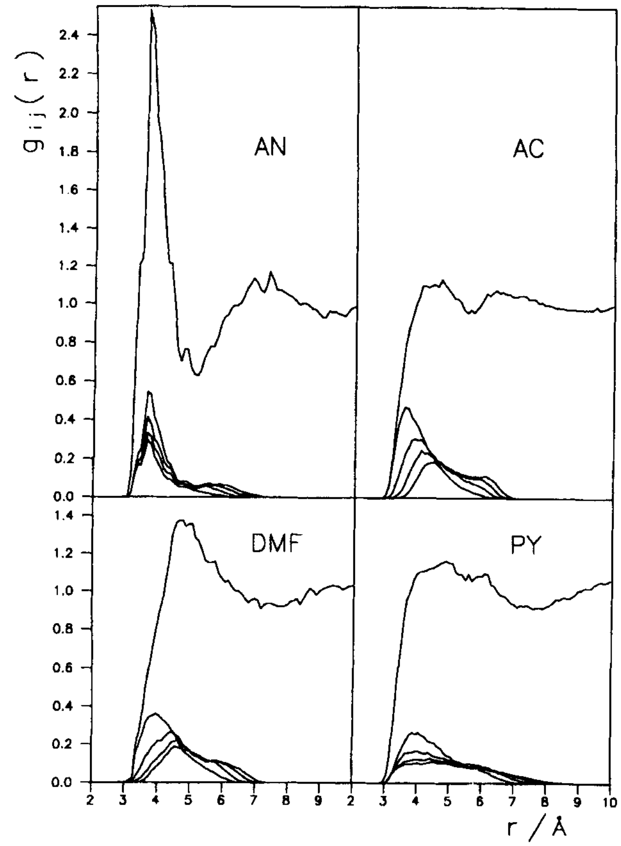

Figure 3 Intermolecular part of a selected partial pair distribution function $g_{ij}(r)$ for each studied liquid: N-Me for acetonitrile, C-O for acetone, N—C for *N*,*N*—dimethylformamide, and N—C_{para} for pyridine. Contributions from the *n*th neighbors ($n = 1,2,3,4$) are shown separately, $n = 1$ is the topmost curve.

concerned. The coordination numbers $C_{\max}$ give the number of j type atoms found around the i type ones within a radius of $r_{\max}$ and measure approximately the numbers of nearest neighboring molecules as well, while $C_{\min}$ inform us about the number of molecules situated within a sphere until the minimum of the $g_{ij}(r)$ function, *i.e.*, within the first coordination shell. Table 3 shows that $C_{\min}$ tends to be 12–13, corresponding to an almost close packing structure, except the AN for which 1–2 molecules are still missing.

In order to draw further conclusions about the differences in the coordination states of the nearest neighboring molecules, separated contributions, arising from the nth coordinating atom j to the $g_{ij}(r)$ functions were also calculated up to $n = 4$. Th r values where the running coordination number reaches n, are listed in Table 3, in the four rightmost columns. It is again obvious that the three liquids with planar molecules exhibit the same structural feature: the related r values practically coincide for AC, DMF and PY, and they are about 0.6–0.8 Å higher than for AN. The $r_{C=k}$ values describe the boundaries of the kth subshell within the coordination shell. The study of the variation in the $r_{C=k}$ values of different liquids provides information about the extension of the subshells, and an investigation of any structural property for each subshell provides the average structure of the neighbors located in the subshells.

Results for an analysis carried out by an opposite approach is demonstrated in Figure 3. Here the sequence number of the subsequent neighboring j atoms was chosen as fixed parameter and the radial distribution of their positions was separately determined. As it can be expected, the first neighbor gives the highest peak at the lowest r-range under the first main peak of $g_{ij}(r)$. The contribution of the first neighbors is asymmetric, but the events when the first neighbor is as far as the minimum position of the partial pdf are negligible. On the contrary, starting from the second neighbors, two changes can be observed on the shapes of the curves. At first, the positions of the first peaks belonging to the 2nd, 3rd and 4th j type atom shift toward the larger r values. The shift is the smallest for AN and PY, but much larger for AC and DMF. This means that the coordination shell is assymmetric: the 2nd, 3rd and 4th molecules occupy further positions than the first ones even if their orientation is the same. The second feature, namely that a well observable second

Table 3 Characteristic values of selected pair distribution functions $g_{ij}(r)$ of the four molecular liquids as determined from computer simulation data.

liquid	*ij*	$r_{\max}$	$c_{\max}$	$r_{\min}$	$C_{\min}$	$r_{C=1}$	$r_{C=2}$	$r_{C=3}$	$r_{C=4}$
AN	N-Me	4.35	2.5	6.15	10.6	3.85	4.20	4.45	4.75
AC	N-C	5.20	3.8	7.25	12.4	4.50	4.85	5.10	5.30
DMF	C-O	5.20	3.2	7.40	12.6	4.50	4.90	5.15	5.40
PY	N-C_{para}	5.60	6.0	7.20	13.0	4.50	4.80	5.00	5.20

$r_{\max}$, $r_{\min}$: the r values in Å where $g_{ij}(r)$ reaches its first maximum and minimum, respectively; $C_{\max}$, $C_{\min}$: coordination numbers belonging to $r_{\max}$ and $r_{\min}$, respectively; $r_{C=k}$: the r value in Å where the coordination number reaches the value k.

maximum emerges together with the decrease of the first peak, suggests that significant changes take place in the orientation of the further neighbors. The double peak is due to the difference in the distances between the two *ij* pairs of molecules. The two distances become identical in case of an anti-dipole alignment which is resulted in a single peak on the corresponding partial pdf.

3.4 Dipole Orientation

The changes in the orientations of the neighboring molecules can be characterized by the orientational distribution of the dipole vectors. Figure 4 shows the distributions $P(\cos\vartheta)$ where ϑ is the angle between a selected vector of the central molecule and of the neighboring molecules within the $k = 1,2,3,4$ subshell. These vectors either coincide with (AN, AC, PY) or are near to the dipole moment vectors (DMF). The completely random dipolar orientation corresponds to a constant value for all $\cos\vartheta$, the anti-parallel alignment gives increased contribution to $\cos\vartheta = -1$, the perpendicular orientation corresponds to $\cos\vartheta = 0$, and the parallel alignment of the dipoles is reflected by extra contributions at $\cos\vartheta = 1$.

Increased contributions at $\cos\vartheta = -1$ are present on the $P(\cos\vartheta)$ distributions of the neighbors in the first subshell in Figure 4 (asterisks), witnessing that more than

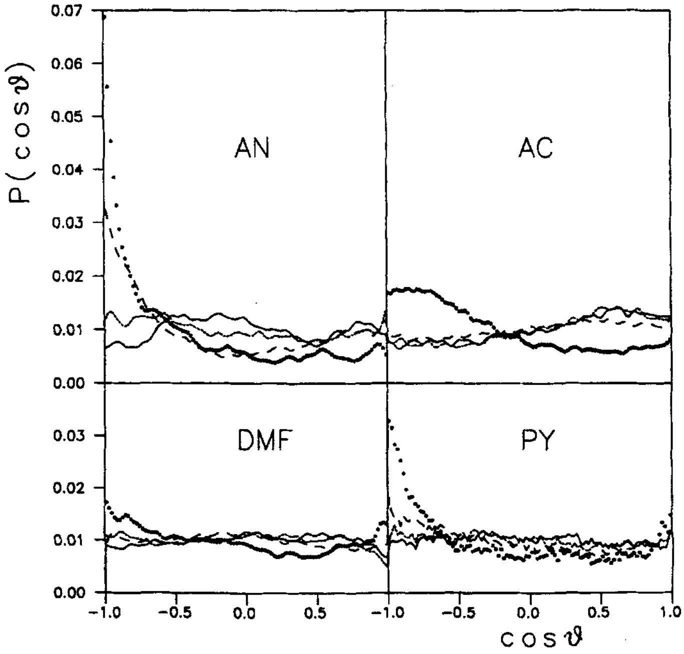

Figure 4 Cosine distributions of the angle ϑ between the dipole moments of the central molecule and of its neighbors in the *n*th "coordination subshell" for the studied liquids: $n = 1$, asterisks, $n = 2$, dashed.

the average number of molecules are aligned in an anti-parallel form around a central one. This is most prominent for AN where the corresponding peak is high and narrow. PY also exhibits a narrow peak for $\cos\vartheta = -1$, but it is much lower. The presence of distinguished anti-parallel alignment for the first subshell can be observed for DMF and AC, too, but for AC the peak is broad and extends to $\cos\vartheta = -0.25$ what indicates that mainly the sign of the dipole moment vector is aligned preferably while the angles scatter largely. Parallelly aligned dipoles are also present in the first subshell at minor extent for all molecules.

The orientational preference decays rapidly in the subsequent coordination subshells. For $n = 2$ the anti-parallel alignment shows a preference only for AN, but in a lesser extent that at $n = 1$, and some spots are found for PY, too (dashed lines). The other two liquids show a random orientation already for the subshell between coordination numbers 1 and 2, and all four molecules exhibit no preferred orientation for $n = 3$ and 4. A slight dispreference for anti-parallel alignment can be observed for AN, $n = 4$, and the tendency of the distribution curves suggests that for AC the alignment of the dipole moment vectors is rather parallel than anti-parallel, but the difference is within 1–2% only.

4 SUMMARY AND CONCLUSIONS

Local order in four aprotic dipolar liquids was discussed on the basis of various computer simulations. The contributions to the pair distribution functions arising from the intermolecular distances were compared to the corresponding distributions determined experimentally by the X-ray diffraction method. The best agreement was found for AN and DMF.

Energy minimization of isolated dimers shows that the most favorable configuration corresponds to the anti-parallel alignment of the dipole moment vectors of the molecules. Detailed analysis of the dipolar orientation demonstrated that in the liquid state the antiparallel alignment is preferred, but for the first or the second neighbors only and it decays rapidly with the increasing number of the neighbors. If this observation is valid, the rough picture which is usually drawn from diffraction experiments for the average geometry of the local order in molecular liquids must be further refined. Thus, conclusions on the often emphasized "predominant" orientation in the first coordination shells must be treated more carefully especially when it is formulated on an either-or basis. Moreover, looking for chain- and ring-like structures even in H-bonded liquids requires much caution and more powerful tools. Our results show that the positional and orientational correlation in the dipolar liquids is determined by concurring effects of the electrostatic and van der Waals type interactions, both of which are interrelated by the size, shape and symmetry of the molecules, and it can lead to remarkable correlations for the first neighbors, but have a smearing effect to the further molecules. The influence of these factors can show an especially wide variety in case of orientational correlations which worth further studying for molecular liquids.

It is worth commenting the capability of the computer simulation techniques in the reproduction of the experimental structural results. The present results demonstrate that a significantly better agreement between the simulated and measured pair distribution function could be reached by the RMC method than by the "traditional" (potential based) simulation methods. This fact is inherent in the methods: the pair-potentials are always approximative, even if they are almost perfect while the RMC is a fitting technique, which naturally produces the best agreement at the level of pair distributions. Therefore, it is plausible to assume that RMC results in more reliable three-dimensional microscopic structures than the traditional molecular dynamics or Monte Carlo methods. It is important to know, however that the comparison of the methods is ended here. At first, the traditional simulations obey the rules of the statistical mechanics, which means that within the accuracy determined by the choice of the potential, a large set of physical and chemical properties of the studied system can be determined by a straightforward way. This opportunity is lost by the RMC method. Moreover, the reproduction of a set of three dimensional particle distributions from a fitting procedure must not necessarily be unique, since a two-particle distribution function can belong to more than one multi-particle distribution function. The experience shows that for simple atomic liquids, provided that the system is subject to pair-potentials only, the agreement in the pair-distribution functions involves strong structural similarities at a multi-particle distribution level, too [22]. The question of the uniqueness of the RMC method in case of hydrogen-bonded molecular liquids has recently been studied for liquid water [23] and remarkable deviations were found in the three-particle correlation functions and also in some parameters of orientational correlation. In the present work, however, the studied system of aprotic dipolar liquids seem to show rather strong similarities even at average orientation of the molecules and this does not seem to depend much on the applied simulation method.

Acknowledgements

This research was partly supported by the Hungarian OTKA Foundation, project numbers 1087 and F013963. One of us (T. R.) is greatly indebted to the organizers of the International Conference on Molecular Simulation, Fukui, Japan, 1994; the Tokyo Institute of Technology; and the Yamada Science Foundation for financial support to this work. We express our thanks to R. McGreevy and M. Howe for providing the RMC code.

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