Available online at www.sciencedirect.com

SCIENCE DIRECT®

Spectrochimica Acta Part A 64 (2006) 156–160

SPECTROCHIMICA
ACTA
PART A

www.elsevier.com/locate/saa

A theoretical prediction of stability in hydrogen-bonded complexes formed between oxirane and oxetane rings with HX (X = F and Cl)

F.C. Ferreira [b], B.G. Oliveira [a], E. Ventura [a],
S.A. do Monte [a], C.F. Braga [a], R.C.M.U. Araújo [a,*], M.N. Ramos [c]

[a] *Departamento de Química, CCEN, Universidade Federal da Paraíba, 58036-300 João Pessoa, PB, Brazil*
[b] *Departamento de Ciências Farmacêuticas, Universidade Federal da Paraíba, 58036-300 João Pessoa, PB, Brazil*
[c] *Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50739-901 Recife, PE, Brazil*

Received 25 May 2005; accepted 3 July 2005

Abstract

The optimised geometries of heterocyclic hydrogen-bonded complexes, $C_2H_4O\cdots HX$ and $C_3H_6O\cdots HX$, where X = F or Cl, were determined at DFT/B3LYP/6-311++G(d,p) computational level. Structural, electronic and vibrational properties of these complexes are used in order to compare the strained ring, which confer the great reactivity of these heterocyclic rings with monoprotic acids, forming a primary hydrogen bond. A secondary hydrogen bond between the hydrogen atoms of the CH_2 groups and the halide specie also takes place, thus causing a nonlinearity (characterized by the θ angle), in the primary hydrogen bond.

Keywords: Oxirane; Oxetane; DFT/B3LYP; Hydrogen bond; Nonlinearity

1. Introduction

In recent years, a great interest in the chemistry of heterocycles has emerged. As examples one can refer to the study of their reactivity through the S_N2 mechanism in organic synthesis [1–3], electrophilic addition with acid-catalysed polymerisation [4], rotational spectrum with a pulsed-nozzle, Fourier-transform microwave spectroscopy (FTMS) [5] as well as through quantum chemistry calculations [6]. One very important field of investigation involving heterocyclic compounds refer to electrophilic addition reactions, whose first step corresponds to the formation of a hydrogen-bonded complex as a stable intermediate.

This type of reaction involving three and four-membered heterocyclic analogue compounds of cyclopropane and cyclobutane, such as oxirane (C_2H_4O) and oxetane (C_3H_6O) are investigated in terms of the stabilization energy of the cyclic structure by monoprotic acids attack at electron *n*-pairs in oxygen atom, facilitating the open-chain reaction, and the intermolecular interaction through hydrogen complex formation reflects in the strain of the ring. Recent experimental investigations of several ground-state microwave rotational spectra with FT have been developed and applied in the study of these heterocyclic hydrogen complexes. Legon and co-workers [7–10] and Alonso and co-workers [11,12] established that the hydrogen bond in any hydrogen-bonded complex is precisely nonlinear, due to the secondary interaction between the Cl or F atoms with the axial hydrogen atoms of the rings. Ab initio molecular orbital calculations are widely used to elucidate the nature of such systems [13,14], and have also confirmed the C_S symmetry and the structure as asymmetric top rotors.

According to Rode [15], four-membered rings complexes formed by the proton donor HCl and oxetane, $C_3H_6O\cdots HCl$, has a defined stereochemistry detected in the supersonic jet technique, showing that the structure in which the HCl is in an equatorial stereochemistry is the more stable one. These conformations can provide different stabilization forms in the hydrogen bonded complexes, resulting in more or less

---

* Corresponding author. Tel.: +55 8321 67438; fax: +55 8321 67437.
E-mail address: regiane@quimica.ufpb.br (R.C.M.U. Araújo).

1386-1425/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2005.07.010

favourable routes of reaction, and theoretical studies show that structural, electronic and vibrational properties can really help one to determine correct mechanisms, and elucidate the great reactivity of these three and four-membered heterocyclic. It is well known that hydrogen bond formation cause significant changes in the aforementioned chemical properties of the C_2H_4O, C_3H_6O, and HX isolated species [16,17]. Thus, in this work we propose a quantum chemistry investigation of these main changes and how these alterations can provide a mechanism for the electrophilic addition reactions from a concise theoretical understanding of the stability of these heterocyclic analogues with the HCl and HF proton donor species.

2. Calculations and computational methods

The calculations have been performed by using the Gaussian 98W program [18]. All structures of the molecular complexes were fully optimised by Density Functional Theory [19–21] with the exchange correlation expressed by the three parameter B3LYP functional [22] with 6-311++G(d,p) basis set. The interaction energies have been correct for the basis set superposition error (BSSE) [23] by using the inherent counterpoise method [24] as well as the zero point vibrational energy (ZPE) [25]. All complexes were characterized as minima in their corresponding potential energies surfaces through vibrational frequency calculations.

3. Results and discussions

3.1. Structural parameters

The fully optimised geometries of $C_2H_4O\cdots HX$ and $C_3H_6O\cdots HX$ hydrogen-bonded complexes are given in Table 1. The complexation effect in the structure of the isolated molecules can be characterized by the modifications in the CO and CC bond lengths upon hydrogen bond formation However, the most pronounced effect occur undoubtedly in the CO bond length, which increases as a result of complexation by the HX eletrophilic species, initiating the open-chain reaction. Such structural changes are an evidenced of the role played by the HX species, thus weakening the CO bonds. The four-membered rings compounds present larger enhancements in CO bond length, with 0.0125 Å and 0.0126 Å in complexes formed by oxetane with HCl and HF acid species, respectively, while in the corresponding oxirane complexes such bond increases by 0.0100 Å and 0.0120 Å, respectively. Such behaviour is in parallel to the obtained intermolecular distances, $R_{\text{H-bond}}$, with the smaller values corresponding to the oxetane complexes, where the fluoride acid provides the most stable heterocycle. The hydrogen bond distances are in good agreement with the available experimental data.

Concerning structural properties, with respect to the most significant changes that can be used to describe the preferential stereochemistry and consequently the proposal of a mechanism, the microwave spectroscopy with FT has shown a secondary interaction between the F and Cl halides with the α axial hydrogen atoms of the ring, illustrated in Fig. 1. The DFT/B3LYP calculations have predicted such interaction, which is characterized by the nonlinearity angle, θ, in this series of heterocyclic complexes. The greater stability of the four-membered ring, as evidenced by a shortest intermolecular distance, culminates in a less pronounced secondary interaction, characterized by the θ angle (see Fig. 1). In the $C_2H_4O\cdots HX$ complexes, the $R_{\text{H-bond}}$ values are 1.7860 Å and 1.6620 Å, and the nonlinearity parameter (θ) have values of 9.1° and 9.2° for HCl and HF, respectively, while for the same proton donors in the $C_3H_6O\cdots HX$ complexes, the smaller intermolecular distances of 1.6940 Å and 1.6134 Å provide a weakest secondary interaction, with θ values of 5.9° and 5.4°. Despite the non-negligible deviations of about 5–7° between calculated and experimental θ values, the trend of decreasing values (see Table 1) in the series $C_2H_4O\cdots HCl > C_3H_6O\cdots HCl > C_3H_6O\cdots HF$ is reproduced by our results.

3.2. Electronic parameters

The Table 2 shows the calculated intermolecular energies and their corresponding zero point vibrational energy and

Table 1

Optimized structural parameters obtained for the $C_2H_4O\cdots HX$ and $C_3H_6O\cdots HX$ complexes along with the more pronounced changes, δr_{CO}, δr_{CC} and δr_{HX} which occur after hydrogen complexes formation, and with the intermolecular distance values, $R_{\text{H-bond}}$, and the nonlinearity parameter, θ

Heterocyclic hydrogen complexes	δr_{CO}	δr_{CC}	δr_{HX}	$R_{\text{H-bond}}$	θ (degree)
$C_2H_4O\cdots HCl$	0.0100	−0.0010	0.0300	1.786 (1.841)[a]	9.1 (16.5)[a]
$C_2H_4O\cdots HF$	0.0120	−0.0010	0.0250	1.662 (1.700)[b]	9.2 (–)
$C_3H_6O\cdots HCl$	0.0125	−0.0016	0.0426	1.694 (1.730)[c]	5.9 (12.0)[c]
$C_3H_6O\cdots HF$	0.0126	−0.0014	0.0304	1.613 (1.660)[d]	5.4 (10.0)[d]

δr_{CO} and δr_{CC} correspond to changes in CO and CC bond length in the heterocycles; δr_{HX} refers to enhancement in HX distance; The $R_{\text{H-bond}}$ corresponds to the distance between the isolated electron n-pairs in oxygen atom to the hydrogen atom in HX species; distance units in Å; nonlinearity parameter, θ angle, is given in degrees; the experimental values are given in parentheses.

[a] Ref. [8].

[b] Ref. [7].

[c] Ref. [11].

[d] Ref. [12].