VOLUME 354, NOS. 1–3 10 December 2008
Complete in one Volume

ISSN 0301-0104

ELSEVIER

Chemical Physics

A journal devoted to experimental and theoretical research involving problems of both a chemical and a physical nature

On-line access via: www.elsevier.com/locate/chemphys

Chemical Physics 354 (2008) 202–210

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Weak intermolecular bonding in *N*,*N*′-dimethylethyleneurea dimers and *N*,*N*′-dimethylethyleneurea–water systems: The role of the dispersion effects in intermolecular interaction

A. Bende [a], L. Almásy [b,c,*]

[a] Molecular and Biomolecular Physics Department, National Institute for Research and Development of Isotopic and Molecular Technologies, Donath Street, No. 65-103, Ro – 400293, Cluj-Napoca, Romania
[b] Research Institute for Solid Sate Physics and Optics, P.O. Box 49, Budapest – 1525, Hungary
[c] Laboratory for Neutron Scattering, PSI and ETH Zürich, 5232 Villigen, Switzerland

ARTICLE INFO

Article history:
Received 19 May 2008
Accepted 17 October 2008
Available online 22 October 2008

Keywords:
Van der Waals interaction
Tetramethylurea
1,3-Dimethyl-2-imidazolidinone
Hydrophobic interaction
Symmetry adapted perturbation theory–SAPT
Dispersion effects

ABSTRACT

Using first principle quantum chemical methods based on Hartree–Fock, density functional theory and second order Møller–Plesset perturbational theory, equilibrium configurations of *N*,*N*′-dimethylethyleneurea (DMEU) dimer and DMEU–water systems were studied using the D95**+ full double-zeta, cc-pVXZ and aug-cc-pVXZ (X = D, T, Q) basis sets. Three different structures for DMEU dimer and two for DMEU–water systems were found. Method of the symmetry-adapted perturbational theory was applied for intermolecular interaction energy decomposition in order to elucidate the role of the physically relevant energy components. For all studied equilibrium configurations, dispersion effects are significant, while the contributions of the other energy components are relatively smaller. Two out of the three studied configurations of the DMEU dimers are strong enough to be not destroyed by binding with further water molecules. Such configurations are suggested to play role in dilute aqueous solutions of DMEU, in which DMEU aggregation was recently observed.

1. Introduction

Structure and properties of aqueous solutions of organic molecules, as well as the intermolecular interactions in the solutions are widely studied by different experimental and theoretical techniques [1–15]. The present study contributes to understanding of the intermolecular interactions in aqueous solutions of hydrophobic-hydrophilic molecules. *N*,*N*′-Dimethylethyleneurea (1,3-dimethyl-2-imidazolidinone; DMEU) is a cyclic molecule having an asymmetric ring structure – an urea core and a methylene group on the opposite sides of the non-aromatic ring. DMEU represents a cyclic analogue of the more familiar tetramethylurea (TMU) molecule; it contains – instead of two methyl groups – an ethylene group which closes the ring.

Both DMEU and TMU possess large hydrophobic entities, still they are fully miscible with water at any concentrations due to hydrogen bonds formed with water. They display similar behaviour in their dilute aqueous solutions – both show a tendency to self-association as evidenced from neutron scattering and density measurements [4–7]. The mechanism of the self-association is, however, different. TMU shows a typical hydrophobic type of association, in which the water hydrogen bond network plays a dominant role [4,6]. In contrast, the self-association of DMEU was found to be insensitive to temperature [7]. This may be an indication of the possible direct association of the solute molecules, which is less influenced by the aqueous environment.

This marked difference of aqueous solutions of TMU and DMEU makes these otherwise rather similar systems an interesting model for investigating the role of intermolecular interactions in the structural and dynamical behaviour in the condensed state. Calculations of intermolecular interactions by *ab initio* methods are frequently used to get closer view on the solute–solvent and solute–solute interactions. Quantum chemistry calculations can provide a plausible geometry of molecular clusters, which may sustain also in the liquid phase of neat liquids or mixtures [16–21]. However, quantitative results obtained for the gas phase cannot be transferred directly to the structural or thermodynamic properties of the solutions, therefore studies are usually performed for a group of related solute or solvent molecules, with subsequent analysis of characteristic trends and correlations with various experimental data. As a nice example, a linear correlation between the strength of water–amide group hydrogen bonding in 1:1 complexes of water with several methyl-substituted pyridines, and the limiting excess partial enthalpies of the corresponding mixtures were shown by Marczak et al. [22,23].

* Corresponding author.
E-mail address: almasy@sunserv.kfki.hu (L. Almásy).

0301-0104/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2008.10.016

In binary mixtures with competing solute-solute, and solute–solvent interactions, the comparison of these pair interactions as obtained by theoretical methods can be related to the thermodynamic behaviour of the solutions, and this was the purpose of our present work.

The DMEU monomer has been studied by Otero et al., the ring puckering and internal rotation energy barriers were calculated by semi-empirical and *ab initio* methods [24]. The molecular geometry was found to have either C_2 or C_{2v} symmetry in energy minimum state with energy differences between 0.2 and 11.0 kJ/mol varying with the approximation used. In a parallel spectroscopy study the vibration bands could be assigned on the basis of the C_{2v} symmetry. Following the behaviour of the C=O vibrations depending on the solvent quality, the DMEU was suggested to interact with water mainly by its oxygen lone pair electrons [25].

The TMU–water system has been studied by *ab initio* calculations by Jancsó et al. [26], and by using Monte Carlo methods in the liquid state by Freitas et al. [27]. In the gas phase, the water molecule forms nearly linear hydrogen bonds with the oxygen of the carbonyl group and also with the nitrogen atom in the region of the amide group [26], while in the liquid phase only water–oxygen hydrogen bonds were observed [27].

In the present work we performed *ab initio* studies of intermolecular interactions between DMEU molecules as well as between DMEU and water molecules, aiming to elucidate the possible conformations and strength of the intermolecular interactions. Stable configurations of DMEU dimers and DMEU–water pairs have been found and analysed using different levels of theory including Hartree–Fock (HF), density functional theory (DFT) and second-order Møller–Plesset many-body perturbation theory (MP2). The correction of basis set superposition error (BSSE) was taken into account – using the "counterpoise" (CP) method – in order to remove the mathematical artefacts of finite basis sets. Decomposition of the intermolecular interaction energy into distinct physical components was performed applying a special procedure of the Symmetry-Adapted Perturbation Theory (SAPT), a short theoretical description of which will be presented in the next section. Further calculations have been performed using the local methods of the second-order Møller–Plesset many-body perturbation (LMP2) and coupled-cluster (LCCSD(T)) theories combined with density fitting technique in order to achieve accurate description for dispersion effects as well as for intermolecular interactions.

2. Computational method

The calculations were carried out in Cluj-Napoca on an AMD Opteron cluster running under Linux. The standard HF, B3LYP, MP2, and the CP-corrected HF, B3LYP, MP2 energy calculations were performed by the Gaussian 03 computer code [28]. The three investigated DMEU dimer and two DMEU–water geometries were optimized at the MP2 level using D95**+ [29] basis sets, considering polarization and diffuse functions on heavy atoms and only polarization functions on hydrogen atoms. The motivation of using the D95 (Dunning/Huzinaga full double zeta) basis set family was that in our previous work [30] the D95 was found to be a more balanced basis set with less BSSE content compared to different type 6-31G Pople's basis sets. The potential energy curves for the intermolecular interaction were calculated considering these optimized MP2 geometry structures of DMEU and water monomers. The effects of basis set superposition error (BSSE) were eliminated applying the widely known "counterpoise" correction scheme [31,32]. The intermolecular interaction energy decomposition procedure was performed using the Symmetry-Adapted Perturbation Theory, developed by the group of Szalewicz and Jeziorski [33–37]. The basic working formulas are briefly presented here.

In the SAPT theory, the total (supermolecular) Hamiltonian of the dimer system is partitioned as $H = F + V + W$, where $F = F_A + F_B$ is the sum of Fock operators for monomers A and B, V is the intermolecular interaction

$$E_{int} = \sum_{n=1}^{\infty}\sum_{j=0}^{\infty}\left(E_{pol}^{(nj)} + E_{exch}^{(nj)}\right), \tag{1}$$

with indexes n and j denoting the orders in the operators V (intermolecular) and W (intramolecular), respectively. The polarization energies $E_{pol}^{(nj)}$ are similar to the corrections given by the classical Rayleigh–Schrödinger theory, while the exchange correction part $E_{exch}^{(nj)}$ is derived from the application of a global antisymmetrizer operator in order to force the correct permutation symmetry ("symmetry adaptation") of the dimer wavefunction in each order.

The SAPT interaction energy can be computed at the different levels of intramolecular correlation. If one considers the 0th order in W the sum of the polarization and exchange corrections gives in a good approximation the supermolecular Hartree–Fock energy, E_{int}^{HF}:

$$E_{int}^{HF} = E_{elst}^{(10)} + E_{exch}^{(10)} + E_{ind,resp}^{(20)} + E_{exch-ind,resp}^{(20)} + \delta E_{int,resp}^{HF} \tag{2}$$

where $\delta E_{int,resp}^{HF}$ represents all the third- and higher-order induction and exchange-induction terms together. Including the intramolecular correlation up to the second order (equivalent to the supramolecular second-order many-body perturbation theory (MBPT)), one obtains the second-order interaction energy in the SAPT framework:

$$E_{int}^{SAPT2} = E_{int}^{HF} + E_{elst,resp}^{(12)} + \varepsilon_{exch}^{(1)}(2) + {}^{t}E_{ind}^{(22)} + {}^{t}E_{exch-ind}^{(22)} + E_{disp}^{(20)} + E_{exch-disp}^{(20)} \tag{3}$$

where the notation $\varepsilon^{(n)}(k) = \sum_{j=1}^{k} E^{(nj)}$ has been used. The highest routinely used level of SAPT, approximately equivalent to the supermolecular MBPT theory through fourth order, is defined as

$$E_{int}^{SAPT} = E_{int}^{SAPT2} + E_{elst,resp}^{(13)} + [\varepsilon_{exch}^{(1)}(CCSD) - \varepsilon_{exch}^{(2)}(2)] + \varepsilon_{disp}^{(2)}(2) \tag{4}$$

where $\varepsilon_{exch}^{(1)}(CCSD) = E_{exch}^{(1)}(CCSD) - E_{exch}^{(10)}$ is the part of $\varepsilon_{exch}^{(1)}(\infty)$ with intramolecular excitations at the CCSD (coupled cluster theory with single and double excitations) level only.

Due to the huge computer storage capacity required and memory limitations we were obliged to make a compromise in using sufficiently large basis sets. Accordingly, we considered the D95* basis set (including polarization functions on heavy atoms with a total number of 280 basis functions) in case of DMEU dimers and D95** (including polarization functions on all type of atoms with a total number of 200 basis functions) for DMEU–water structures. For the same reasons we considered the SAPT theory only up to the second order contribution (SAPT2 as defined by Eq. (3)). The intermolecular equilibrium geometries for SAPT-type calculations were considered by taking the BSSE corrected MP2-CP intermolecular distances.

3. Results and discussions

3.1. Structure and interaction energy

3.1.1. Dimethylethyleneurea dimers

The optimization at the second order Møller–Plesset perturbation theory level leads to three equilibrium configurations of DMEU dimers. In the first structure both DMEU monomers are situated in the same molecular plane (defined by the ring) and we call it planar structure (Fig. 1, left). The second one shows a parallel position of the two molecules with opposite direction of the O=C bonds, we call it parallel configuration (Fig. 1, middle). In the third

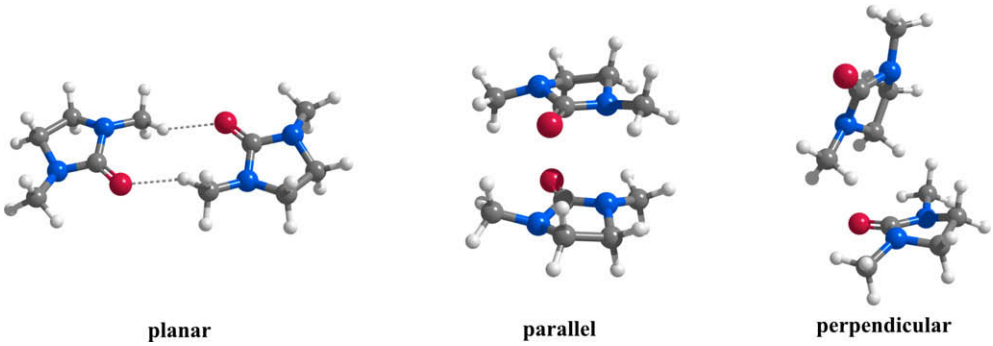

Fig. 1. The planar, parallel and perpendicular geometry structures of DMEU dimers.

one the two molecular planes are nearly perpendicular; this case is referred to as perpendicular structure (Fig. 1, right).

Fig. 2 shows the different potential energy curves obtained for planar geometry structure of DMEU dimer with the standard HF, B3LYP, MP2, and the CP-corrected HF, B3LYP, MP2 levels of theory, where the parameter *R* is defined by the distance of H atom from methyl group and O atom of the another DMEU monomer. In Fig. 3 the potential energy curves are shown for the parallel geometry structure of DMEU dimer, here the parameter *R* is defined by the distance of C atom from monomer carbonyl group and O atom of another DMEU monomer. For the perpendicular geometry structure, the parameter *R* is defined by the distance of H atom from methyl group and O atom of the other DMEU monomer, as for the planar structure; the potential energy curves are shown in Fig. 4. Table 1 compiles the equilibrium intermolecular distances and intermolecular interaction energies for the three (planar, parallel and perpendicular) DMEU dimer structures.

Using normal mode analysis and *ab initio* Hartree–Fock calculations, Otero et al. [24] and Cervellati et al. [38] have already shown that the DMEU molecule has non-planar ring equilibrium geometry with C_2 molecular symmetry. It is generally accepted that the correlation effects can accentuate the non-planarity of the N-atom orbitals in such ring structures [39]. This effect can be observed also for the dimer structures at MP2 level of theory, where the individual DMEU molecules have non-planar structures as well (Fig. 1).

The perturbational methods usually give a better description for the intermolecular interactions than DFT or HF methods. Therefore we will compare the results for the interactions energies and equilibrium geometries of different conformations as obtained with the

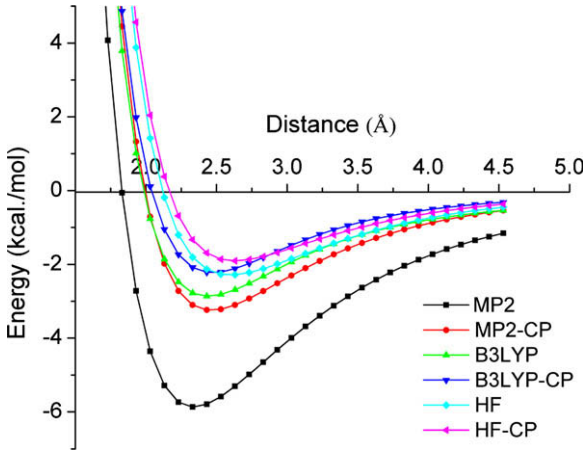

Fig. 2. Potential energy curves of planar structure of DMEU dimer obtained at HF, B3LYP and MP2 levels of theory, with and without BSSE corrections.

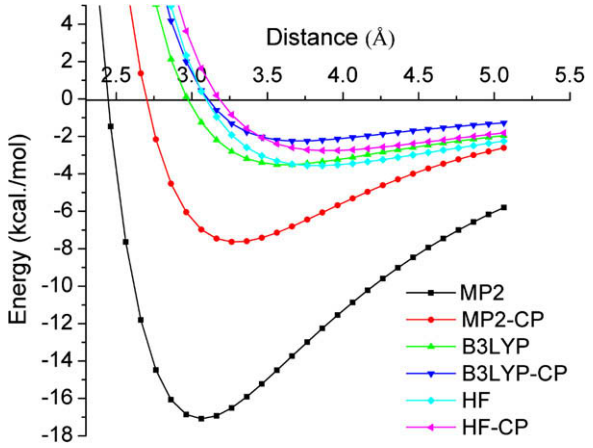

Fig. 3. Potential energy curves of parallel structure of DMEU dimer obtained at HF, B3LYP and MP2 levels of theory with and without BSSE corrections.

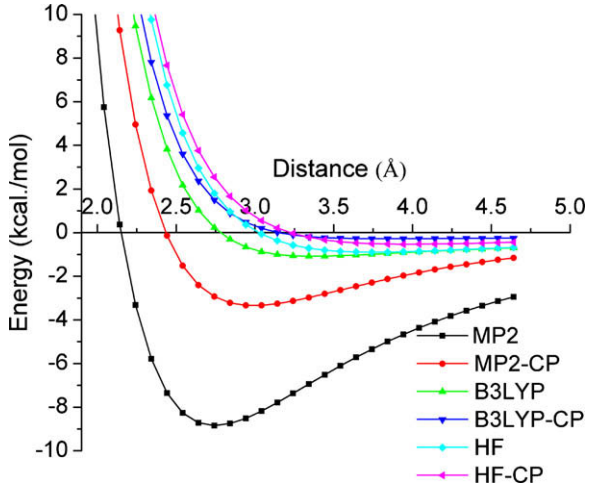

Fig. 4. Potential energy curves of perpendicular structure of DMEU dimer obtained at HF, B3LYP and MP2 levels of theory.

MP2-CP method, where the BSSE effects were excluded by applying the "counterpoise" correction scheme.

There are large differences between the intermolecular interaction energies for different dimer conformations, as seen in Table 1. The strongest interaction is found in the parallel conformation (−7.647 kcal/mol at MP2-CP), while the other two conformations (planar and perpendicular) have similar magnitudes of interaction at MP2-CP level (−3.249 kcal/mol for the planar configuration and

Table 1
Equilibrium intermolecular distances and intermolecular interaction energies for the three (planar, parallel and perpendicular) DMEU dimer structures.

Method	Planar		Parallel		Perpendicular	
	R (Å)	ε (kcal/mol)	R (Å)	ε (kcal/mol)	R (Å)	ε (kcal/mol)
HF	2.602	−2.285	3.38	−3.558	3.756	−0.896
HF-CP	2.636	−1.904	3.903	−2.758	3.98	−0.531
B3LYP	2.445	−2.866	3.626	−3.516	3.37	−1.084
B3LYP-CP	2.475	−2.228	3.707	−2.249	3.842	−0.278
MP2	2.331	−5.867	3.063	−17.091	2.742	−8.846
MP2-CP	2.468	−3.249	3.296	−7.647	2.992	−3.343

−3.343 kcal/mol for the perpendicular one). The electron correlation in the energy values is important, but the different treatment of electron correlation effects (perturbative or DFT functional type) show large discrepancy. While the second order Møller–Plesset perturbation correction (MP2) gives a significant electron correlation contribution in contrast to the Hartree–Fock (HF) values, the B3LYP-type DFT functional show noticeable correlation contribution (0.324 kcal/mol) only for the planar case (in comparison to the HF values), but is still smaller than the corresponding MP2 value (1.02 kcal/mol). This fact points out that the long-range dispersive interactions, which are usually neglected by construction from the DFT functionals [40] become important in all three cases, while the DFT-type correlation effects give only small contributions. In accordance with the Cremer's paper [41], the DFT functionals (including the hybrid ones) could reproduce the electron correlation effects with a very good approximation only in the atomic and bond regions of the molecule, while in the non-bonded part they gave a rather poor description. Dispersion interactions in vdW complexes depend on fluctuations of the density in the tails of the monomers forming the complex, therefore they depend strongly on the proper theoretical description of electron correlations in the density in the vdW region. The DFT functionals are not able to describe these fluctuations correctly; this leads to the failure of the DFT methods in the case of vdW complexes [42,43]. Better results are obtained for vdW complexes dominated by electrostatic forces (interaction between permanent and induced multipole moments). There are several attempts to improve DFT methods in order to describe correctly the weakly bound vdW interactions. These methods are based on the semi-empirical correction by adding to the density functional a long-range attractive pair-potential (proportional to R^{-6}) multiplied by a damping function that shuts it off at short distances [44–46]. These results are very promising due to the low computational cost, comparable with the original method without the long-range dispersion correction. Yet, further parameterization studies are required in order to obtain accurate results for dispersion effects in the general case of weakly bound vdW interactions [44].

In the DMEU monomer the dominant part of the DFT-type electron correlation effects comes from the atomic and bond regions situated in the plane formed by the heavy atoms of the DMEU molecule. The different B3LYP results of correlation effects which are observed between the planar structure on one hand and parallel and perpendicular structures on the other hand are caused by the juncture of polarization effects due to the intermolecular interaction and bond formation. For the planar structure these two effects can be found approximately in the same plane and thus the polarization effects could influence the intermolecular interactions, while in the other two cases they act in different planes. Accordingly, the correlation effect arising from the bond formations will be also perceptible in the intermolecular interaction energy for the planar structure, while in the other two cases this contribution will almost be missing. Even so, the magnitude of this DFT-type electron correlation is much less than the magnitude of the MP2 correlation.

It is well-known that the weakly binding vdW interaction is the result of different type correlation effect (exchange, electrostatic, polarization, dispersion, etc.) contributions. Dispersion-type effects are generally shielded by the other components of correlation, but in some special cases when these other components are missing (e.g. the absence of the permanent dipole–dipole interaction), the role of the dispersion forces (interaction between two instantaneous dipoles) becomes crucial [47]. Following these considerations on the correlation effects, it is seen that in all three geometry conformations of the DMEU dimer, the contribution of the dispersion forces in intermolecular interaction energy is essential. The most evident case is the parallel conformation where the HF-CP and B3LYP-CP methods give, respectively, −2.758 kcal/mol and −2.249 kcal/mol for the interaction energy, while the MP2-CP method gives −7.647 kcal/mol. For the planar dimer this difference is smaller than that in the other two cases, but is still relevant for the interaction energy.

The MP2 values are affected significantly by the so-called basis set superposition error (BSSE) due to the use of finite basis sets, which leads to an incomplete description of the individual monomers. These errors have purely mathematical origin, which should be corrected for when weakly bound molecular systems are described. Moreover, it can be observed that the significant contribution of the dispersion interaction in the interaction energy involves large BSSE effects in the electron correlation. While for the planar dimer case the BSSE contribution in energy is around 45%, for the parallel conformation it amounts to 55% and for the perpendicular case it is more than 62% of the total uncorrected interaction energy values (Table 1 and Figs. 2–4). The BSSE corrections are much less for the HF and B3LYP methods (Table 1 and Figs. 2–4). This result shows that the BSSE is a relevant attendant of the dispersion forces in the DMEU dimers.

Inspecting the potential energy profiles it is seen that only the MP2 and MP2-CP curves show a bound system for all three spatial arrangements (Figs. 2–4). The HF, HF-CP, B3LYP and B3LYP-CP potential curves exhibit well defined minima only in case of the planar structure (see Fig. 2). In the other two conformational cases, the HF and DFT methods give a very weak interaction with a wide potential curvature. Applying these two methods, the parallel and perpendicular arrangements cannot be considered as bound conformations.

Comparing these results for the strength of the dimer interaction one can see that the strongest bound system is the parallel one (−7.647 kcal/mol at MP2-CP level), while the planar and perpendicular conformations show much weaker intermolecular interactions (−3.249 and −3.343 kcal/mol, respectively).

3.1.2. Dimethylethyleneurea–water systems

Starting geometry optimization procedure at arbitrary initial positions (but taking into the account the possible DMEU atomic sites where water molecules could form hydrogen bonds), two different equilibrium configurations were found at the MP2 level of theory. In the first configuration – denoted as structure I – the water molecule is situated in the plane of the DMEU molecular ring, forming a hydrogen bond with the O atom of DMEU and at the same time showing an attractive interaction in the direction of the DMEU's methyl group (Fig. 5, left). In the second case (structure II) the water molecule is located above the DMEU ring forming a hydrogen bond with the N atom of the ring (Fig. 5, right).

In Table 2 the equilibrium intermolecular separations (R) and intermolecular interaction energies are collected for the two (structure I and structure II) DMEU–water systems. Fig. 6 shows the different potential energy curves obtained for structure I geometry structure of DMEU–water with the standard HF, B3LYP, MP2, and the CP-corrected HF, B3LYP, MP2 levels of theory. The parameter R is defined as the distance of H atom of water molecule and O

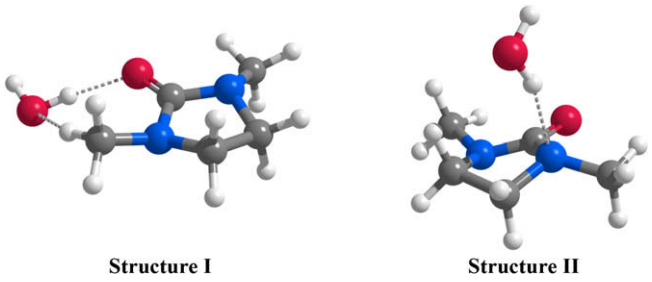

Fig. 5. Geometry structures (I and II) of DMEU–water complexes.

Table 2
Equilibrium intermolecular distances and intermolecular interaction energies for the two (structure I and structure II) DMEU–water complexes.

Method	Structure I		Structure II	
	R (Å)	ε (kcal/mol)	R (Å)	ε (kcal/mol)
HF	1.961	−7.116	2.198	−4.673
HF-CP	1.983	−6.371	2.255	−3.705
B3LYP	1.846	−8.215	2.036	−5.99
B3LYP-CP	1.864	−7.35	2.068	−4.802
MP2	1.852	−10.704	1.955	−10.701
MP2-CP	1.939	−6.929	2.076	−5.754

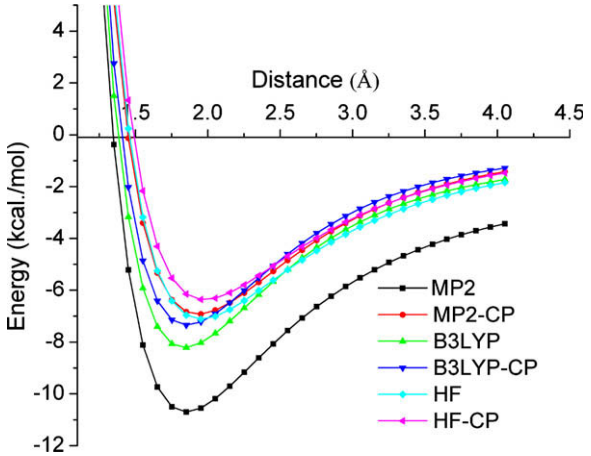

Fig. 6. Potential energy curves of DMEU–water structure I obtained at HF, B3LYP and MP2 levels of theory, with and without BSSE corrections.

atom of DMEU monomer. For Structure II the parameter R is defined by the distance of H atom of water molecule and N atom of DMEU monomer ring, these curves are shown in Fig. 7.

For structure I, there are no strong differences in the intermolecular interaction energies and intermolecular distances as obtained at DFT and MP2 levels of theory (the energy values are −7.350 kcal/mol and −6.929 kcal/mol, the intermolecular distances are 1.864 Å and 1.939 Å for B3LYP-CP and MP2-CP, respectively). Accordingly, it seems that the effects of dispersion forces are much less important in this case, as compared to the DMEU dimer interactions (see later). At the same time the HF contribution to the interaction energy is much stronger than that in case of the DMEU dimers, it accounts for 85% of the total interaction energy.

In the case of structure II, the intermolecular interaction picture is more subtle than it is for structure I. The interaction energies are smaller and a considerable dispersion contribution appears in the energy which is mostly due to the interaction of the DMEU ring atoms with the lone pairs of the O atom of water. The MP2-CP values are around 1.0 kcal/mol larger than those are in B3LYP-CP case, due to these dispersion forces.

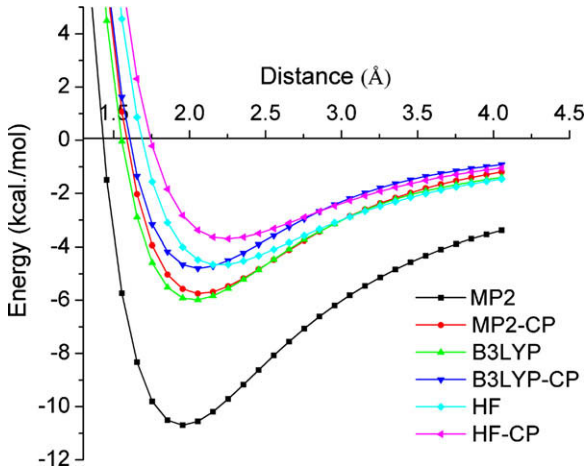

Fig. 7. Potential energy curves of DMEU–water structure II obtained at HF, B3LYP and MP2 levels of theory, with and without BSSE corrections.

Similar to the case of the DMEU dimer systems, the BSSE effects are also very important here. For structure II, the BSSE is larger by about 1 kcal/mol, which can be also related to the larger dispersion effects. In case of structure I the total interaction energy is mostly given by the HF-type energy contribution, which represents more than 90% from the total energy. For structure II the electron correlation effects become important, giving more than 35% contribution to the total interaction energy.

The potential energy profiles indicate that both structures are bound interacting systems. The shapes of MP2-CP and B3LYP-CP curves are quite similar for structure I, while for structure II the difference between these two curves is caused by the dispersion interaction.

3.2. SAPT-type intermolecular interaction energy decomposition

In order to study the basis set and size effects, first we present the interaction energy decomposition scheme for DMEU–water system, which is a smaller molecular system than the DMEU dimer and the various polarization and diffuse functions could be applied more easily.

3.2.1. Dimethylethyleneurea–water systems

Values of the physically interesting intermolecular interaction energy components (given by Eqs. (2) and (3)), for the two DMEU–water configurations, as obtained by applying the SAPT decomposition scheme up to the second-order level of theory, are collected in Table 3. Calculations with two different basis sets (D95 and D95**) were performed for elucidating the role of the polarization functions. The results unambiguously show major differences between energy component values obtained with and without the polarization functions. Thus, for structure I, E_{int}^{HF} = −8.245 kcal/mol and $SAPT_{corr}$ = −0.128 kcal/mol in case of D95 basis set, and E_{int}^{HF} = −6.364 kcal/mol and $SAPT_{corr}$ = −1.094 kcal/mol for D95** basis set. For structure II the energies are respectively: E_{int}^{HF} = −4.920 kcal/mol and $SAPT_{corr}$ = −0.714 kcal/mol in case of D95 basis set, and E_{int}^{HF} = −3.571 kcal/mol and $SAPT_{corr}$ = −1.784 kcal/mol for D95** basis set. In particular, by applying polarization functions the first order energy E_{int}^{HF} value decreases, while the $SAPT_{corr}$ correlation part shows a very pronounced increase. The main reason for decrease of the E_{int}^{HF} energy is the significant change of $E_{elst}^{(10)}$ electrostatic component. This fact suggests us that the polarization effects increase the electrostatic and exchange interactions between monomers when we apply polarization functions in our calculations. The

Table 3
The different SAPT energy components (in kcal/mol) of two equilibrium DMEU–water complexes at SCF and second-order correlation level of SAPT theory, using D95 and D95** basis sets.

Correction	Structure I		Structure II	
	D95	D95(d,p)	D95	D95(d,p)
SCF				
$E_{elst}^{(10)}$	−13.808	−11.963	−10.718	−9.394
$E_{exch}^{(10)}$	8.734	8.601	8.502	8.397
$E_{ind,resp}^{(20)}$	−4.010	−3.834	−4.238	−4.130
$E_{exch-ind,resp}^{(20)}$	1.958	1.926	2.625	2.592
$\delta E_{int,resp}^{HF}$	−1.118	−1.094	−1.091	−1.037
E_{int}^{HF}	−8.245	−6.364	−4.920	−3.571
$SAPTSCF_{resp}$	−7.126	−5.270	−3.828	−2.534
Correlation				
$E_{elst,resp}^{(12)}$	0.495	0.429	−0.742	−0.520
$E_{exch}^{(11)}$	−0.211	−0.073	−0.138	0.007
$E_{exch}^{(12)}$	2.199	1.808	1.856	1.398
$^tE_{ind}^{(22)}$	−0.762	−0.654	−0.977	−0.763
$^tE_{exch-ind}^{(22)}$	0.372	0.328	0.605	0.479
$E_{disp}^{(20)}$	−1.615	−2.633	−2.005	−3.180
$E_{exch-disp}^{(20)}$	0.308	0.465	0.363	0.526
$SAPT_{corr}$	−0.128	−1.094	−0.714	−1.784

opposite effect occurs at the correlation level, but the increasing of $SAPT_{corr}$ energy is the result of the collective contributions of the different correlation energy components having repulsive or attractive interaction character. The most pronounced change occurs in the dispersion contribution $E_{disp}^{(20)}$ for which the energy increases by about 60% for both structure I and structure II cases. The polarization effects could also generate significant changes in other second-order energy components, like e.g. $E_{exch}^{(11)}$. At the same time, comparing these values for structure I and structure II, one can see that the magnitude of several correlation (first or second-order) energy contributions are very different. This fact means that the given energy component strongly depends on the orientations of the atomic orbitals. On the other hand, considering only the correlation effects, the dispersion contribution appears to be the most relevant component of the correlation energy ($E_{disp}^{(20)}$ = −2.633 kcal/mol for structure I and $E_{disp}^{(20)}$ = −3.180 kcal/mol for structure II, using D95** basis sets in both cases). This result confirms the statement formulated on the basis of the MP2 and DFT calculations that dispersion effects are very important for the description of these weakly bound molecular associates. In addition, the SAPT results prove also another previous statement. Namely, the ε intermolecular interaction energy and R intermolecular distance for structure I obtained with counterpoise corrected MP2 and DFT levels of theory are much closer than the corresponding values in cases of structure II and the various DMEU dimers. This fact is due to the more significant contribution of the first order (HF) energy and smaller second-order correlation energy for structure I in comparison with structure II geometry. This case could be considered similar to those discrepancies which were found for the planar and perpendicular arrangements of the DMEU dimers using two different (MP2 and B3LYP) methods (see Section 3.1.1).

Large dispersion effects were also found for TMU–water complexes [26], accompanied by a large BSSE. Those results were obtained applying the London formula as an addition at the HF level, hence the other second-order electron correlation effects were missing, which could probably diminish the effect of the dispersion contribution.

3.2.2. Dimethylethyleneurea dimers

In the previous subsection we have shown the importance of polarization functions in the accurate description of intermolecular interaction. However, using *d* functions for heavy atoms and *p* functions for hydrogen atoms the number of basis functions would increase in such extent that the limited computer capacity would prevent us from performing SAPT calculation. As a realistic compromise for DMEU dimer calculations, we kept only the *d* polarization functions on heavy atoms, using the D95* basis set. The physically interesting intermolecular interaction energy components (Eqs. (2) and (3)) for the three different DMEU dimers are collected in Table 4. The strongest intermolecular interaction is obtained for the parallel configuration ($E_{int} = E_{int}^{HF} + SAPT_{corr}$ = − .135 kcal/mol), while the weakest one is found for the perpendicular structure (E_{int} = −2.057 kcal/mol). For all the three dimer configurations the correlation contribution is higher then the first order part. But the most conspicuous of them is the parallel structure where the second order contribution is higher by about one order of magnitude. The major contribution in the correlation energy is given by the dispersion effects ($E_{disp}^{(20)}$ = −2.067 kcal/mol for planar structure, $E_{disp}^{(20)}$ = −7.981 kcal/mol for parallel structure and $E_{disp}^{(20)}$ = −3.801 kcal/mol for perpendicular case). The other second order energy components are smaller. Summarizing them the positive and negative energy components partially cancel each other and finally result in a small positive contribution in E_{int}^{SAPT2} energy.

The first order corrections do not show any systematical behaviour. These energies are compounded from several electrostatic parts with negative signs and exchange parts having positive signs. The lack of pronounced trends is due to the different magnitudes of electrostatic and exchange contributions in the different dimer configurations. Thus, for planar case $SAPT_{SCF}$ = −1.320 kcal/mol, for parallel one $SAPT_{SCF}$ = −0.132 kcal/mol, and in case of perpendicular structure $SAPT_{SCF}$ = 0.928 kcal/mol.

Another important remark can be made for the $\delta E_{int,resp}^{HF}$ term. As it was mentioned in Section 2, it represents all the third- and higher-order induction and exchange-induction terms together. This energy component has the largest value in case of the parallel structure, but in the other two cases its contribution is still significant, and can substantially influence the magnitude of $SAPT_{SCF}$

Table 4
The different SAPT energy components (in kcal/mol) of planar, parallel and perpendicular DMEU dimer structures at SCF and second-order correlation level of SAPT theory, using D95* basis set.

Correction	Planar	Parallel	Perpendicular
SCF			
$E_{elst}^{(10)}$	−3.911	−7.670	−2.366
$E_{exch}^{(10)}$	3.454	8.966	3.635
$E_{ind,resp}^{(20)}$	−1.411	−4.633	−1.345
$E_{exch-ind,resp}^{(20)}$	0.549	3.205	1.004
$\delta E_{int,resp}^{HF}$	−0.319	−0.727	−0.215
E_{int}^{HF}	−1.638	−0.858	0.713
$SAPTSCF_{resp}$	−1.320	−0.132	0.928
Correlation			
$E_{elst,resp}^{(12)}$	−0.007	−0.138	−0.528
$E_{exch}^{(11)}$	−0.154	−0.296	−0.093
$E_{exch}^{(12)}$	0.915	2.382	0.860
$^tE_{ind}^{(22)}$	−0.122	−1.121	−0.328
$^tE_{exch-ind}^{(22)}$	0.048	0.775	0.245
$E_{disp}^{(20)}$	−2.067	−7.981	−3.801
$E_{exch-disp}^{(20)}$	0.237	0.963	0.347
$SAPT_{corr}$	−1.821	−5.277	−2.770

term. Since the equilibrium geometry in the case of SAPT calculations was taken at the MP2-CP geometry configuration, the SAPT energies are hardly comparable with HF, B3LYP or either MP2 results, mainly because of the different intermolecular separations obtained by the different *ab initio* and DFT methods.

Even so, inspecting the contribution of first and second order SAPT energy corrections for all three geometry configurations, we can explain why HF and DFT results give larger intermolecular separation for parallel and perpendicular structures in comparison with MP2 values. The answer is given by the dominant role of dispersion effects in the intermolecular interaction energy. These attraction-type dispersion forces have purely electron correlation character which is not included neither in the HF theory nor in the correlation part of the DFT exchange-correlation functionals. Their contribution could be decisive in such cases when the sum of the first order energy components gives a relatively small negative value or even a positive contribution [47].

3.3. Local correlation treatment of intermolecular interactions

The results presented in the previous two Sections 3.1 and 3.2 show that the amount of the dispersion effects gives the major contribution to the magnitude of the intermolecular interaction energies of DMEU dimers. In case of DMEU–water systems their effects remain also very important, in comparison with the HF contribution, especially in case of structure II conformation. It is well-known that dispersion forces have a long-range character and therefore an adequate description of the intermolecular space which is contained in the structure of basis set is indispensable. Thus, beside of the split-valence basis set (at least a double-zeta basis function) the use of the augmented basis functions together with the large shells of the polarization functions (aug-cc-pVDZ, aug-cc-pVTZ...) are required. Considering the D95**+ basis set used for geometry optimization as well as the D95* and D95** basis sets for SAPT-type intermolecular interaction decomposition, it can be easily seen that these basis sets are not large enough to properly reproduce the dispersion effects in the studied systems. On the other hand, using standard MP2 methods with aug-cc-pVTZ basis would lead to a very expensive computational job (780 basis functions) for the geometry optimization calculation. For the computation of intermolecular interactions, local electron correlation methods [48–50] have proven to give values which are very close to the standard MP2 results and by construction they are virtually free of BSSE [49,50]. Linear scaling of the computational cost as a function of the system size [51] makes it possible to treat much larger systems or using much larger basis sets. Using the density fitting (DF) approximation of the electron repulsion integrals [52–54] one can reduce again the computation time by about one order of magnitude applying it both in HF and LMP2 cases (DF-HF and DF-LMP2). In particular, the efficiency of DF-LMP2 method in describing π-stacked intermolecular interaction in case of benzene dimer structures dominated by the dispersion forces was clearly demonstrated by Hill et al. [55].

Table 5
Equilibrium intermolecular distances and intermolecular interaction energies for the three (planar, parallel and perpendicular) DMEU dimer structures, using the LMP2 method.

Method	Planar		Parallel		Perpendicular	
	R (Å)	ε (kcal/mol)	R (Å)	ε (kcal/mol)	R (Å)	ε (kcal/mol)
MP2-CP/D95**+	2.47	−3.249	3.30	−7.647	2.99	−3.343
DF-LMP2/vdz	2.38	−3.292	3.23	−9.029	3.06	−4.361
DF-LMP2/vtz	2.42	−3.727	3.33	−9.013	3.14	−3.908
DF-LMP2/avtz	2.39	−3.666	3.20	−9.107	3.00	−5.161

Table 6
Intermolecular interaction energies for the three DMEU dimer structures, using the LMP2 method. The optimized geometry was obtained with aug-cc-pVTZ basis set.

Method	Planar	Parallel	Perpendicular
	ε (kcal/mol)	ε (kcal/mol)	ε (kcal/mol)
DF-LMP2/avdz	−3.701	−9.996	−4.780
DF-LMP2/avtz	−3.666	−9.107	−5.161
DF-LMP2/avqz	−3.548	−8.455	−3.691
DF-LCCSD(T)/avtz	−3.551	−8.793	−3.822
E_{disp}	−2.370	−9.480	−4.888

Table 7
Equilibrium intermolecular distances and intermolecular interaction energies for the two (structures I and II) DMEU–water structures, using the LMP2 method.

Method	Structure I		Structure II	
	R (Å)	ε (kcal/mol)	R (Å)	ε (kcal/mol)
MP2-CP/D95**+	1.939	−6.929	2.076	−5.754
DF-LMP2/vdz	1.966	−9.096	2.394	−9.146
DF-LMP2/vtz	1.914	−7.832	2.414	−6.842
DF-LMP2/vqz	1.879	−7.695	2.374	−6.138
DF-LMP2/avdz	1.908	−7.310	2.134	−5.812
DF-LMP2/avtz	1.871	−7.519	2.030	−6.173
DF-LMP2/avqz	1.869	−7.539	2.013	−6.371

Using the DF-LMP2 method implemented in the Molpro program package suite [56] and taking the program parameter settings as presented [55] we have performed geometry optimization for DMEU (planar, parallel and perpendicular) dimers and for DMEU–water (structure I and structure II) systems, respectively, using cc-pVXZ (X = D, T, Q) with and without augmented diffuse functions (see Tables 5 and 7). Taking the optimized geometry obtained with the aug-cc-pVTZ (avtz), the intermolecular interaction energies were calculated for the above mentioned basis sets. In all these cases we considered the DF-LMP2 and DF-LCCSD(T) methods together with the dispersion energy components which derive from the local character of occupied and virtual orbitals in the local correlation treatment [57]. The values of intermolecular energies for different basis sets and the dispersion energy contribution obtained with DF-LMP2 using aug-cc-pVTZ basis set are collected in Tables 6 and 8.

3.3.1. Dimethylethyleneurea dimers

In the first step we have compared the optimized geometry structures obtained with the standard MP2 and with the local MP2 methods. We have found that in case of LMP2, no conformational changes in planar, parallel and perpendicular structures could be observed compared with the previously obtained standard MP2 values. Significant differences are seen in the intermolecular bond distances. For the R coordinate, (Table 5,) we have 2.39 Å, 3.20 Å, and 3.00 Å bond distances for the planar, parallel and perpendicular DMEU dimer structures at DF-LMP2/avtz, which differ from the MP2-CP/D95**+ results by about 0.1 Å. For the intermolecular interaction energies (Table 5) the discrepancy between the standard and local MP2 values are much more pronounced than the differences in the distances. This result is attributed to

Table 8
Intermolecular interaction energies for the two DMEU–water structures, using the LMP2 method. The optimized geometry was obtained with aug-cc-pVTZ basis set.

Method	Structure I	Structure II
	ε (kcal/mol)	ε (kcal/mol)
DF-LMP2/avdz	−7.204	−5.264
DF-LMP2/avtz	−7.519	−6.173
DF-LMP2/avqz	−7.433	−6.382
DF-LCCSD(T)/avtz	−6.777	−4.848
E_{disp}	−2.226	−2.959

the effect of applying larger and well-balanced basis sets belonging to the augmented correlation-consistent polarized basis set family and in this way the long-range contributions are taken into account more precisely. In case of parallel and perpendicular DMEU dimer structures the $\varepsilon^{\text{DF-LMP2}}$ intermolecular interaction energies are by 1.460 kcal/mol and 1.818 kcal/mol larger than in case of standard MP2-CP methods obtained D95**+ basis sets, corresponding to an increase of 20% and 50%, respectively. Contrary to the previous two cases, for planar structure the energy difference between the MP2 and DF-LMP2 results is only ≈13%. This fact confirms the previous conclusions from Section 3.2, that the dispersion contributions are much more significant in case of parallel and perpendicular DMEU dimer configurations. Furthermore, comparing the results (intermolecular bonds and interaction energies of different optimized geometry) obtained with different consistent correlated split-valence basis sets, one could observe some differences between the double-ξ and triple-ξ basis sets as well as between basis sets with and without diffuse basis functions (see again Table 5). In order to see the effects of different basis sets, in Table 6 are presented the intermolecular energies obtained with augmented double-, triple- and quadruple-ξ basis sets (avdz, avtz and avqz), applied to the same (DF-LMP2/avtz) geometry structure. Moreover, singles and doubles coupled cluster theory with perturbative treatment of triple excitations (CCSD(T)) is currently believed to be the most accurate method for computing dispersion interactions. It provides binding energies of excellent quality, if at least a basis set of aug-cc-pVTZ quality is used [58,59]. From Table 6 one can see that the DF-LMP2/avqz and DF-LCCSD(T) results are quite close, while in other cases significant differences can be found (e.g. the DF-LMP2/avtz values of the perpendicular geometry). As regarding to the dispersion component of the intermolecular interaction energy obtained with DF-LMP2 method, one can conclude that the long-range contribution given by the large basis sets is essential, they become twice as large as the SAPT results (in planar case: $\varepsilon_{disp}^{SAPT}$ = 1.584 kcal/mol – $\varepsilon_{disp}^{DF-LMP2}$ = 2.370 kcal/mol, in parallel case: $\varepsilon_{disp}^{SAPT}$ = 4.264 kcal/mol – $\varepsilon_{disp}^{DF-LMP2}$ = 9.480 kcal/mol and for perpendicular case: $\varepsilon_{disp}^{SAPT}$ = 2.423 kcal/mol – $\varepsilon_{disp}^{DF-LMP2}$ = 4.888 kcal/mol).

3.3.2. Dimethylethyleneurea–water systems

Comparing the optimized geometries obtained with MP2-CP and DF-LMP2 methods for DMEU–water structures, similarly to the DMEU dimer cases, no conformational changes were found. Comparing the intermolecular bond distances *R* presented in Table 7, one can see that *R* becomes shorter by about 0.1 Å in case of structure I and by about 0.06 Å shorter for structure II when applying the DF-LMP2 method. One should also mention the fact that the free O–H water bond, not participating in the intermolecular bonding is strongly basis set sensitive. The out-of-plane angle (the molecular plane which is approximately defined by the DMEU heavy atoms and the other O–H bond of water) can vary in a range of 20–30 °C. Analyzing the intermolecular interaction energies obtained for both structures I and II conformations, one can notice that the increase of energy values is not so significant like in case of parallel and perpendicular structures of DMEU dimer (considering the DF-LMP/avqz results, 0.610 kcal/mol for structure I and 0.617 kcal/mol for structure II, see Table 7). Following the basis set dependency of the interaction energy, as presented in Table 8, the order of the split-valence basis set (double, triple or quadruple) has a large influence on the energy results, especially in case of structure II. Comparing with the DF-LCCSD(T) results, it appears that the DF-LMP2 method slightly overestimates the intermolecular interaction energies for the DMEU–water systems. Aside from this different behaviour of DF-LMP2 and DF-LCCSD(T) methods the dispersion energy has the same trend like for the DMEU dimers, namely, it is larger by more than 100% compared with the MP2-CP/D95V** results (in structure I case: $\varepsilon_{disp}^{SAPT}$ = 0.629 kcal/mol – $\varepsilon_{disp}^{DF-LMP2}$ = 2.226 kcal/mol and for perpendicular case: $\varepsilon_{disp}^{SAPT}$ = 1.258 kcal/mol – $\varepsilon_{disp}^{DF-LMP2}$ = 2.959 kcal/mol).

3.4. Interactions in the liquid phase

The computational results allow us to shed some light on the structure and behaviour of dilute DMEU solutions. Comparing the DMEU dimer structures and DMEU–water systems the strongest interaction occurs for the parallel DMEU dimer with binding energy −9.107 kcal/mol (at DF-LMP2/avtz level). The two optimized DMEU–water structures have somewhat lower energies, −7.539 kcal/mol and −6.371 kcal/mol (at DF-LMP2/avqz level). The remaining two DMEU dimer (planar and perpendicular) configurations have roughly twice smaller energies. The strongest interaction, on the pair-wise level, is thus seen for the parallel DMEU dimer. Such attraction should have considerable effect on the intermolecular interactions in the liquid phase as well. The DMEU–water hydrogen bonding occurs via the oxygen site and partially the molecular ring of the DMEU, and does not hinder sterically the DMEU–DMEU bonding. Thus, in the dilute aqueous solution, the quantum chemistry permits the formation of bound DMEU pairs, or eventually aggregates. Calculation of larger structures, although computationally feasible, was left out of the scope of the present study, since such results would not reflect reliably the interactions in the real liquid. Nevertheless, test calculations of [DMEU dimer]–water structures resulted in stable configuration *in vacuo*, with a parallel DMEU dimer and a water molecule bound to the DMEU oxygen site, indicating that larger solute aggregates may also exist, not being destroyed by the water network.

These quantum chemistry results help us to understand the observed temperature-independent aggregation of DMEU in their dilute aqueous solutions [7]. The temperature dependence of the physicochemical properties is a sensitive indicator of the intermolecular interactions. The pair-wise vdW attraction is independent of the temperature, while in the liquid phase, the solute–solute interactions are always perturbed by the solvent. In aqueous TMU solutions, the TMU–TMU interactions follow the temperature dependence of the dynamics of water, while in case of the DMEU, the solute-solute attraction is insensitive to the temperature, indicating that it is dominated by the contact solute-solute bonding. In this respect, the properties of the DMEU–water mixture are close to those of TMU–carbon disulfide mixture, in which a similar kind of temperature-independent solute-solute attraction was observed [60]. In our case, the relatively strong bonding between DMEU molecules can effectively counterbalance the solute–solvent interaction, while in case of the inert solvent carbon disulfide (in the TMU–CS_2 system), the solute–solvent interactions are rather weak and thus do not influence the solute–solute attraction.

4. Conclusions

In this study we performed quantum chemical *ab initio* calculations for the geometries and intermolecular interaction potential curves of the three different (planar, parallel and perpendicular) DMEU dimers and two different DMEU–water systems. The geometry optimization has been taken at second order Møller–Plesset perturbation theory level using D95**+ basis set, as well as at DF-LMP2 theory using consistent correlated basis sets (aug-cc-pVXZ, X = D, T, Q). Comparisons have been made for the intermolecular interaction potential energy curves obtained at HF, B3LYP and MP2 levels of theory. There is a significant difference between the B3LYP and MP2 energy values, which is mainly due to the missing of the long-range dispersive interactions from the B3LYP exchange-correlation functional. The influence of BSSE is fairly significant for the standard MP2 results, and less important for the HF and B3LYP results.

Performing quantum mechanical treatment of SAPT method for interaction energy decomposition into physically relevant terms, we have shown the role of the dispersion effects in DMEU–DMEU and DMEU–water intermolecular interactions. Furthermore, it was found that the "counterpoise corrected" MP2-CP intermolecular interaction energy values are close to the SAPT values, which is obtained as a sum of the first and second order SAPT correction contributions ($E_{int}^{SAPT} = E_{int}^{HF} + SAPT_{corr}$).

For larger basis sets (aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, etc.) the contribution of the dispersion energy strongly increases, pointing to the importance of using suitably large basis sets in addition to the correct electron correlation method.

The strong DMEU–DMEU bonding is suggested to be responsible for the DMEU association in its aqueous solutions. Further studies along these lines may be useful for better understanding the role of hydration and van der Waals interactions in solutions of hydrophobic molecules.

Acknowledgments

A.B. acknowledges the support of Romanian Ministry of Education and Research through the Grant Nos. CEEX ET-30/08.10.2005 and CEEX ET-60/30.04.2006. The authors thank Dr. F. Bogár for helpful comments on the manuscript and the anonymous Referee for pointing out the relevancy of some special theoretical considerations in case of the weakly bounded molecular systems.

References

[1] Y. Koga, Y. Miyazaki, Y. Nagano, A. Inaba, J. Phys. Chem. B 112 (2008) 11341.
[2] A. Perera, F. Sokolić, L. Almásy, P. Westh, Y. Koga, J. Chem. Phys. 123 (2005) 024503.
[3] G. Jancsó, J. Solution Chem. 35 (2006) 991.
[4] V.Yu. Bezzabotnov, L. Cser, T. Grósz, G. Jancsó, Yu.M. Ostanevich, J. Phys. Chem. 96 (1992) 976.
[5] S. Borbély, L. Cser, T. Grósz, G. Jancsó, Physica B 213 (1995) 513.
[6] L. Almásy, A. Len, N.K. Székely, J. Plestil, Fluid Phase Equilibr. 257 (2007) 114.
[7] N.K. Székely, L. Almásy, G. Jancsó, J. Mol. Liq. 136 (2007) 184.
[8] G. D'Arrigo, R. Giordano, J. Teixeira, Eur. Phys. J. E 10 (2003) 135.
[9] L. Almásy, P. Bánki, M.C. Bellissent-Funel, M. Bokor, L. Cser, G. Jancsó, K. Tompa, J.M. Zanotti, Appl. Phys. A 74 (Suppl.) (2002) S516.
[10] K. Jerie, A. Baranowski, S. Koziol, J. Gliński, A. Burakowski, Chem. Phys. 309 (2005) 277.
[11] Y. Takasu, I. Nishio, J. Phys. Soc. Jpn. 72 (2003) 2106.
[12] M. Musso, M.G. Giorgini, H. Torii, J. Mol. Liq. in press, doi:10.1016/j.molliq.2008.08.006.
[13] A. Idrissi, J. Mol. Liq. 134 (2007) 23.
[14] A. Idrissi, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. 61 (2005) 1.
[15] T. Pradhan, P. Ghoshal, R. Biswas, J. Phys. Chem. A 112 (2008) 915.
[16] S. Bálint, I. Bakó, T. Grósz, T. Megyes, J. Mol. Liq. 136 (2007) 257.
[17] T. Megyes, S. Bálint, T. Grósz, T. Radnai, I. Bakó, L. Almásy, J. Chem. Phys. 126 (2007) 164507.
[18] E.C. Yang, X.J. Zhao, H. Fang, Indian J. Chem. A 44 (2005) 291.
[19] S. Kunsági-Máté, G. Vasapollo, K. Szabó, I. Bitter, G. Mele, L. Longo, L. Kollár, J. Incl. Phenom. Macrocycl. Chem. 60 (2008) 71.
[20] A. Heintz, D. Wandschneider, U. Lüning, W. Marczak, Fluid Phase Equilibr. 248 (2006) 123.
[21] I. Pápai, G. Jancsó, J. Phys. Chem. A 104 (2000) 2132.
[22] W. Marczak, J.K. Lehmann, A. Heintz, J. Chem. Thermodyn. 35 (2003) 269.
[23] W. Marczak, A. Heintz, M. Bucek, J. Chem. Thermodyn. 36 (2004) 575.
[24] J.C. Otero, J.I. Marcos, E. López-Cantarero, A. Chacón, Chem. Phys. 157 (1991) 201.
[25] E.I. Harnagea, P.W. Jagodzinski, Vib. Spectrosc. 10 (1996) 169.
[26] K. Tóth, P. Bopp, G. Jancsó, J. Mol. Struct. 381 (1996) 181.
[27] P. Belletato, L.C.G. Freitas, E.P.G. Arêas, P.S. Santos, Phys. Chem. Chem. Phys. 1 (1999) 4769.
[28] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzews.ki, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
[29] T.H. Dunning Jr., P.J. Hay, in: H.F. Schaefer III (Ed.), Modern Theoretical Chemistry, vol. 3, Plenum, New York, 1976, p. 1.
[30] A. Bende, S. Suhai, Int. J. Quantum Chem. 103 (2005) 841.
[31] H.B. Jansen, P. Ros, Chem. Phys. Lett. 3 (1969) 140.
[32] S.B. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.
[33] B. Jeziorski, R. Moszyński, K. Szalewicz, Chem. Rev. 94 (1994) 1887.
[34] K. Szalewicz, B. Jeziorski, in: S. Scheiner (Ed.), Molecular Interactions – from van der Waals to strongly bound complexes, Wiley, New York, 1997, p. 3.
[35] B. Jeziorski, K. Szalewicz, P. von Ragué Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, P.A. Kollman, H.F. Schaefer, P.R. Schreiner (Eds.), Encyclopedia of Computational Chemistry, vol. 2, Wiley, Chichester, UK, 1998, p. 1376.
[36] B. Jeziorski, K. Szalewicz, in: S. Wilson (Ed.), Handbook of Molecular Physics and Quantum Chemistry, vol. 3, Wiley, 2003, p. 232 (Part 2, Chapter 9).
[37] Program SAPT2006: "An Ab Initio Program for Many-Body Symmetry-Adapted Perturbation Theory Calculations of Intermolecular Interaction Energies" by R. Bukowski, W. Cencek, P. Jankowski, B. Jeziorski, M. Jeziorska, S.A. Kucharski, V.F. Lotrich, A.J. Misquitta, R. Moszynski, K. Patkowski, R. Podeszwa, S. Rybak, K. Szalewicz, H.L. Williams, R.J. Wheatley, P.E.S. Wormer, P.S. Żuchowski.
[38] R. Cervellati, A. Degli Esposti, D.G. Lister, P. Palmieri, J. Mol. Struct. 189 (1988) 81.
[39] A. Masunov, J.J. Dannenberg, J. Phys. Chem. A 103 (1999) 178.
[40] M. Elstner, P. Hobza, T. Frauenheim, S. Suhai, E. Kaxiras, J. Chem. Phys. 114 (2001) 5149.
[41] D. Cremer, Mol. Phys. 99 (2001) 1899.
[42] S. Kristyán, P. Pulay, Chem. Phys. Lett. 229 (1994) 175.
[43] P. Hobza, J. Šponer, T. Reschel, J. Comput. Chem. 16 (1995) 1315.
[44] S. Grimme, J. Comput. Chem. 25 (2004) 1463.
[45] S. Grimme, J. Comput. Chem. 27 (2006) 1787.
[46] V. Barone, M. Biczysko, M. Pavone, Chem. Phys. 346 (2008) 247.
[47] A. Bende, Á. Vibók, G.J. Halász, S. Suhai, Int. J. Quantum Chem. 101 (2005) 186.
[48] P. Pulay, Chem. Phys. Lett. 100 (1983) 151.
[49] S. Saebø, P. Pulay, Annu. Rev. Phys. Chem. 44 (1993) 213.
[50] C. Hampel, H.-J. Werner, J. Chem. Phys. 104 (1996) 6286.
[51] G. Hetzer, M. Schütz, H. Stoll, H.-J. Werner, J. Chem. Phys. 113 (2000) 9443.
[52] M. Schütz, J. Chem. Phys. 113 (2000) 9986.
[53] M. Schütz, H.-J. Werner, J. Chem. Phys. 114 (2001) 661.
[54] O. Vahtras, J. Almlöf, M.W. Feyereisen, Chem. Phys. Lett. 213 (1993) 514.
[55] J.G. Hill, J.A. Platts, H.-J. Werner, Phys. Chem. Chem. Phys. 8 (2006) 4072.
[56] MOLPRO, version 2006.1, a package of ab initio programs, H.-J. Werner, P.J. Knowles, R. Lindh, F.R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T.B. Adler, R.D. Amos, A. Bernhardsson, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A.W. Lloyd, R.A. Mata, A.J. May, S.J. McNicholas, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, A. Wolf Available from: <http://www.molpro.net>.
[57] M. Schütz, G. Rauhut, H.-J. Werner, J. Phys. Chem. A (1998) 5997.
[58] J. Šponer, P. Hobza, Chem. Phys. Lett. 267 (1997) 263.
[59] S. Tsuzuki, T. Uchimaru, K. Matsumura, M. Mikami, K. Tanabe, Chem. Phys. Lett. 319 (2000) 547.
[60] L. Cser, G. Jancsó, P. Jóvári, G. Káli, J. Phys. Chem. B 102 (1998) 2313.