Journal of Molecular Structure: THEOCHEM 895 (2009) 100–106

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

Density functional theory and ab-initio computational study of molecular structure, tautomerism, and geometrical isomerism of ethynyl-bridged dipyridinones: In the gas phase and dielectric media

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ARTICLE INFO

Article history:
Received 6 August 2008
Received in revised form 17 October 2008
Accepted 17 October 2008
Available online 30 October 2008

Keywords:
Lactam–lactim tautomerizm
Isomerism
Dipyridinone
Solvent effect
Density functional theory

ABSTRACT

The geometries and relative stabilities for the different isomers and tautomers of ethynyl-bridged dipyridinones were calculated with full geometry optimizations using DFT method. Solvent effects have been analysed using the self-consistent reaction field theory with Onsager and continuum models for three different solvent, $CHCl_3$, CH_3OH and H_2O. The geometrical parameters of all structures were almost unaffected by the solvent. Except **3a** and **3b**, all compounds were found to have planar structure in the gas phase and in solutions. For the **3a** and **3b** tautomers were observed small divergence from planarity. The keto forms were calculated considerably to be more stable than the enol forms in the gas phase and in all solutions. The differences in relative energy values between tautomers were increased in general by the effect of solvent.

1. Introduction

Hydrogen-bonded compounds have received considerable attention with a view toward application to material science biological systems, and so forth. As for intermolecular hydrogen bonding compounds, DNA is very famous for its double helical structure using hydrogen binding and other interactions [1]. Although hydrogen bonds between neutral organic molecules are not among the strongest non-covalent interactions, they hold a prominent place in supramolecular chemistry due to their directionality and versatility [2–4]. The relationship between the degree of polymerization and the strength of the non-covalent interaction between monomers in a supramolecular polymer implies that multiple hydrogen bonds with a high association constant are required to obtain significant degrees of polymerization.

Combining several hydrogen bonds in a functional unit is a valuable tool to increase the strength of this interaction. Moreover, employing a particular arrangement of the hydrogen bonding sites enhances its specificity. The strength of single hydrogen bonds basically depends on the nature of donor and acceptor, although it is influenced to a large extent by the solvent. Association strength between multiple hydrogen bonding units obviously depends on the same factors, as well as on the number of hydrogen bonds. It has also been shown that the particular arrangement of neighboring donor (D) and acceptor (A) sites is an additional factor, which significantly affects the strength of the complexation. Very stable complexes can be obtained when quadruple hydrogen bonding units are employed [5–9]. Aspects of multiple hydrogen bonding units that are of special importance with respect to application in supramolecular polymers are the self-complementarity of DADA and DDAA arrays, and the possibility of tautomerism. The latter may lead to loss of complexation when complementarity is lost, or when a DDAA array tautomerizes to a DADA array with a higher number of repulsive secondary interactions.

Ducharme and Wuest [10] have synthesized ethynyl-bridged dipyridone **1** (Scheme 1) featuring a self-complementary array of four hydrogen bonding sites and have compared its association properties with those of symmetric, non-self-complementary dipyridone **2**. The isomeric form dipyridone 3 was synthesized as part of on going study of substituted pyridones [11]. Dipyridinone **1** incorporates a quadruple DADA pattern, which is self-complementary and thereby permits formation of cyclic dimer in solution and in the solid state. In contrast, the quadruple ADDA pattern of hydrogen-bonding sites in dipyridone **2** is not self-complementry. It produced oligomeric chains. In a significant extension of these studies of dipyridinone **1** and **2**, Meijer and co-worker [12] devised elegantly simple way to make a variety of new quadruple linear hydrogen-bonding motifs and other groups [13,14,1b] have also constructed related arrays of hydrogen-bonding sites designed to

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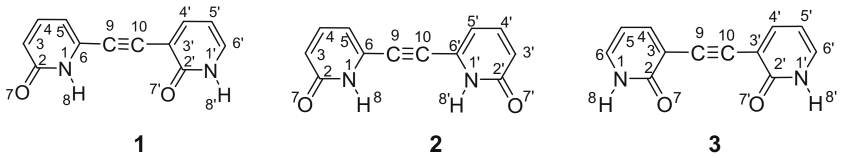
doi:10.1016/j.theochem.2008.10.031



Scheme 1.

control association. These studies also have helped stimulate further development of two exciting new fields of research in supramolecular chemistry: supramolecular polymers [15,1a] and molecular tectonics [16–21].

Ethynyl-bridged dipyridinone molecule may appear in various tautomeric forms as illustrated in Fig. 1. It is important to note that no attention has been paid to the tautomeric forms of dipyridone. It is well known that the heterocyclic tautomerism depends on the environment. Recently Matsumoto and coworkers [22] have studied the behaviors of the 2-dipyridone both in chloroform and methanol solutions and have clarified that dimer formation can be controlled by changing solvents. The features of the absorption spectra indicate that the molecule **1** exists as the keto form in the ground state. This result contrast with the fact that 2-pyridone taken the enol form in nonpolar solvent at low concentration [23]. One of the reasons for this work is the lack of experimental and theoretical findings for dipyridinone tautomers. Theoretical investigations represent a practicable way for obtaining in formation about the energetics of tautomers. In the present work, it has been investigated the structural and energetic features of possible tautomers, isomers and conformers of the present compounds in the gas phase and in dielectric media, using the ab initio and density functional theory calculations.

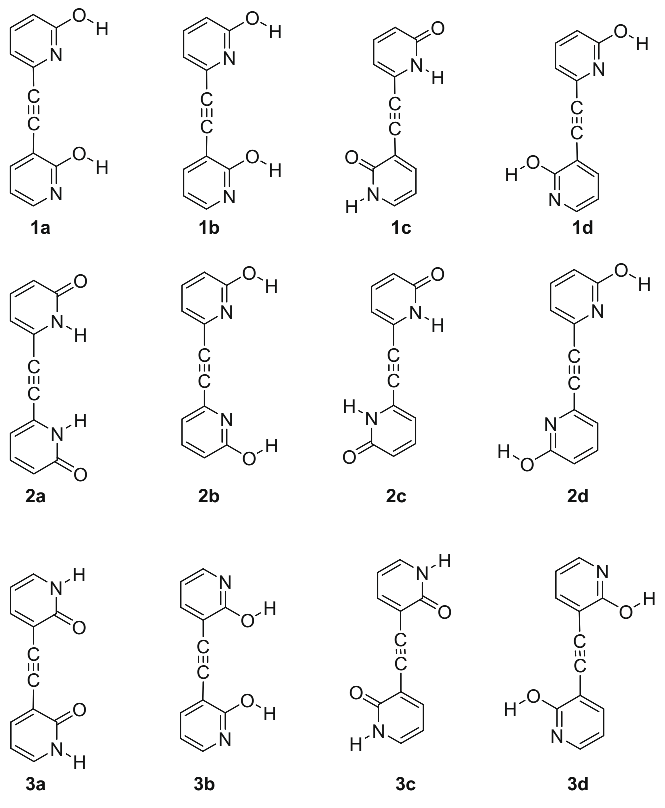


Fig. 1. The possible tautomeric and rotameric structures of the main compounds.

2. Computational details

All the calculations were carried out with the GAUSSIAN 03 [24] package program. Full geometry optimizations of all species were performed at the B3LYP/6-31+G* level in the gas phase and in solutions. Since the sizes of the systems under consideration prevent the use of large basis sets. Initially, all optimizations were carried out at B3LYP/6-31+G* level in the gas phase, and the resulting geometries were used as starting points in the further calculations. Frequency calculations showed that all structures were stationary points in the geometry optimization procedures, and none showed imaginary frequencies in the vibrational analyses.

The solute–solvent interaction was evaluated using the self-consistent reaction field (SCRF) method, which is based on Onsager's reaction field theory [25] of electrostatic solvation and using isodensity polarized continuum (IPCM) model [26]. The simplest SCRF model is the Onsager reaction field model. In this method, the solute occupies a fixed spherical cavity of radius a_0 within the solvent field. A dipole in the molecule will induce a dipole in the polar medium, and the electric field applied by the solvent dipole will in turn interact with the molecular dipole, leading to net stabilization. The isodensity polarized continuum model (IPCM) defines the cavity as an isodensity surface of the molecule. This isodensity is determined by an iterative process in which and SCF cycle is performed and converged using the current isodensity cavity. Heterocyclic tautomerism is very sensitive to the solvent [27]. Therefore much effort, both experimental and theoretical has been devoted to the study of solvent effects on tautomerism processes in various compounds [28–32]. Geometry optimization in the solvent with $e = 4.9$ to simulate $CHCl_3$, $e = 36.72$ to simulate CH_3OH and $e = 78.54$ to simulate H_2O were carried out at the 6-31+G* level using Onsager model.

3. Results and discussion

DFT calculations have been performed for the tautomeric equilibria 2-dipyridinone (DP) and 2-hydroxydipyridines (HDP). More than one conformer was found in each HDP, and the most stable conformers are chosen for further analyses. As shown in Fig. 1, these conformers are stabilized by possible intramolecular hydrogen bonds (N···OH, O···HN). As pronounced before, for 2-hydroxypyridine N—C—O—H cis rotamer is calculated to be more stable by 8.7 kcal/mol than the trans rotamer [33]. The possible tautomeric and rotameric structures of DPs and HDPs are given in Fig. 1. The structural forms of DPs are designated as **1a**, **2a**, **3a** for lactam (keto) isomers, **1b**, **2b**, **3b** for the lactim (enol) isomers, **1c**, **2c**, **3c** and **1d**, **2d**, **3d** for their rotamers, respectively.

3.1. Structures

The geometric optimizations were carried out at the B3lyp/6-31+G* level that is known to provide reliable geometries, without imposing any symmetry. Table 1 gives all the important geometrical parameters of investigated compounds in the gas phase. It was found that the SCRF has a small influence on the molecular geometries and most of the computed geometrical parameters in the gas