

Basicity of the aziridine, solvent and substituent effects: A theoretical study

R. Hadjadj-Aoul^a, A. Bouyacoub^a, A. Krallafa^a, F. Volatron^{b,*}

^a Laboratoire de Chimie Physique Macromoléculaire (LCPM), Dpt. Chimie, Faculté des Sciences, Université Oran (Es-Senia), Oran 31000, Algeria

^b Laboratoire de Chimie Théorique CNRS (UMR 7616), Université de Paris VI (Pierre et Marie Curie), Site le Raphaël, 94200 IVRY, France

Received 11 July 2007; received in revised form 25 September 2007; accepted 26 September 2007

Available online 1 October 2007

Abstract

Ab initio investigations of the protonation of the aziridine and the *para*-X-phenylaziridine (X = NO₂, H and MeO) are carried out at the MP2 level of theory with the 6-31G* basis set. In gas phase the phenylaziridine is found to have a greater proton affinity than the aziridine. When the solvent effects are taken into account, a reverse behavior is observed in agreement with the experimental data. In addition, our calculations show that the electronic effects are transmitted through the phenyl cycle; a π -donor substituent located at the *para* position of the phenyl increases the proton affinity of the *para*-X-phenylaziridine. Conversely, a π -acceptor substituent decreases the proton affinity of the *para*-X-phenylaziridine.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Aziridine; Basicity; Solvent effect; Substituent effect

1. Introduction

Basicity of amines has been the subject of lot of experimental [1–4] and theoretical works [5–20]. In the case of alkyl amines, the main question under study is the different evolution of the amine basicity in gas-phase and water upon nitrogen substitution: it increases continuously from NH₃ to NMe₃ in gas-phase whereas Me₂NH is the most basic amine in water. This effect may be adequately reproduced in theoretical calculations when a combined discrete-continuum description of the solvent is used [21].

To our knowledge, the basicity of cyclic amines has been subject of much less studies. Substituent effects have been shown experimentally to be important in the case of aziridine: for instance, phenylaziridine in water has been found to be less basic than the unsubstituted aziridine by 1.5 pK unit [23]. In addition, substitution at the *para* position of the phenyl ring has been shown to have a noticeable influence on the aziridine basicity: the pK_a of the *para*-MeO-

C₆H₄-aziridine is equal to 8.7 i.e. it is more basic by 2.2 pK units than the unsubstituted phenylaziridine [23].

No theoretical study analogous to that made in acyclic amines is available on the solvation and substitution effects on cyclic amine basicity. In a recent study, Ohwada et al. [22] have analyzed the evolution in gas-phase of small cyclic amines basicity with the size of the heterocycles.

The aim of this paper is to study the solvent effect on the basicity of the aziridine. Following Mo and coworkers [21], a combined discrete-continuum description of the solvent has been used. Calculations were made with one and two water molecules included in the discrete part of the solvent. In a first part, the basicities of aziridine and phenylaziridine are studied in gas-phase and in solvent. In a second part, substitution effects at the *para* position of the phenyl ring are considered. A π -donor substituent (MeO) is studied as in the experimental study [23]. In addition we have also examined the influence of a π -acceptor substituent (NO₂). In each case, gas-phase and solvated species have been calculated to evaluate the importance of solvent effects.

* Corresponding author. Tel.: +33 1 44 27 96 63.

E-mail address: volatron@lct.jussieu.fr (F. Volatron).

2. Computational methods

Since we are interested in studying substituent and solvent effects on aziridine basicity, we need a computational method which gives reasonable results without being too much time consuming. Test calculations have been made on aziridine gas-phase proton affinity (PA) at various level of theory. We have used the Pople's standard basis sets 6-31G*, 6-31G** and the more extended 6-311G(2d,p) at the MP2, B3LYP and CCSD(T) levels. At each level of calculations, the geometries have been fully optimized. The results are given in Table 1.

It should be noted that at any level of calculation the 6-31G** basis set gives results systematically larger (by 3–6 kcal/mol) than the more extended 6-311G(2d,p) basis set (Table 1). Since we need a basis set of moderate size, we have chosen the 6-31G* basis set that will be used at the MP2 level. We are aware that the coincidence of the values obtained at the MP2/6-31G* and CCSD(T)/6-311G(2d,p) is fortuitous and probably comes from errors cancellation at the lowest calculation level. However, since hydrogen bonding will be involved in our study, we will test the difference between 6-31G* and 6-31G** more in detail in the following.

All gas-phase geometries of neutral aziridine and aziridinium cation interacting with zero, one or two water molecules have been optimized using an analytical gradient method. Characterizations of the stationary points have been performed at the MP2/6-31G* level by analytical frequencies calculations.

The effects of solvent are taken into account using the Polarized Continuum Model (PCM United Atom model) which includes non electrostatic effects. In this model, the solvent (water) is modeled by a continuum of uniform permittivity ($\epsilon = 78.4$). The solute is placed in a cavity defined as the union of a series of overlapping spheres centered on heavy atoms [24].

All calculations have been performed with the GAUSSIAN 03 [25] package.

3. Results

3.1. Unsubstituted aziridine

3.1.1. Gas-phase unsubstituted aziridine

The gas-phase basicity of the unsubstituted aziridine has been found to be equal to 226.6 kcal/mol (see preceding section). In order to take into account part of the solvent

effect, one and two water molecule(s) has(have) been added in the coordination sphere of the neutral aziridine and of the aziridinium cation.

3.1.1.1. With one water molecule. In the case of the aziridine, two structures are considered. In the first one (**1**), the nitrogen of the aziridine is a proton acceptor, whereas it is a proton donor in the second (**2**) (Fig. 1). The interaction energy between the aziridine and water molecules is found to be 9.5 kcal/mol (N...H–O bond) and 5.3 kcal/mol (N–H...O bond) (Table 2). The hydrogen bond involving the nitrogen lone pair is therefore found to be stronger than that involving the oxygen lone pair. Two stationary points were located in the case of mono-solvate of the aziridinium cation (Fig. 1). In the first (**3**), the water oxygen atom is bound to only one hydrogen of the cation. This structure is found to be a real minimum in which the interaction energy between the water and the cation is equal to 22.1 kcal/mol. This value is substantially greater than in the preceding case because of the cationic nature of the complexed system. In the second structure (**4**), the oxygen atom is symmetrically bound to the two hydrogen atoms; this structure was characterized as a transition state and is located 4.3 kcal/mol above the minimum **3**. This transition state allows the interconversion of two equivalent minima with H₂O bound to one or other H atom.

Since the interaction energy between H₂O and the cation (22.1 kcal/mol, Table 2) is noticeably greater than that of the neutral aziridine (9.5 kcal/mol, Table 2), the PA substantially increases (from 226.6 to 239.2 kcal/mol) when one solvent molecule is taken into account.

3.1.1.2. With two water molecules. The case of the aziridinium cation is rather simple: since two protons are available on nitrogen, each water molecule interacts with one of them. This structure (**5**, Fig. 2), was characterized as a minimum, the interaction energy being equal to 41.3 kcal/mol with respect to separated species (Table 2).

The situation is a little more complicated in the aziridine case. We first optimized a structure in which the nitrogen atom acts both as a proton-donor and as a proton acceptor. This structure (**6**, Fig. 2) was characterized as a real minimum. However, since the NH...O binding energy (5.3 kcal/mol in **2**) is smaller than the binding energy in H₂O dimer (7.3 kcal/mol at our level of calculation), we also optimized structures in which the N lone pair interacts with a H₂O dimer. Two other minima were located (**7** and **8** in Fig. 2). As expected, both are found to be lower in energy than **6**. It should be noted that in the lowest energy structure (**8**), an additional hydrogen bond between hydrogen and the oxygen atom may occur (the H...O distance is about 2.09 Å). All interaction energies and relative energies of the various species (**1–8**) are summarized in Table 2.

The PA of aziridine solvated by two water molecules is found to be 245.5 kcal/mol, a value larger than that in the mono-solvate case (239.2 kcal/mol) and much larger than

Table 1
Calculated aziridine proton affinity (in kcal/mol) at various level of calculations

	MP2	B3LYP	CCSD(T)
6-31G*	226.6	228.0	228.1
6-31G**	230.3	229.8	231.9
6-311G(2d,p)	224.8	226.6	226.6

Download English Version:

<https://daneshyari.com/en/article/5418622>

Download Persian Version:

<https://daneshyari.com/article/5418622>

[Daneshyari.com](https://daneshyari.com)