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

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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].

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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

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

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}:

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

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:

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

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

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

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