

Naphthazarin derivatives in the light of intra- and intermolecular forces.

Autorzy

Karol Kułacz

Michał Pocheć

Aneta Jezierska

Jarosław J. Panek

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Streszczenie

Our long-term investigations have been devoted the characterization of intramolecular hydrogen bonds in cyclic compounds. Our previous work covers naphthazarin, the parent compound of two systems discussed in the current work: 2,3-dimethylnaphthazarin (**1**) and 2,3-dimethoxy-6-methylnaphthazarin (**2**). Intramolecular hydrogen bonds and substituent effects in these compounds were analyzed on the basis of Density Functional Theory (DFT), Møller–Plesset second-order perturbation theory (MP2), Coupled Clusters with Singles and Doubles (CCSD) and Car-Parrinello Molecular Dynamics (CPMD). The simulations were carried out in the gas and crystalline phases. The nuclear quantum effects were incorporated a posteriori using the snapshots taken from ab initio trajectories. Further, they were used to solve a vibrational Schrödinger equation. The proton reaction path was studied using B3LYP, ω B97XD and PBE functionals with a 6-311++G(2d,2p) basis set. Two energy minima (deep and shallow) were found, indicating that the proton transfer phenomena could occur in the electronic ground state. Next, the electronic structure and topology were examined in the molecular and proton transferred (PT) forms. The Atoms In Molecules (AIM) theory was employed for this purpose. It was found that the hydrogen bond is stronger in the proton transferred (PT) forms. In order to estimate the dimers' stabilization and forces responsible for it, the Symmetry-Adapted Perturbation Theory (SAPT) was applied. The energy decomposition revealed that dispersion is the primary factor stabilizing the dimeric forms and crystal structure of both compounds. The CPMD results showed that the proton transfer phenomena occurred in both studied compounds, as well as in both phases. In the case of compound **2**, the proton transfer events are more frequent in the solid state, indicating an influence of the environmental effects on the bridged proton dynamics. Finally, the vibrational signatures were computed for

both compounds using the CPMD trajectories. The Fourier transformation of the autocorrelation function of atomic velocity was applied to obtain the power spectra. The IR spectra show very broad absorption regions between 700 cm⁻¹–1700 cm⁻¹ and 2300 cm⁻¹–3400 cm⁻¹ in the gas phase and 600 cm⁻¹–1800 cm⁻¹ and 2200 cm⁻¹–3400 cm⁻¹ in the solid state for compound **1**. The absorption regions for compound **2** were found as follows: 700 cm⁻¹–1700 cm⁻¹ and 2300 cm⁻¹–3300 cm⁻¹ for the gas phase and one broad absorption region in the solid state between 700 cm⁻¹ and 3100 cm⁻¹. The obtained spectroscopic features confirmed a strong mobility of the bridged protons. The inclusion of nuclear quantum effects showed a stronger delocalization of the bridged protons.

Słowa kluczowe

intramolecular hydrogen bonds, gas phase, crystalline phase, DFT, MP2, CCSD, AIM, SAPT, nuclear quantum effects, CPMD

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