Non-covalent forces in Naphthazarin—cooperativity or competition in the light of theoretical approaches.

Autorzy

Aneta Jezierska

Kacper Błaziak

Sebastian Klahm

Arne Lüchow

Jarosław J. Panek

Rok wydania

2021

Czasopismo

International Journal of Molecular Sciences

Numer woluminu

22

Strony

8033/1-8033/22

DOI

10.3390/ijms22158033

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Non-covalent interactions responsible for molecular features and self-assembly in Naphthazarin C polymorph were investigated on the basis of diverse theoretical approaches: Density Functional Theory (DFT), Diffusion Quantum Monte Carlo (DQMC), Symmetry-Adapted Perturbation Theory (SAPT) and Car-Parrinello Molecular Dynamics (CPMD). The proton reaction paths in the intramolecular hydrogen bridges were studied. Two potential energy minima were found indicating that the proton transfer phenomena occur in the electronic ground state. Diffusion Quantum Monte Carlo (DQMC) and other levels of theory including Coupled Cluster (CC) employment enabled an accurate inspection of Potential Energy Surface (PES) and revealed the energy barrier for the proton transfer. The structure and reactivity evolution associated with the proton transfer were investigated using Harmonic Oscillator Model of Aromaticity - HOMA index, Fukui functions and Atoms In Molecules (AIM) theory. The energy partitioning in the studied dimers was carried out based on Symmetry-Adapted Perturbation Theory (SAPT) indicating that dispersive forces are dominant in the structure stabilization. The CPMD simulations were performed at 60 K and 300 K in vacuo and in the crystalline phase. The temperature influence on the bridged protons dynamics was studied and showed that the proton transfer phenomena were not observed at 60 K, but the frequent events were noticed at 300 K in both studied phases. The spectroscopic signatures derived from the CPMD were computed using Fourier transformation of autocorrelation function of atomic velocity for the whole molecule and bridged protons. The computed gas-phase IR spectra showed two regions with OH absorption that covers frequencies from 2500 cm−1 to 2800 cm−1 at 60 K and from 2350 cm−1 to 3250 cm−1 at 300 K for both bridged protons. In comparison, the solid state computed IR spectra revealed the environmental influence on the vibrational features. For each of them absorption regions were found between 2700–3100 cm−1 and 2400–2850 cm−1 at 60 K and 2300–3300 cm−1 and 2300–3200 cm−1 at 300 K respectively. Therefore, the CPMD study results indicated that there is a cooperation of intramolecular hydrogen bonds in Naphthazarin molecule.

Słowa kluczowe

Naphthazarin C, photoluminescence, 8-dihydroxynaphthalene-1, 4-dione, hydrogen bond, gas phase, crystalline phase, DFT, MP2, DQMC, CC, HOMA index, Fukui function, AIM, SAPT, CPMD

Adres publiczny

http://dx.doi.org/10.3390/ijms22158033

Strona internetowa wydawcy

http://www.mdpi.com/journal/metals