

# A comparison of intermolecular vibrations and tautomerism in benzimidazole, benzotriazole and their binary water clusters

Ch. Jacoby, W. Roth\*, M. Schmitt\*\*

Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 26.43.02, 40225 Düsseldorf, Germany

Received: 2 March 2000/Revised version: 31 May 2000/Published online: 5 October 2000 – © Springer-Verlag 2000

**Abstract.** Resonance-enhanced two-photon ionization spectra of benzotriazole, benzimidazole and their water clusters have been taken in a molecular beam. The tautomerism of the benzotriazole and benzimidazole monomers is studied.

In order to obtain an assignment of the vibronic bands of the benzotriazole- and benzimidazole-water clusters, ab initio calculations have been performed, which allow the assignment of the intermolecular vibrations and the determination of the most stable cluster structures. In the case of benzotriazole the cyclic cluster of the 2H-tautomer has been found to be the most stable one, whereas for benzimidazole the most stable cluster could be shown to have a linear arrangement, with the benzimidazole moiety acting as proton donor.

**PACS:** 36.40.Mr; 31.15.Ar

NH–O and OH–N type hydrogen bonds are important in many fields of chemistry and biology. The hydrogen-bonded clusters of benzimidazole and benzotriazole are of interest as model systems due to several facts. First of all the water molecule(s) are able to attach at different positions of the solute. Second, even small water clusters may form cyclic structures, due to the close vicinity of proton-donating and proton-accepting groups in the solute. Both benzotriazole and benzimidazole contain proton-donating and proton-accepting functional groups, as well as an aromatic  $\pi$ -system. All three regions are potential sites for the binding of one or more water molecules.

But even the minimum-energy structure of the monomers is not indubitable due to an equilibrium between different tautomeric forms, which differ in the position of one H-atom and exhibit nearly equal energies. The 1H- and 3H-tautomers are identical, whereas the 2H-tautomers differ in energy. For the benzotriazole monomer we could show experimentally, that the most stable form is the 1H-tautomer (equal to the 3H-tautomer) [1]. The energy difference between the 1H- and

the 2H-tautomer amounts only to  $417\text{ cm}^{-1}$ , which explains the great expenditure both in theoretical methods and in basis sets, which has to be pursued in determining the most stable structures.

A vibrationally resolved spectrum of the benzimidazole monomer in a supersonic jet has been presented by Jalviste and Treshchalov [2]. Velino et al. reported the microwave spectrum of benzimidazole and its N-deuterated isotopomer [3], which showed that benzimidazole is a planar asymmetric rotor in the electronic ground state. The rotational constants of the electronically excited state have been obtained by a band-contour analysis of the electronic origin of benzimidazole in the vapor phase [4]. Berden et al. presented a rotationally resolved laser-induced fluorescence (LIF) spectrum of benzimidazole in a supersonic jet [5]. From their excited-state rotational constants they concluded that benzimidazole is planar also in the  $S_1$ -state. Schoone et al. published a matrix-isolation FT-IR study of hydrogen-bonded benzimidazole–water clusters [6] and compared the intramolecular vibrational frequencies to the results of ab initio calculations. They found two different conformers of the binary cluster to be present in the matrix and assigned their intramolecular vibrations.

Benzotriazole has been studied both experimentally and theoretically to a much larger extent. The microwave spectra of 1H-benzotriazole have been taken both in a gas cell [7] and in a molecular beam [8]. The vibrationless  $S_1 \leftarrow S_0$  transition of benzotriazole at  $34\,920\text{ cm}^{-1}$ , which had been observed first by Jalviste et al. [2] could be shown to be due to the 2H-tautomer using rotationally resolved LIF spectroscopy [9]. The dispersed fluorescence spectra of benzotriazole taken in our group could be assigned to be solely due to 2H-benzotriazole [10]. Fourier-transform infrared spectra of benzotriazole in a molecular beam which have been taken in the range between  $650$  and  $1700\text{ cm}^{-1}$  showed vibrational bands, which could be attributed to 2H-benzotriazole [11], whereas infrared spectra in the solid state could be assigned as belonging to 1H-benzotriazole [11, 12].

From a comparison of the UV band spectra of benzotriazole with the spectra of the 1- and 2-methylsubstituted derivatives at different temperatures Catalán et al. concluded, that up to 20% of 2H-BT are present in the gas phase

\*Present address: University of Leeds, School of Chemistry, Leeds LS2 9JT, UK

\*\*Corresponding author.

Dedicated to Prof. Dr. J. Wolfrum on the occasion of his 60th birthday.

at 90 °C [13,14]. Whereas Hartree–Fock calculations predict the 1H-tautomer to be favored by  $\approx 800\text{--}1000\text{ cm}^{-1}$ , this ordering is reversed when electron correlation effects are included via second-order Møller–Plesset perturbation theory [14].

The electronic spectra of some benzotriazole–water clusters have been published recently without assignment of the vibronic bands [15].

In this publication we present an interpretation of the resonance-enhanced two-photon ionization (R2PI) spectra of benzimidazole–water and benzotriazole–water clusters. Furthermore the tautomeric equilibrium, which leads to two distinct forms in the case of benzotriazole and benzimidazole, is studied.

## 1 Experimental setup

The experimental setup for the resonance enhanced two-photon ionization (R2PI) and UV–UV spectral hole burning (SHB) is explained in detail elsewhere [10, 16]. Briefly, the apparatus consists of a source chamber pumped with a 1000 l/s oil diffusion pump (Alcatel) in which the molecular beam is formed by expanding a mixture of helium and benzimidazole through the 300  $\mu\text{m}$  orifice of a pulsed nozzle (General Valve, Iota One). Dried benzimidazole was heated to 120 °C prior to expansion in He. The spectra of the deuterated substances were recorded by simply flowing  $\text{D}_2\text{O}$  vapor at a partial pressure of 18 mbar over the solid benzimidazole sample and recording successively the R2PI spectra. The water clusters were formed by coexpanding water at a partial pressure of 10 mbar. The skimmed molecular beam (Beam Dynamics Skimmer, 1-mm orifice) crosses the laser beams at right angles in the ionization chamber. The ions are extracted in a gridless Wiley–McLaren-type time-of-flight (TOF) spectrometer (Bergmann Meßgeräte Entwicklung) perpendicular to the molecular beam and laser direction and enter the third (drift) chamber where they are detected using multi-channel plates (Galileo). Ionization and drift chamber are both pumped with a 150 l/s rotatory pump (Leybold). The vacuum in the three chambers with molecular beam on was  $1 \times 10^{-3}$  mbar (source),  $5 \times 10^{-5}$  mbar (ionization) and  $1 \times 10^{-7}$  mbar (drift), respectively.

The resulting TOF signal was digitized by a 500-MHz oscilloscope (TDS 520A, Tektronix) and transferred to a personal computer, where the TOF spectrum was recorded and stored.

The R2PI measurements were carried out using the frequency-doubled output of a Nd:YAG (Spectra Physics, GCR170) pumped dye laser (LAS, LDL205) operated with Fluorescein 27. For hole burning spectroscopy the second harmonic of a Nd:YAG (Spectra Physics GCR3)-pumped dye laser (LAS, LDL205) operated with the Fluorescein 27 dye was used. Both lasers have been calibrated by comparison with the tabulated transition frequencies to the iodine spectrum.

## 2 Theoretical methods

All ab initio calculations have been performed using the Gaussian 98 program package [17]. The SCF energy con-

vergence criterion was  $10^{-8}$  hartree and the convergence criterion for the gradient optimization of the molecular geometry was  $1.5 \times 10^{-5}$  hartree/bohr and hartree/degree, respectively.

The geometry optimization has been performed at Hartree–Fock (HF) and Møller–Plesset perturbation theory at second-order (MP2) level using the 6-31G(d,p) basis set. The vibrational frequencies have been calculated using the analytical second derivatives of the potential energy surface. Although these frequencies represent ground-state values, they can be compared to the frequencies of the R2PI spectra. The agreement between the theoretical MP2 frequencies and experimental  $S_1$  intermolecular frequencies has been found to be sufficient in comparable cluster systems in order to assign vibronic transitions. One has to keep in mind, that this comparison has to be made with great caution, regarding the fact that although the form of the normal mode (and therefore its reduced mass) does change a little upon electronic excitation, the force constants may differ considerably. Furthermore a harmonic description is in many cases not adequate. Nevertheless the calculation give a good hint as to the energetic order of the normal modes. An accidental agreement of calculated and experimental frequencies should not be taken as a measure of the quality of the calculations.

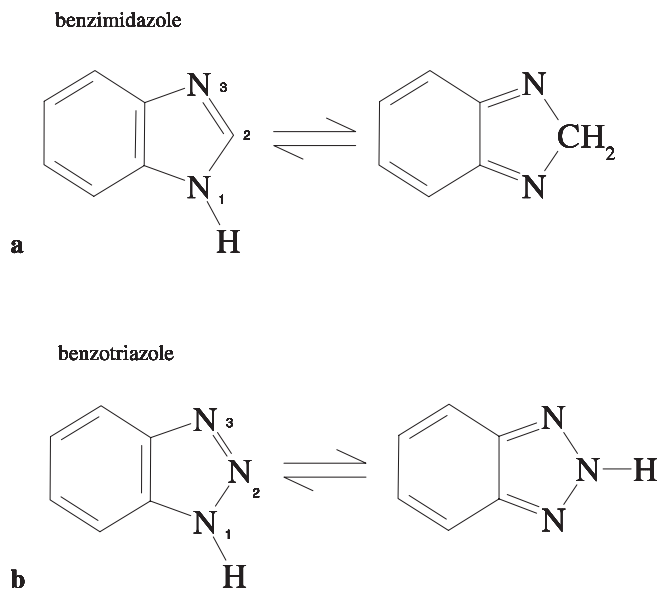
The different benzimidazole tautomers were calculated at the MP2/6-31G(d,p) level of theory, including the unscaled zero-point energy (ZPE) contribution. In order to study the relative energies of the two tautomers of benzotriazole, we carried out single-point calculations (on the MP2/6-311G(d,p) optimized geometry) using the coupled-cluster method with single and double excitations (CCSD) and contributions from triple excitations (CCSD(T)). Using the optimized structures, the unscaled zero-point energy contribution was calculated through normal mode analysis using the analytical second derivatives. Scaling factors as proposed by Scott and Radom [18] change the relative energies of the tautomers only by a few wavenumbers and do not lead to a change in their relative stability.

The stabilization energies  $D_e$  and  $D_0$  for the clusters were obtained as differences of the cluster and monomer energies and are corrected for the zero-point energy (ZPE) and the basis-set superposition error (BSSE) using the counterpoise method of Boys and Bernardi [19].

## 3 Results and discussion

### 3.1 Benzimidazole

The structures of the 1H, 2H- and 2H, 2H-tautomers of benzimidazole are shown in Fig. 1a. In order to study the tautomerism in the benzimidazole monomer the R2PI spectra of some of the deuterated species have been taken. Deuteration has been performed by flowing 18 mbar of  $\text{D}_2\text{O}$  over the benzimidazole sample, while taking the R2PI spectra. The progressive deuteration can be observed by an increase of the signal at the respective mass channels in the mass spectrum. Figure 2 shows the R2PI spectra in the region of the electronic origins of benzimidazole at the mass channels 118 amu, 119 amu and 120 amu which correspond to the  $\text{H}_2$ -benzimidazole, H,D-benzimidazole and  $\text{D}_2$ -benzimidazole, respectively. The electronic origins of the differently

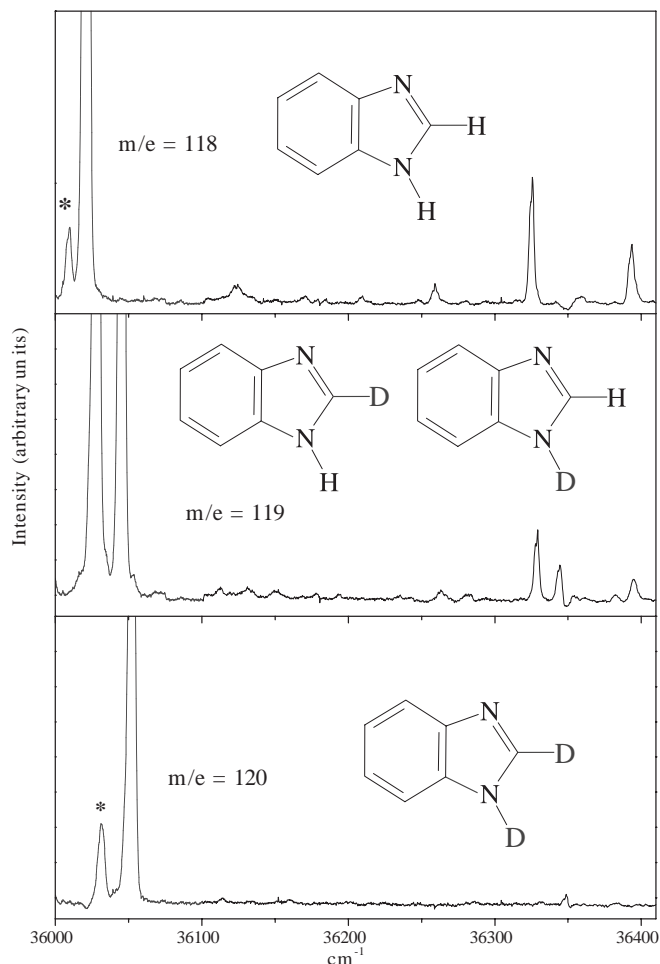


**Fig. 1.** a The atom numbering, structure and tautomerism of benzimidazole. b The atom numbering, structure and tautomerism of benzotriazole

deuterated species are given in Table 1. The electronic origin of  $\text{H}_2$ -benzimidazole is located at  $36022.2\text{ cm}^{-1}$ . The observation of only one electronic origin for  $\text{H}_2$ -benzimidazole indicates that only one tautomer absorbs in this spectral region. The mass trace 119 of the monodeuterated species exhibits two electronic-origin bands. They can be explained by the existence of two differently deuterated monomers, namely the 1D,2H-benzimidazole and the 2D,1H-benzimidazole. Both monodeuterated species are formed to equal amounts, which can be pursued by the simultaneous increase of both mass signals during deuteration. The small spectral shift relative to  $\text{H}_2$ -benzimidazole shows the small influence of deuteration on the electronic structure. The existence of two different electronic origins of the monodeuterated benzimidazole further proves that the absorbing species is the 1H,2H-tautomer, because the two monodeuterated H,D-tautomers would be identical. While a rapid  $\text{H} \leftrightarrow \text{D}$  exchange in 1-position seems to be easily explainable by the acidity of the NH group, the mechanism for the similarly rapid exchange at the 2-position (CH) is not so obvious.

In order to investigate this behavior, the TOF spectra of 1-methyl-benzimidazole have been taken at the mass trace 131 while flowing  $\text{D}_2\text{O}$  under the same experimental conditions as in the case of benzimidazole over the sample of 1-methyl-benzimidazole. If the  $\text{H} \leftrightarrow \text{D}$  exchange at the CH group was due to a direct deuteration mechanism, an equally rapid deuteration as in the case of benzimidazole would be expected. Only a very weak signal appears at the mass trace 132, which is due to 1-methyl-2-deutero-benzimidazole, showing that under comparable conditions to the benzimidazole case no (or only slow) direct deuteration takes place in the case of 1-methyl-benzimidazole.

Therefore we conclude that the deuteration in 2-position can be explained by a rapid tautomeric equilibrium (compare with Fig. 1a), which exchanges the hydrogen atoms of the NH and CH groups. The same mechanism is responsible for the rapid bideuteration of benzimidazole.



**Fig. 2.** R2PI spectra of the different isotopically substituted forms of the benzimidazole monomer. From top to bottom  $\text{H}_2$ -, H,D- and  $\text{D}_2$ -benzotriazole are shown. For the distinction of the two isomeric form of H, D-benzotriazole see text. The bands marked with \* are hot bands

**Table 1.** Electronic origins and spectral shifts of benzotriazole, benzimidazole and their water clusters

	Electronic origin / $\text{cm}^{-1}$	Spectral shift / $\text{cm}^{-1}$
1H,2H-benzimidazole	36022.2	–
1H,2D-benzimidazole	36028.4	6.2
1D,2H-benzimidazole	36046.0	23.8
1D,2D-benzimidazole	36051.6	29.4
1H,2H-benzimidazole( $\text{H}_2\text{O}$ ) <sub>1</sub>	35951.8	–70.4
2H-benzotriazole	34917.8	–
2D-benzotriazole	34971.5	53.7
2H-benzotriazole( $\text{H}_2\text{O}$ ) <sub>1</sub>	35039.2	121.4
2H-benzotriazole( $\text{H}_2\text{O}$ ) <sub>2</sub>	35049.3	131.5
2H-benzotriazole( $\text{H}_2\text{O}$ ) <sub>3</sub>	35071.0	153.2

The tautomerism between 1H,2H- and 2H,2H-benzimidazole, which interconverts the aromatic and orthoquinoidal forms is equivalent to the tautomerism of benzotriazole, which has been studied extensively in the gas phase [1, 2, 9–11, 13, 14]. Up to now, we have not observed the electronic origins of the 1H-tautomer of benzotriazole and of the 2H,2H-tautomer of benzimidazole. Both might be spectrally shifted outside the observed range.

**Table 2.** Stabilization energies of 1H,2H-, 2H,2H- and 1H,3H-benzimidazole, calculated at the HF/6-31G(d,p) and MP2/6-31G(d,p) level of theory including ZPE corrections

	HF			MP2		
	Energy / hartree	ZPE / hartree	$\Delta E$ / kJ/mol	Energy / hartree	ZPE / hartree	$\Delta E$ / kJ/mol
1H, 2H-BI	-377.48878	0.12717	0	-378.72953	0.11860	0
2H, 2H-BI	-377.44025	0.12639	125.3	-378.67778	0.11691	131.4
1H, 3H-BI	-377.45330	0.12729	93.5	-378.68133	0.11912	127.9

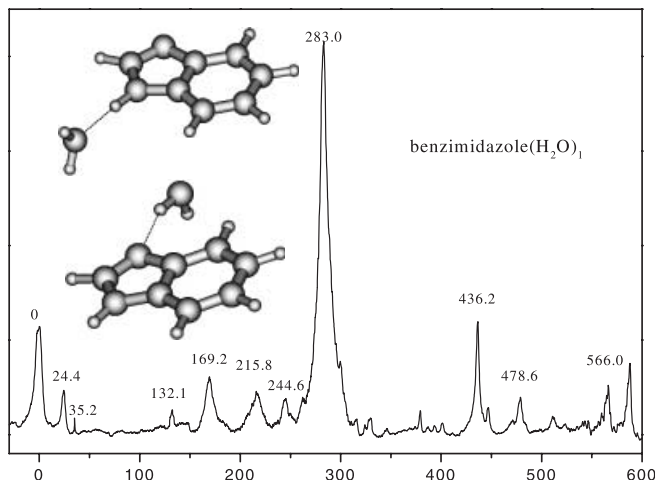
**Table 3.** Experimental  $S_1$  vibronic frequencies ( $\text{cm}^{-1}$ ) of 1H,2H-benzimidazole compared to calculated harmonic vibrational frequencies at the HF/6-31G(d,p) and MP2/6-31G(d,p) level of theory

Experiment Relative frequency	Assignment	harm. freq.	
		HF	MP2
0	origin	0	0
237.2	“butterfly”	244.4	212.5
303.6	“twist”	279.6	232.4
371.4	$N_{\text{inv}}$	447.6	352.8
398.6	“cogwheel”	448.1	397.6

Table 2 gives the stabilities of three benzimidazole tautomers, namely the benzenoid 1H,2H-, the ortho-quinoidal 2H, 2H- and the carbenoid 1H, 3H-tautomer, calculated at the HF and MP2/6-31G(d,p) level of theory, including ZPE corrections. The 1H,2H-benzimidazole has been found to be the most stable tautomer. The other two tautomers are between 90 and 130 kJ/mol higher in energy, depending on the method. Table 3 presents the lowest vibronic frequencies of 1H, 2H-benzimidazole, which can be attributed to mutual ring motions and to the N(1) inversion vibration, together with the theoretical frequencies of an ab initio normal mode analysis for the 1H,2H-tautomer.

### 3.2 Benzimidazole–water clusters

Figure 3 shows the R2PI spectrum of the binary benzimidazole–water cluster. The electronic origin at  $35951.8 \text{ cm}^{-1}$  is redshifted by  $70.4 \text{ cm}^{-1}$  with respect to the origin of the monomer. This shows a stabilization of the cluster in the electronically excited state compared to the ground state. Due to the small spectral shift relative to the origin of the monomer, we conclude that the water cluster is formed via the 1H,2H-tautomer. Several positions at the benzimidazole monomer are conceivable, where the water moiety may attach. Geometry optimizations at the MP2/6-31G(d,p) level showed two stable structures for the binary water cluster. The water moiety might be bound linearly to the  $-\text{NH}$  group, which acts as proton donor, or to the N(3)-atom, which acts as proton acceptor. No stable geometries of the water moiety bound to the  $-\text{CH}$  group of the five-membered ring (acting as proton donor), nor stable  $\pi$ -bonded structures (via the



**Fig. 3.** R2PI spectrum of the benzimidazole–water cluster in the region of the intermolecular vibrations. The inset shows the two most stable cluster structures, cf. Table 4

five- and six-membered ring, respectively) could be obtained. Table 4 presents the absolute and relative stabilities of both conformers including BSSE and ZPE corrections. The conformer in which the water moiety acts as proton acceptor is found to be stabilized by  $370 \text{ cm}^{-1}$  with respect to the other conformer. This difference is too small to conclude finally which of these conformers is the observed one. Schoonen et al. gave a value of  $117 \text{ cm}^{-1}$  for the energy difference using the larger 6-31++G(d,p) basis set [6]. Table 5 gives the calculated vibrational frequencies of both conformers of benzimidazole( $\text{H}_2\text{O}$ )<sub>1</sub> in the region of the intermolecular vibrations compared to the experimental  $S_1$  vibronic frequencies. The intermolecular vibrational frequencies which are calculated for the proton donating benzimidazole are in much better agreement than for the proton accepting benzimidazole. From this comparison it seems to be clear that the R2PI spectrum is due to the cluster with 1H,2H-benzimidazole acting as proton donor. The forms of the intermolecular vibrational modes of benzimidazole( $\text{H}_2\text{O}$ )<sub>1</sub> are very similar to those of the phenol( $\text{H}_2\text{O}$ )<sub>1</sub> cluster. Therefore we adopted the nomenclature for the intermolecular vibrations of Schütz et al. [20]. As in the case of the phenol–water cluster, three

**Table 4.** Absolute and relative stabilization energies of 1H,2H-benzimidazole( $\text{H}_2\text{O}$ )<sub>1</sub> clusters at the MP2/6-31G(d,p)//HF/6-31G(d,p) level. Both  $D_e$  and  $D_0$  include corrections for the BSSE

geometry	SCF energy / hartree	MP2 corr. <sup>a</sup> / hartree	$D_e$ / kJ/mol	ZPE / hartree	$D_0$ / kJ/mol
1H, 2H-BI( $\text{H}_2\text{O}$ ) <sub>1</sub>					
BI proton donor	-453.52292	-0.00404	-35.3	0.15245	-29.8
BI proton acceptor	-453.52319	-0.00499	-34.0	0.15363	-25.4

<sup>a</sup> The stabilization energies at fully optimized MP2/6-31G(d,p) level are  $-454.96317$  and  $-454.96464$  hartree for donor and acceptor cluster, respectively

**Table 5.** Experimental vibrational frequencies ( $\text{cm}^{-1}$ ) of the 1H,2H-benzimidazole( $\text{H}_2\text{O}$ )<sub>1</sub> cluster in the  $S_1$ -state compared to calculated harmonic vibrational frequencies of both stable conformers. The assignment, given in the table is valid for the 1H,2H-benzimidazole( $\text{H}_2\text{O}$ )<sub>1</sub>-cluster in which benzimidazole acts as proton donor. The form of the vibrational modes of the other conformer differ considerably and cannot be described in terms of the used notation

Experiment rel. freq.	Assignment	BI proton donor HF/6-31G(d,p)	BI proton acceptor HF/6-31G(d,p)
0	origin	0	0
24.4	$\varrho_1$	20.7	44.4
35.2	$\beta_1$	38.9	65.5
–	$\tau$	104.0	135.3
–	$\beta_2$	116.4	183.4
132.1	$\sigma$	137.8	244.1
169.2	$\sigma + \beta_1$		
215.8	$\varrho_2$	218.4	273.3
244.6	“butterfly”	252.9	312.7
283.0	“twist”	285.9	448.6
436.2	“cogwheel”	451.1	636.9
478.6	ring oop	475.8	
566.0	6a	590.9	
587.8	6a + $\varrho_1$		

of the vibrations are of rotational parentage of the water moiety ( $\beta_2$ ,  $\tau$ ,  $\varrho_2$ ), while the others are of translational parentage ( $\beta_1$ ,  $\varrho_1$ ,  $\sigma$ ). The agreement between the calculated harmonic and the experimental intermolecular vibrational frequencies is satisfactory. The vibronic assignment, which is given in Table 5 refers to the most stable conformer. The vibrational frequencies of the other conformer are given just for comparison and do not match the assignments due to their different nature. Nevertheless it cannot be excluded that some of the observed vibronic bands are due to the other conformer. We will clarify this point in the future using IR-UV double-resonance spectroscopy in the range of the OH and NH stretching vibrations for both the benzotriazole and benzimidazole clusters.

The next three vibrations at 244.6, 283.0 and 436.2  $\text{cm}^{-1}$  can be assigned to intramolecular vibrations of the benzimidazole moiety and represent mutual ring motions (butterfly, twist and cogwheel), which are similar to the monomer frequencies. The band at 478.6  $\text{cm}^{-1}$  represents an out-of-plane motion mainly located in the benzenoid ring. The vibrational transition at 566  $\text{cm}^{-1}$  can be attributed to the in-plane 6a vibration of the benzene ring.

In the electronic spectrum of the binary water cluster we found no indication of bands due to the second conformer. This conformer, in which benzimidazole acts as proton acceptor, has been identified by Schoonen et al., using matrix-isolation FT-IR spectroscopy [6]. Under supersonic jet conditions this conformer appears not to be formed, or its absorption is shifted outside the observed region. This, however, seems unlikely, because spectral shifts due to different binding sites in hydrogen-bonded clusters are in the range of some 100 wavenumbers.

### 3.3 Benzotriazole

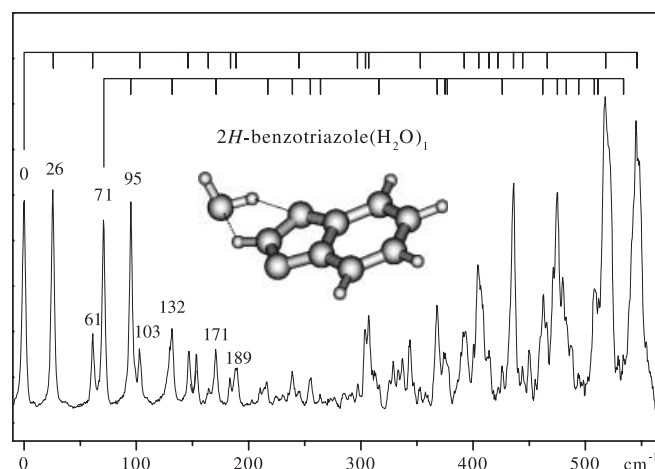
The vibrations and the tautomeric equilibrium between the 1H- and 2H-benzotriazole monomer has been studied in detail in two preceding publications [1, 10]. Thus we will only

briefly recall the relevant results. The two different tautomeric forms of benzotriazole are shown in Fig. 1. From a temperature-dependent FTIR study, the 1H-tautomer has been found to be stabilized by 417  $\text{cm}^{-1}$  with respect to the 2H-tautomer [1]. The energetic order of the two tautomers could be reproduced satisfactory at the CCSD and CCSD(T) level of theory. Nearly independent of the method and basis set used, the ZPE of 2H-benzotriazole is about  $230 \pm 20 \text{ cm}^{-1}$  larger than that of 1H-benzotriazole. Using this approximation for the ZPE, a value of  $D_0$  of approximately 430 and 180  $\text{cm}^{-1}$  for CCSD and CCSD(T), respectively, has been obtained.

A UV-UV double-resonance spectrum in a molecular beam has been taken in order to prove that all transitions in the absorption spectrum of benzotriazole belong to one species. This has shown to be the 2H-tautomer by a rotationally resolved LIF spectrum by Berden et al. [9]. A thorough search of 2000  $\text{cm}^{-1}$  to the red and 4000  $\text{cm}^{-1}$  to the blue of the electronic origin of 2H-benzotriazole gave no additional bands, which could be assigned to the second tautomer.

### 3.4 Benzotriazole–water clusters

Figure 4 shows the R2PI spectrum of the benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> cluster. The electronic origin which is given in Table 1 is blueshifted with respect to the origin of the monomer by 121.4  $\text{cm}^{-1}$ . This shows a destabilization of the cluster in the  $S_1$ -state in contrast to the findings for the benzimidazole–water cluster. The electronic origins of benzotriazole( $\text{H}_2\text{O}$ )<sub>2,3</sub> also given in Table 1 are blueshifted by 131.5 and 153.2  $\text{cm}^{-1}$ , respectively. This similar blueshift points to structures for the higher clusters, which are related to the binary cluster. A UV-UV double-resonance spectrum has been taken for the benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> cluster which proves that all vibronic transitions in the R2PI spectrum belong to only one conformer of the benzotriazole–water cluster. Within 6000  $\text{cm}^{-1}$  in the monomer R2PI spectrum no bands could be found which belong to the water cluster of the 1H-tautomer. Therefore we conclude that the only slightly



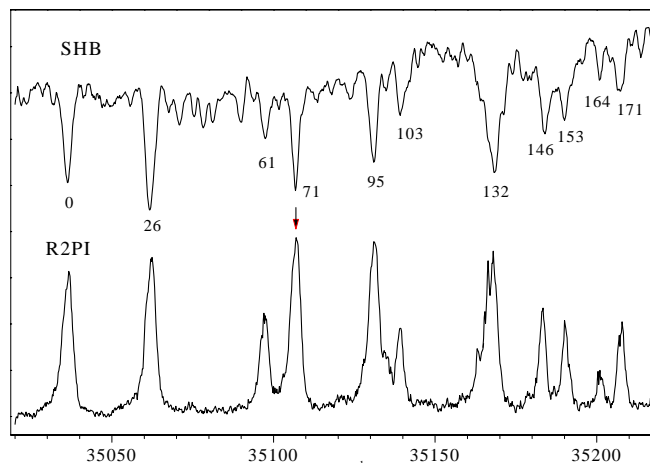
**Fig. 4.** R2PI spectrum of the binary benzotriazole–water cluster. The two band systems, which are 71  $\text{cm}^{-1}$  apart are marked by combs, indicating that they belong to one of the systems. The inset shows the most stable cluster structure

shifted origin of the benzotriazole–water spectrum belongs to the 2H-tautomer. The same holds true for the  $n = 2$  and 3 clusters.

A closer look to the R2PI spectrum of 2H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> reveals that it consists of two band systems, which are separated by only  $71\text{ cm}^{-1}$ . The UV–UV double-resonance spectrum (Fig. 5) clearly shows that both band-system origins and all observed bands belong to the same ground-state species. Therefore the existence of a tunneling splitting in the electronic ground state which might lead to the observed two nearly identical band systems can be ruled out. Nevertheless a splitting in the  $S_1$ -state cannot be ruled out to be responsible. In the following we will present an approach to explain a possible splitting in the  $S_1$ -state.

Due to the =N and NH functions in the five-membered ring of the 1H- and 2H-tautomer of benzotriazole, this molecule can act both as proton donor and acceptor in a hydrogen bond towards a water molecule. Furthermore, the water moiety can be bound via the  $\pi$ -electron cloud of the five- or six-membered ring [21].

A large variety of starting geometries have been chosen for the structure optimization covering all of the mentioned types of hydrogen bonding. The most stable ones are those with the benzotriazole moiety acting as proton donor. The calculations yield linear and  $\text{NH}\cdots\text{OH}\cdots\text{N}$  cyclic arrangements as nearly equally stable structures. At the HF level of theory, the linear structure of 2H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> is a first-order saddle point leading to the cyclic cluster geometry.

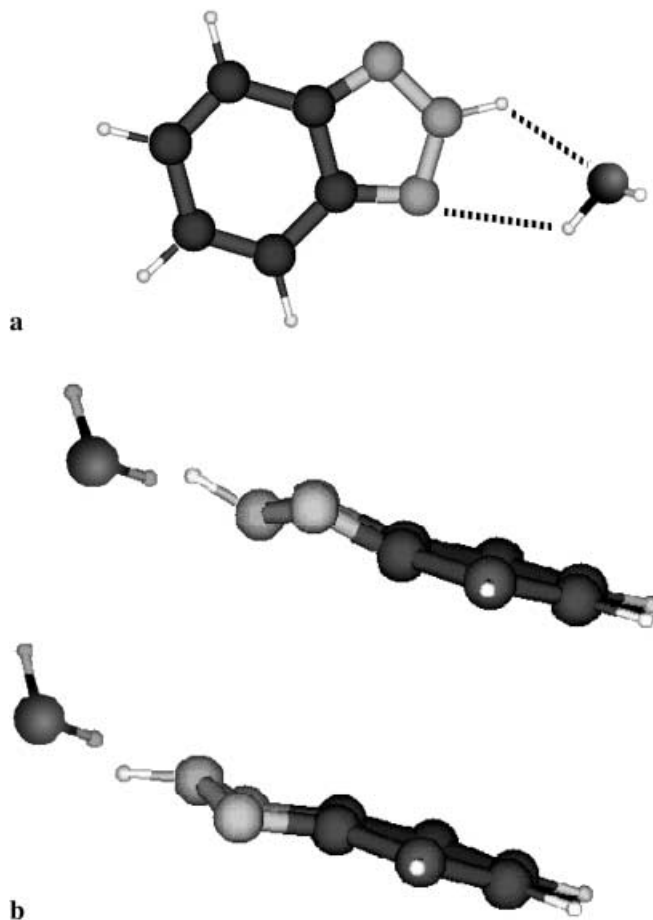


**Fig. 5.** UV–UV double-resonance spectrum of 1H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> (upper trace). The lower trace shows the respective R2PI spectrum of the cluster

**Table 6.** Absolute and relative stabilization energies of 1H- and 2H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> clusters. All calculations have been performed with the 6-31G(d,p) basis set. Both  $D_e$  and  $D_0$  include corrections for the BSSE

geometry	method	energy / hartree	$D_e$ / kJ/mol	ZPE / hartree	$D_0$ / kJ/mol
linear					
1H-BT( $\text{H}_2\text{O}$ ) <sub>1</sub>	HF	−469.46904	−26.9	0.14030	−20.3
2H-BT( $\text{H}_2\text{O}$ ) <sub>1</sub>	HF	−469.46473	−25.8	0.14109	−20.1
2H-BT( $\text{H}_2\text{O}$ ) <sub>1</sub>	MP2	−470.95171	−25.5	0.13168	−18.6
cyclic					
1H-BT( $\text{H}_2\text{O}$ ) <sub>1</sub>	HF	−469.46948	−25.9	0.14085	−17.8
2H-BT( $\text{H}_2\text{O}$ ) <sub>1</sub>	HF	−469.46536	−25.3	0.14183	−17.6
2H-BT( $\text{H}_2\text{O}$ ) <sub>1</sub>	MP2	−470.95305	−29.9	0.13229	−21.4

The discussion of the absolute and relative cluster stabilities is complicated by the difficulties arising from the calculated relative energies of the two tautomers as discussed in [1]. However, we believe that the relative stabilization energies of the 1H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> and 2H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> isomers calculated at the HF/6-31G(d,p) level of theory provide a good estimate. The calculated absolute and relative energies are given in Table 6. We also reoptimized the most stable linear and cyclic structures of the 2H-tautomer at the MP2/6-31G(d,p) level where the linear form turns out to be a true minimum energy of the potential energy surface. Including BSSE and ZPE corrections, the cyclic form of benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> could be shown to be



**Fig. 6.** **a** Most stable structure of the benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> cluster in the  $S_0$ -state. **b** The (uu) and (du) diastereomers of 2H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> in the  $S_1$ -state. The deviation from planarity is exaggerated in order to illustrate the diastereomeric forms more clearly

**Table 7.** Vibronic frequencies of the two band systems (b.s.) of 2H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub>, together with the calculated vibrational frequencies at the HF//6-31G(d,p) and MP2//6-31G(d,p) level of theory

b.s. 1	HF	MP2	ass.	b.s. 2	b.s. 2–71 cm <sup>-1</sup>
0	0	0	0,0	71	0
26	48	51	$\nu_1$	95	24
61	58	82	$\nu_2$	132	61
103			$2\nu_2$	171	100
146	155	164	$\nu_3$	217	146
164	175	217	$\nu_4$	239	168
184				255	184
190	237	220	$\nu_5$	264	193
245				316	245
304	292	256	$\nu_6$	375	304
307				377	306
392				462	391
405				475	404
414				483	412
422				494	423
436				508	437
444				511	440
466				534	463
518	585		6a	590	519
546				614	543
578				650	579

the most stable structure in the electronic ground state. It is shown in Fig. 6a.

Geometry optimizations at the CIS level with the 6-311G(d,p) basis set predict a nonplanar geometry of the benzotriazole monomer [22, 23] in the  $S_1$ -state, which is in accordance with the larger inertial defect in the electronically excited state, as obtained by Berden et al. [9]. The N(2) atom of benzotriazole (compare with Fig. 1b) is shifted out of the aromatic plane. Thus the hydrogen atom of the -NH group also points out of the plane. The position above or below the aromatic plane leads to indistinguishable structures which are converted into each other via the inversion vibration at N(2). They represent enantiomers, and are thus of equal energy. In the case of the benzotriazole–water cluster the free (not hydrogen-bonded) H-atom of the water moiety points out of the plane defined by the aromatic system. Therefore we have two distinguishable structures with different energies in the  $S_1$ -state of the benzotriazole–water cluster. In one of them both hydrogen atoms point upwards (uu). In the other structure one points upwards and the other downwards (ud). In the electronic ground state these structures are identical due to the planarity of the aromatic system.

The splitting in the excitation spectrum could thus be explained by transitions to two different  $S_1$ -states which differ only slightly in their geometry. This leads to very similar vibrational frequencies and intensities of both band systems. The latter can be explained by the very small geometry change, which leads to similar Franck–Condon factors for both transitions. Table 7 compares the experimental and theoretical vibrational frequencies of the most stable cyclic 2H-benzotriazole( $\text{H}_2\text{O}$ )<sub>1</sub> cluster.

The origins of the  $n = 2$  and 3 cluster are shifted by only some wavenumbers to higher energy compared to  $n = 1$ , which points to similar structures. Nevertheless, the assumption of cyclic structures for these clusters, in which the water bridge between N(1)-H and N(2) is less strained has to be supported by further experiments and calculations.

## 4 Conclusions

The benzimidazole monomer exhibits a tautomerism, which leads to corresponding tautomers as in the case of benzotriazole. Whereas the electronic spectrum of benzotriazole around 285 nm could be attributed to the ortho-quinoidal 2H-tautomer, the absorption of benzimidazole around 278 nm is due to the benzenoid 1H, 2H-benzimidazole. Nevertheless we could show that the ortho-quinoidal tautomer plays an important role in the tautomerism of benzimidazole.

Whereas the binary water cluster in case of benzotriazole forms a cyclic arrangement with benzotriazole acting both as proton donor and acceptor, a linear geometry is found for the benzimidazole–water cluster, in which benzimidazole acts as proton donor. The comparably stable cluster in which benzimidazole acts as proton acceptor could be ruled out by comparison of the vibronic frequencies. No indication for a stable conformer with a bridging water moiety could be found for benzimidazole.

*Acknowledgements.* We would like to thank Professor Kleineremanns for his continuous support, for his steady interest in this work and for many helpful discussions. We thank the Deutsche Forschungsgemeinschaft for financial support of this work.

## References

1. W. Roth, D. Spangenberg, C. Janzen, A. Westphal, M. Schmitt: *Chem. Phys.* **248**, 17 (1999)
2. E. Jalviste, A. Treshchalov: *Chem. Phys.* **172**, 325 (1993)
3. B. Velino, A. Trombetti, E. Cané: *J. Mol. Spec.* **152**, 434 (1992)
4. E. Cané, A. Trombetti, B. Velino, W. Caminati: *J. Mol. Spec.* **150**, 222 (1991)
5. G. Berden, W.L. Meerts, E. Jalviste: *J. Chem. Phys.* **103**, 9596 (1995)
6. K. Schoone, J. Smets, L. Houben, M.K.V. Bael, L. Adamowicz, G. Maes: *J. Phys. Chem.* **102**, 4863 (1998)
7. B. Velino, E. Cané, L. Gagliardi, A. Trombetti, W. Caminati: *J. Mol. Spec.* **161**, 136 (1993)
8. F. Negri, W. Caminati: *Chem. Phys. Lett.* **260**, 119 (1996)
9. G. Berden, E. Jalviste, W.L. Meerts: *Chem. Phys. Lett.* **226**, 305 (1994)
10. W. Roth, C. Jacoby, A. Westphal, M. Schmitt: *J. Phys. Chem. A* **102**, 3048 (1998)
11. G. Fischer, X. Cao, R.L. Purchase: *Chem. Phys. Lett.* **262**, 689 (1996)
12. A. Bigotto, A.N. Pandey, C. Zerbo: *Spect. Lett.* **29**, 511 (1996)
13. J. Catalán, P. Pérez, J. Elguero: *J. Org. Chem.* **58**, 5276 (1993)
14. F. Tomás, J. Catalán, P. Pérez, J. Elguero: *J. Org. Chem.* **59**, 2799 (1994)
15. C. Jacoby, P. Hering, M. Schmitt, W. Roth, K. Kleineremanns: *Chem. Phys.* **239**, 23 (1998)
16. M. Schmitt, C. Jacoby, K. Kleineremanns: *J. Chem. Phys.* **108**, 4486 (1998)
17. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople: *Gaussian 98, Revision A.7.* (Gaussian, Inc., Pittsburgh, PA 1998)
18. A.P. Scott, L. Radom: *J. Phys. Chem.* **100**, 16502 (1996)
19. S.F. Boys, F. Bernardi: *Mol. Phys.* **19**, 553 (1970)
20. M. Schütz, T. Bürgi, S. Leutwyler: *J. Mol. Struct.* **276**, 117 (1992)
21. T.M. Korter, J. Küpper, D.W. Pratt: *J. Chem. Phys.* **111**, 3946 (1999)
22. W. Roth: Ph.D. thesis, Heinrich-Heine-Universität Düsseldorf, 1998
23. P. Imhof, W. Roth, M. Schmitt: (2000) manuscript in preparation