Exploring intra- and intermolecular interactions in selected *N*-oxides : the role of hydrogen bonds.

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Streszczenie

Intra- and intermolecular interactions have been explored in selected N-oxide derivatives: 2-(N,N-dimethylamino-N-oxymethyl)-4,6-dimethylphenyl (**1**) and 5,5'-dibromo-3-diethylaminomethyl-2,2'-biphenol N-oxide (**2**). Both compounds possess intramolecular hydrogen bonding, which is classified as moderate in **1** and strong in **2**, and resonance-assisted in both cases. Density Functional Theory (DFT) in its classical formulation as well as Time-Dependent extension (TD-DFT) were employed to study proton transfer phenomena. The simulations were performed in the gas phase and with implicit and explicit solvation models. The obtained structures of the studied N-oxides were compared with experimental data available. The proton reaction path was investigated using scan with an optimization method, and water molecule reorientation in the monohydrate of **1** was found upon the proton scan progress. It was found that spontaneous proton transfer phenomenon cannot occur in the electronic ground state of the compound **1**. An opposite situation was noticed for the compound **2**. The changes of nucleophilicity and electrophilicity upon the bridged proton migration were analyzed on the basis of Fukui functions in the case of **1**. The interaction energy decomposition of dimers and microsolvation models was investigated using Symmetry-Adapted Perturbation Theory (SAPT). The simulations were performed in both phases to introduce polar environment influence on the interaction energies. The SAPT study showed rather minor role of induction in the formation of homodimers. However, it is worth noticing that the same induction term is responsible for the preference of water molecules' interaction with N-oxide hydrogen bond acceptor atoms in the microsolvation study. The Natural Bond Orbital (NBO) analysis was performed for the complexes with water to investigate the charge flow upon the polar environment introduction. Finally, the TD-DFT was applied for isolated molecules as well as for microsolvation models showing that the presence of solvent affects excited states, especially when the N-oxide acceptor atom is microsolvated.

Słowa kluczowe

N-oxides, microsolvation, DFT, IEF-PCM, Fukui functions, SAPT, NBO, TD-DFT

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