Pergamon

Tetrahedron Letters 42 (2001) 3897–3899

TETRAHEDRON
LETTERS

Intermolecular hydrogen transfers in 2,3-dihydroimidazol-2-ylidene and 2,3-dihydrothiazol-2-ylidene: a theoretical study

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Received 21 March 2001; accepted 12 April 2001

Abstract—The remarkable stability of *N*-heterocyclic carbenes has been an area of great interest in chemistry. However, prototype carbenes of these molecules, i.e. those with hydrogen atoms bearing on the nitrogens, have not been isolated as stable compounds. It is clear from our theoretical study that these prototype carbenes (2,3-dihydroimidazol-2-ylidene and 2,3-dihydrothiazol-2-ylidene) should undergo intermolecular hydrogen transfers (forming imidazole and thiazole) easily at room temperature. © 2001 Elsevier Science Ltd. All rights reserved.

N-Heterocyclic carbenes are compounds of great interest due to their manifold catalytic applications in chemistry.[1] Since the first isolation of an imidazol-2-ylidene in 1991,[2] related carbenes were isolated and characterized in condensed phase.[3] Theoretical works were devoted to the understanding of the extraordinary stability of these species.[4] However, imidazol-2-ylidene bearing hydrogen atoms on the nitrogens (2,3-dihydroimidazol-2-ylidene (**1**), see Fig. 1) has not been isolated as a stable compound.

Very recently, **1** was characterized in the gas phase and in matrix isolation.[5,6] In the matrix isolation experiment, irradiation of imidazole-2-carboxylic acid in argon matrix at 10 K resulted in the complex between **1** and carbon dioxide.[6] Annealing of the matrix at 60 K (complete evaporation of the argon) led to the disappearance of the spectrum of **1**. Due to the fact that imidazole (**5**) was formed from imidazole-2-carboxylic acid during annealing, it was not possible to decide whether **1** rearranged into **5** at 60 K. According to theoretical predictions at the B3LYP level, the activation energy (E_a) of the 1,2-hydrogen shift of **1** (into **5**) was very high (39.8 and 41.5 kcal mol^{-1} at the 6-31G* and 6-311G** basis sets, respectively),[5,6] intramolecular rearrangement of **1** is thus unlikely.

Thiazol-2-ylidenes play an important role in biochemical systems and have great potential in catalytic processes.[1,7] The synthesis of the first stable thiazol-2-ylidene was reported in 1997.[8] The quest for the prototype compound 2,3-dihydrothiazol-2-ylidene (**1′**, see Fig. 1) has resulted in the successful identification of **1′** in the gas phase and in matrix isolation.[9,10] The theoretically predicted E_a of the intramolecular 1,2-hydrogen shift of **1′** was also very high (40.9 and 42.3 kcal mol^{-1} using B3LYP and MP4 approaches, respectively).[9,10] However, it was observed that **1′** rearranges to thiazole (**5′**) upon warming the argon matrix to 60 K.[10] The observation urged the researchers to suggest that there is intermolecular hydrogen transfer between two molecules of **1′**. 1,2-Hydrogen shifts of *N*-heterocyclic carbenes via intermolecular processes have not been reported. However, an example of intermolecular 1,2-silyl migration of the 1,2,4-triazol-5-ylidene system was reported.[11]

The potential energy surfaces of **1** and **1′**, including dimerization and the intermolecular hydrogen transfer, were studied using the B3LYP and MP2 levels of theories.[12,13] The species involved in the reactions are illustrated in Fig. 1, point groups of the species involved are indicated in parentheses. The computed energetics are summarized in Table 1, in which numbers are relative energies with respect to those of the hydrogen-bonded complexes **2** and **2′**. In a previous publication, the authors showed that the E_a values for the dimerizations of stable diaminocarbenes of type **1** are much lower than those of intramolecular 1,2-rearrangements.[4]

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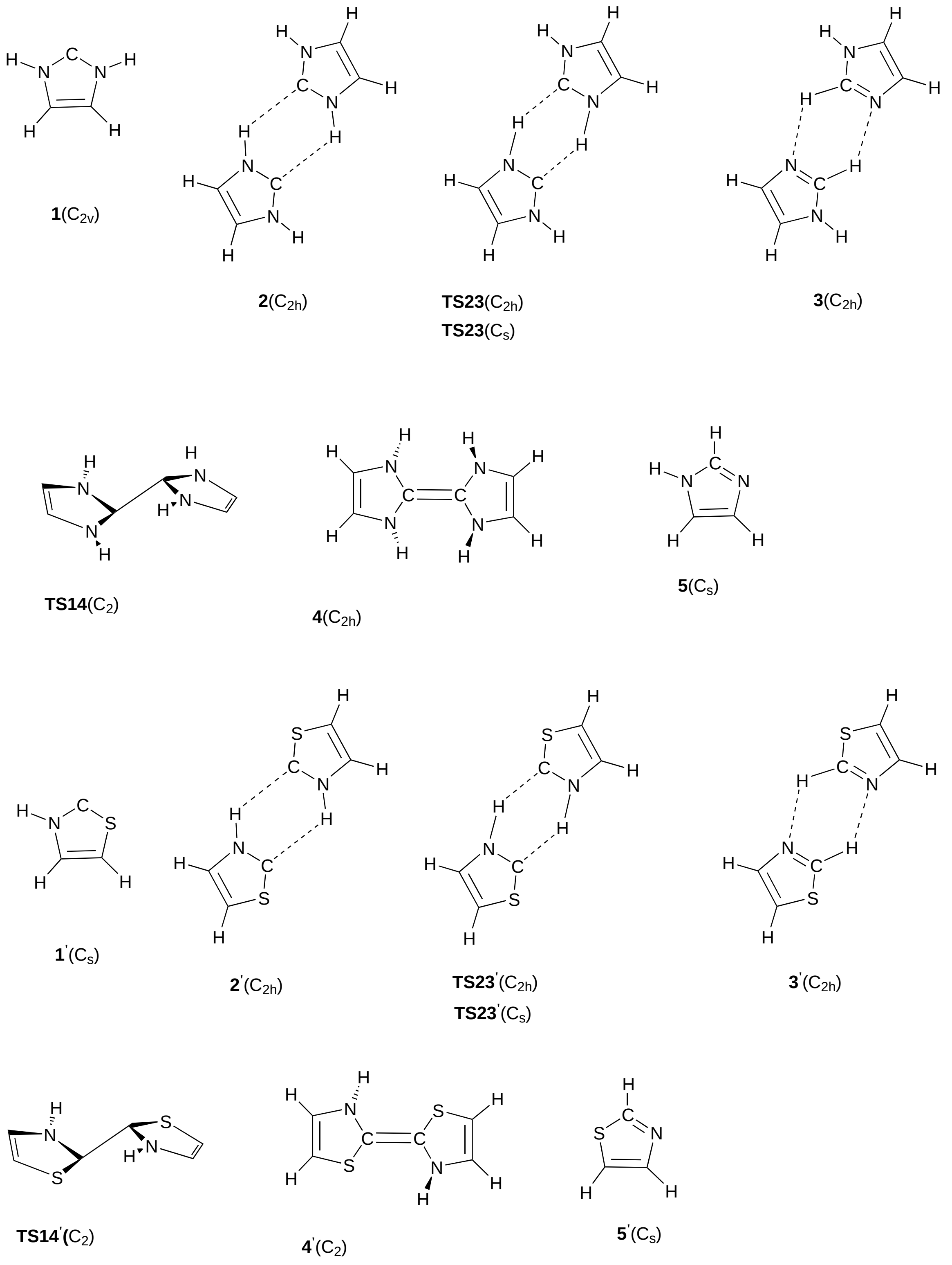
PII: S0040-4039(01)00605-0



1(C_{2v})

2(C_{2h})

TS23(C_{2h})
TS23(C_s)

3(C_{2h})

TS14(C_2)

4(C_{2h})

5(C_s)

1'(C_s)

2'(C_{2h})

TS23'(C_{2h})
TS23'(C_s)

3'(C_{2h})

TS14'(C_2)

4'(C_2)

5'(C_s)

Figure 1. Species involved in the intermolecular hydrogen transfer and the dimerization of 2,3-dihydroimidazol-2-ylidene (**1**) and 2,3-dihydrothiazol-2-ylidene (**1′**).

Two molecules of **1** form the hydrogen-bonded complex (**2**) at the first stage of the reaction (Fig. 1 and Table 1). With the B3LYP/aug-cc-pVDZ approach, the predicted hydrogen bond strength is 13.5 kcal mol^{-1}. From complex **2**, a small amount of activation energy (4.8 kcal mol^{-1}) is sufficient to form the imidazole dimer (**3**). The computed energetics indicate that the transition state (TS) of intermolecular hydrogen transfer (**TS23**) is much lower in energy than that of dimerization (**TS14**). Two saddle points were located for the hydrogen transfer of **2**. The first saddle point is symmetric (**TS23**, C_{2h}), while the second one is asymmetric

Table 1. Relative energies (in kcal mol^{-1}) of the species involved in the reactions of 2,3-dihydroimidazol-2-ylidene (**1**) and 2,3-dihydroimidazol-2-ylidene (**1′**). Energies are calculated with those of **2** and **2′** set to zero. The notation 2× represent 2 mol of free molecules. The energies including zero-point vibrational energy corrections are included in parentheses

	MP2/ 6-31G*	B3LYP/ 6-31G*	B3LYP/ 6-311G**	B3LYP/ aug-cc-pVDZ
		2,3-Dihydroimidazol-2-ylidene[c]		
2×**1**	21.1 (19.9)	19.5 (18.1)	16.5 (15.4)	14.6 (13.5)
TS23(C_{2h})[a]	9.4 (3.0)	9.4 (3.4)	11.0 (4.9)	10.9 (4.8)
TS23(C_s)[b]	9.1 (4.4)	9.2 (3.6)	10.5 (6.2)	10.2 (6.1)
3	−51.9 (−52.7)	−46.6 (−47.2)	−42.0 (−42.6)	−40.8 (−41.5)
2×**5**	−44.1 (−45.7)	−40.6 (−42.1)	−35.8 (−37.3)	−36.1 (−37.7)
TS14	43.9 (41.5)	38.6 (36.0)	38.8 (36.3)	37.2 (34.8)
4	7.1 (6.5)	2.6 (2.2)	5.6 (5.0)	4.3 (3.5)
		2,3-Dihydrothiazol-2-ylidene[c]		
2×**1′**	22.8 (22.0)	19.7 (18.7)	17.5 (16.5)	15.7 (14.7)
TS23′(C_{2h})[a]	5.7 (−0.1)	7.0 (1.3)	8.1 (2.3)	8.2 (2.3)
TS23′(C_s)[b]	5.7 (0.7)	6.9 (2.3)	7.9 (3.5)	7.9 (3.7)
3′	−56.9 (−57.4)	−50.6 (−50.8)	−46.1 (−46.5)	−44.4 (−44.8)
2×**5′**	−50.0 (−51.2)	−45.7 (−46.7)	−41.1 (−42.2)	−40.6 (−41.8)
TS14′	30.0 (29.1)	26.2 (25.1)	26.3 (25.3)	25.7 (24.6)
4′	−19.8 (−19.6)	−20.3 (−19.8)	−18.0 (−17.7)	−18.9 (−18.7)

[a] Symmetric transition state with two imaginary vibrational frequencies.

[b] Asymmetric transition state with one imaginary vibrational frequency.

[c] Refer to Fig. 1 for the notation of species.

(**TS23**, C_s) with nonequivalent N–H···C distances. The C_{2h} structure has two imaginary vibrational frequencies, and the C_s structure has one. At all levels of theory, the uncorrected energy of the symmetric saddle point is higher than that of the asymmetric one. However, energy of the symmetric saddle point becomes lower when the zero-point vibrational energy (ZPVE) corrections are included. An index to judge the bonding features and relative energies of **TS14** and **TS23** lies in the bond dissociation energies (BDEs) of **3** and **4** (with respect to 2×**1**), where BDE of the former is much larger.

The potential energy surface of **1′** is similar to that of **1**. Two saddle points were located for the intermolecular hydrogen transfer. The ZPVE corrected energy of the symmetric TS (**TS23′**, C_{2h}) is lower in energy than that of the asymmetric (C_s) one. **TS23′** is much lower in energy than that of dimerization (**TS14′**, C_2). From complex **2′**, an E_a of only 2.3 kcal mol^{-1} is needed to surmount the energy barrier (at the B3LYP/aug-cc-pVDZ level), forming the thiazole dimmer **3′**.

In conclusion, it is clear from our computations that carbenes **1** and **1′** should undergo intermolecular hydrogen transfers readily under normal conditions. The present study confirms the assumption made by Maier, Endres and Reisenauer that intermolecular hydrogen transfers occur in **1′**.[10]

Acknowledgements

We are grateful to the National Science Council of Taiwan for financial support, and to the National Center for High-performance Computing for computing facilities.

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12. The computations were performed using the GAUSSIAN98 program. Harmonic vibrational frequencies were computed for the stationary points at all levels of approaches, and the zero-point vibrational energies were included in the energies. We use the B3LYP/aug-cc-pVDZ energies for discussions in the text.
13. GAUSSIAN98; Gaussian: Pittsburgh, PA, 1998.