Journal of Molecular Structure: THEOCHEM 867 (2008) 78–84

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

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

Density functional theory study of intermolecular interactions of cyclic tetrazole dimers

Alireza Najafi Chermahini [a,*], Aseyeh Ghaedi [a], Abbas Teimouri [b], Fariborz Momenbeik [a], Hossein A. Dabbagh [c]

[a] Department of Chemistry, Faculty of Science, Yasouj University, Yasouj, Iran
[b] Payame Noor University, Isfahan, Iran
[c] Department of Chemistry, Isfahan University of Technology, Isfahan, Iran

ARTICLE INFO

Article history:
Received 22 April 2008
Received in revised form 23 July 2008
Accepted 23 July 2008
Available online 31 July 2008

Keywords:
Tetrazole
Substituent effect
Intermolecular hydrogen bonding
DFT
NBO
Vibrational analysis

ABSTRACT

In this study the density functional theory at B3LYP/6-31++G(d,p) level was employed to evaluate the hydrogen bonding between tetrazole dimers in the gas phase. Four cyclic dimers including one 1H–1H and three 2H–2H dimers were considered. The N...H–N hydrogen bonding which studied in the self assembled structures has been estimated from stabilization energies. The calculated hydrogen-bonding energies of various tetrazole dimers showed a cooperative interaction in the cyclic ones. It was found that 1H–1H dimers are more stable and introduction of an electron-releasing group (ERG) into the tetrazole rings resulted in the formation of more stable hydrogen bonding. Harmonic frequencies of monomers and dimers were calculated and it was found that change in the complexation vibrations is sensitive to the strength of the N...H–N hydrogen bondings. Natural population analysis was performed to predict electrostatic interactions in the cyclic H-bonded complexes.

1. Introduction

Tetrazole derivatives find a wide range of pharmaceutical applications [1] where they act as stimulants or sedatives on the central nervous system. These compounds have antimicrobial, antiinflammatory, antilipemic, and antiallergic activities *cis*-peptide bond mimics [2]. Moreover, such compounds are useful as oxidizers and effective agents for regulating plant growth and as explosives and rocket propellants [3]. In addition, tetrazole compounds have a significant role in medicinal chemical research [4]. In the gas phase, experimental results provide information about the existence of two tautomeric forms for tetrazole and its derivatives [5–7]. On the other hand, theoretical calculations have shown that, in the gas phase, the 2*H* continues to be the lowest energy tautomer on the semiempirical, [8] ab initio HF, [9,10] and DFT levels [11]. Recently some publications describing the tautomerism of 5-substituted tetrazoles by ab initio method became available, for all the substituents at the position 5 of the ring the 2*H*-tautomer is the most stable in the gas phase and the difference in energy between 1*H*- and 2*H*-tautomers depends only slightly on the nature of substituent R [12]. In the solid state, according to X-ray data and vibrational spectroscopy, the crystalline parent tetrazole and some of its derivatives in position 5, 1*H*-tautomers are dominant forms [13]. Recently our calculations have shown that for tetrazoles with electron withdrawing groups in the gas phase and solution 2-H forms are more stable [14].

Hydrogen bond is an important type of noncovalent interaction that is present in many chemical and biological systems [15]. A sound knowledge of hydrogen bond is fundamental to understand chemical structures, enzyme catalysis, material properties, self-assembly phenomena, and functions of molecular and biological devices and machines. Therefore, considerable amount of experimental and theoretical researches has been conducted concerning the structural, spectroscopic, and energetic issues of diverse hydrogen bonds [16–19]. The three types of H-bonding interactions which are most often discussed in the literature are weak, moderate, and strong [20]. In the X–H...Y that X is proton donor and Y is proton acceptor, the hydrogen bonding maybe evaluated geometrically by increase of X–H bond length and decrease of X...Y distance. In addition hydrogen-bond angle for strong hydrogen-bonds ranges from 170–180° [20].

2. Computational procedures

DFT calculations were performed using GAUSSIAN 03 package [21]. Density functional theory was used with Becke3-Lee-Yang-Parr (B3-LYP) exchange-correlation 6-31++G** basis set [22,23].

* Corresponding author. Tel./fax: +98 7412223048.
E-mail addresses: najafi@mail.yu.ac.ir, najafy@gmail.com (A.N. Chermahini).

0166-1280/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2008.07.023

According to recent reports hybrid functionals can provide better description for the systems with hydrogen bonds [24–26]. All geometries were completely optimized and for those compounds that have more than one stable geometry, the most stable one was selected. Vibrational frequencies were calculated to verify the nature of the stationary points found on the potential energy surface. The hydrogen-bonding energy of the studied dimers was corrected both with basis set superposition error (BSSE) and zero-point vibrational energies (ZPVE) [27].

Interaction energies are calculated for the tetrazole–terazole hydrogen bond base on differences between dimer energy and monomer energies.

$$E_{int} = E_{A-B} - (E_A + E_B) \quad (1)$$

where E_A, E_B and E_{A-B} are the electronic energies of tetrazole A, tetrazole B and dimer, respectively. The zero-point vibrational energy (ZPVE) corrections are applied in the present work based on following equations:

$$E_{int(ZPVE)} = E_{A-B(ZPVE)} - E_{A(ZPVE)} - E_{B(ZPVE)} \quad (2)$$

where $E_{A(ZPVE)}$, $E_{B(ZPVE)}$ and $E_{A-B(ZPVE)}$ are the sum of electronic and zero-point energies of tetrazole A, tetrazole B and aggregated system, respectively. To correct the basis set superposition error (BSSE), the counterpoise (CP) method is employed as followed:

$$E_{int(BSSE)} = E_{A-B} - E^{AB}_{A'} - E^{AB}_{B'} \quad (3)$$

where $E^{AB}_{A'}$ and $E^{AB}_{B'}$ show alculated energies of tetrazoles A and B with their geometries in the AB complex using the basis function of the complex AB, respectively.Finally the corrected interaction energies $E_{int(corr)}$, was calculated by addition of $E_{int(ZPVE)}$ and $E_{int(BSSE)}$ to interaction energy term (Eq. (1)):

$$E_{int(corr)} = E_{int} + E_{int(ZPVE)} + E_{int(BSSE)} \quad (4)$$

The vibrational frequencies were computed for the optimized geometries of monomers and dimers of tetrazoles. The harmonic frequency shift of the N–H stretching mode in the dimers, υ_{N-H}, was estimated by the following equation:

$$\Delta\nu_{N-H} = \nu_{N-H(dimer)} - \nu_{N-H(monomer)} \quad (5)$$

Precise investigation of the intermolecular interactions was performed by natural bond orbital (NBO) analysis with the NBO program [28].

3. Results and discussion

The structure and numbering of two tautomeric forms of tetrazole monomer (**A** and **B**) and four cyclic dimers including **C** for 1H–1H tetrazole dimers and **D**–**F** for 2H–2H dimres have been presented in Fig. 1 as you can see there is two hydrogen-bonding interactions in symmetrical dimers **C**, which including interaction between N1 hydrogen and N2′ lone pair and between N1′ hydrogen and N2 lone pair. In the symmetrical dimers **D** and **E**, hydrogen-bonding interactions are between N2–H...N1′ and N2–H...N3′ of two rings and in asymmetrical dimers **F** the interactions are between N2–H6...N1′ and N2′–H6′...N3 (Fig. 1).

3.1. Energies

Interaction energies were calculated for the tetrazole–tetrazole hydrogen bonds by taking in to account the energy difference between the monomers and the complex. The relative energies were corrected for both ZPVE and BSSE (basis set super position error) differences. The results of calculations which have been presented in Table 1 reveal that except for NO_2, in all of the substituted tetrazoles the planar 1H–1H dimers (**C** complexes) were found to be the thermodynamically most stable form. For example the hydrogen-bonding strength of 5-NH_2 substituted tetrazole with ZPVE and BSSE corrections are −11.65, −7.89, −8.65 and −8.06 kcal mol^{-1} for dimers **C**–**F**, respectively. However for 5-NO_2 substituted tetrazole, the order of stability of dimers changed to **F**(−7.13) > **E**(7.00) > **D**(6.85) > **C**(6.55) kcal mol^{-1}, which numbers in brackets refers to calculated energies of dimers.

Now we consider effect of substituents on variation of hydrogen-bonding strength. In the best of our knowledge there is a few publications deal with the effect of substituent on the hydrogen-bonding power [29,30]. Kawahara and co-workers studied effect of substituents on the stability and hydrogen bonding of adenine and uracil derivatives and conclude that introduction of an electron-withdrawing group into the uracil ring resulted in the formation of more stable hydrogen bonding [29]. Interestingly the results of our work which presented in Table 1. showed that the total hydrogen-bonding energy of tetrazoles enforced by introduction of ERG's. The order of strength of hydrogen bonding in the 1-H dimers with different substituents are: $NH_2 > CH_3 > H > SH > OH > F > Cl > BH_2 > CF_3 > CN > NO > NO_2$.

As you can see a stronger ERG is more effective for enforcement of the hydrogen bond in the tetrazole tautomers. The difference between the most strong and the weakest dimers is 5.10 kcal mol^{-1}. For the symmetrical and planer tetrazole dimers with structures of **D** and **E** the order of stability was found to be $OH > CH_3 > H > NH_2 > SH > BH_2 > Cl > F > CF_3 > NO_2 > NO > CN$ and $NH_2 > H > BH_2 > Cl > F > OH > CH_3 > CF_3 > SH > NO > CN > NO_2$, respectively. In these two recent dimers the difference between the most strong and the weakest hydrogen bonding in tetrazole dimers was 2.73 and 1.65 kcal mol^{-1}, respectively. Again the most effective hydrogen bonds formed between tetrazoles with electron donating substituents but in comparison with **C** struc-

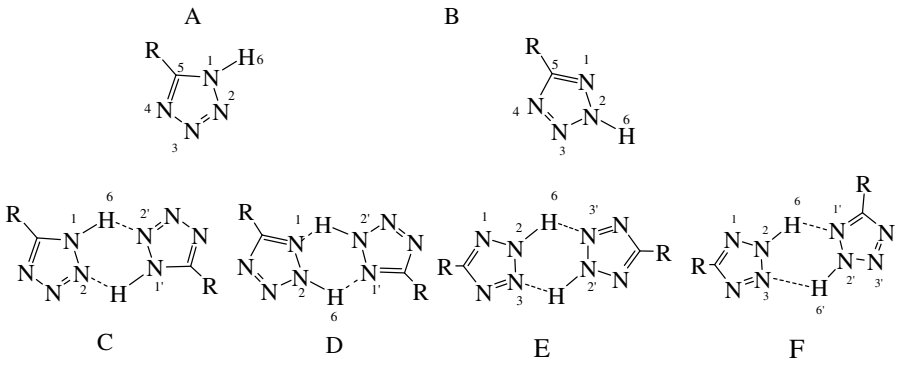

Fig. 1. Structure of tetrazole monomers (**A** and **B**) and dimers (**C**–**F**) which have been considered in this study.