A theoretical study of cooperative and anticooperative effects on hydrogen-bonded clusters of water and the cyanuric acid

Abedien Zabardasti; Ali Kakanejadi; Fatemeh Ghenaatian; Zeinab Bigleri

* Department of Chemistry, Lorestan University, Khoramabad, Iran

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A theoretical study of cooperative and anticooperative effects on hydrogen-bonded clusters of water and the cyanuric acid

Abedien Zabardasti*, Ali Kakanejadi, Fatemeh Ghenaatian and Zeinab Bigleri

Department of Chemistry, Lorestan University, Khoramabad, Iran

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Ab initio and density functional calculations are used to analyse the interaction between a molecule of the cyanuric acid and one, two and three molecules of water at B3LYP/6-311 + + G(d,p) and MP2/6-311 + + G(d,p) computational levels. Also, the cooperative effect (CE) in terms of the stabilisation energy of clusters is calculated and discussed. Depending on the geometry of clusters under study, the cooperative, non- or anti-CE was found with an increasing cluster size. Red shifts of N—H and C=O stretching frequencies illustrate a good dependence on the CE. The atoms in molecules theory is used to analyse the CE on topological parameters.

Keywords: hydrogen-bonded clusters; cooperative effect; cyanuric acid; theoretical studies; triazinetriol

1. Introduction

The cyanuric acid (CA) or 1,3,5-triazine-2,4,6-triol is the cyclic trimer of the cyanic acid [1]. It is an organic chemical compound with the formula C₃H₃N₃O₃. Synonyms include 1,3,5-triazinetriol, 1,3,5-triazine-2,4,6(1H,3H,5H)-trione and the isocyanuric acid. This triazine derivative is a stable, white, odourless and hygroscopic solid at room temperature. It is used as a stabiliser in recreational water treatment to minimise the decomposition of the hypochlorous acid by light in outdoor swimming pools and hot tubes [2]. The ring in this molecule has an aromatic character and the hydroxyl (—OH) groups in the triol form of the molecule take on a phenolic character, becoming somewhat more acidic than hydroxyls in an alcohol [3].

Two chemical structures, shown in Scheme 1, are keto–enol tautomers of the CA. Results of theoretical calculations have shown that the keto form is more stable than the enol form [4].

The importance of non-covalent intermolecular interactions in many areas of contemporary chemical physics has been demonstrated in numerous studies of such systems [5]. Non-covalently bonded molecular clusters are of a certain practical importance in many areas such as atmospheric chemistry and catalysis as well as in biochemically relevant processes.

Among all non-covalent interactions, the hydrogen bonding types are particularly significant. Recently, a large number of studies devoted to the hydrogen bonding phenomenon as well as the cooperative effect (CE) in hydrogen-bonded clusters have been published [6–16].

The presence of several alternative hydrogen bond acceptors (HBA, C=O) and hydrogen bond donors (HBD, N—H), which centres on CA, makes it a suitable molecule for the formation of HB clusters.

Despite the potential importance of CA and water, we could find neither experimental nor theoretical report on their H-bond clusters. In the absence of experimental data, a theoretical analysis of such complexes and their properties would appear to be in order. In the present work, a comparative computational study of the molecular properties of CA(H₂O)ₙ (ₙ = 1–3) is performed.

2. Computational methods

Calculations were performed using the Gaussian 03 system of codes [17]. The geometries of the isolated CA and H₂O molecules and their complexes were fully optimised at B3LYP/6-311 + + G(d,p) and MP2/6-311 + + G(d,p) computational levels. Both MP2 and B3LYP computations have their own supporting instances from the point of agreement between theoretical prediction and experimental measurement [18,19]. Harmonic vibrational frequency calculations at MP2/6-311 + + G(d,p) and B3LYP/6-311 + + G(d,p) levels confirmed the structures as minima and enabled the evaluation of zero point energy (ZPE). The counterpoise procedure [20] was used to correct the interaction energy for the basis-set superposition error.

3. Results and discussion

It seems that adjacent NH···X and CO···Y interactions (X = HBA and Y = HBD) in a cyclic or open Y···O=C—N—H···X form improve each other through both inductive and resonance effects. Clearly, the CO···Y