

The relative stabilities of benzotriazole tautomers determined by a rotational band contour analysis of the N–H stretching vibration

W. Roth¹, D. Spangenberg, Ch. Janzen, A. Westphal, M. Schmitt²

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

Received 14 June 1999

Abstract

The FTIR spectrum of the N–H stretching vibration of 1*H*- and 2*H*-benzotriazole (BT) has been measured in the gas phase in the region between 3440 cm⁻¹ and 3540 cm⁻¹ at six different temperatures. From the deconvolution of the partially resolved rotational band contours the contribution of the two tautomers of BT at each temperature is derived. From this temperature dependency the 1*H*-tautomer could be determined to be stabilized by 417 cm⁻¹ (5 kJ/mol) with respect to the 2*H*-tautomer. This experimental value is compared to results of ab initio calculations on the Hartree–Fock, second order Møller–Plesset and coupled cluster level of theory as well as to different density functional methods. It will be pointed out that the correct order of energies can only be obtained if electron correlation and zero point energy correction is taken into account in the ab initio calculations. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Benzotriazole has been subject to a variety of spectroscopical investigations during the last few years. Ab initio calculations on various levels of theory have been performed parallel to these investigations to interpret the experimental results. It is to be noted that both tautomers of BT, which are shown in Fig. 1, have not been observed simultaneously until now in a single experiment, thus allowing an unequivocal assignment.

The 1*H*-tautomer has been found to be the only stable isomer in the solid state by X-ray crystallography [1]. Infrared spectra of BT in the solid state

could also be assigned to this tautomer [2,3]. Furthermore BT was examined by microwave spectroscopy both in a gas cell [4] and in a molecular beam [5]. The rotational constants showed clearly that only microwave transitions due to the 1*H*-tautomer were observed.

In contrast to these findings, the vibrationless $S_1 \leftarrow S_0$ transition of BT at 34920 cm⁻¹, which had been observed first by Jalviste et al. [6] could unambiguously be attributed to the 2*H*-tautomer using rotationally resolved LIF spectroscopy [7]. The dispersed fluorescence spectra of benzotriazole taken after resonant excitation of the electronic origin, as well as of several vibronic bands could be assigned to be due to the 2*H*-tautomer of BT [8]. FTIR spectra in a molecular beam taken in the range between 650 and 1700 cm⁻¹ showed vibrational bands, which also could be attributed to the 2*H*-tautomer of BT [3].

¹ Present address: University of Leeds, School of Chemistry, Leeds LS2 9JT, UK.

² Corresponding author.

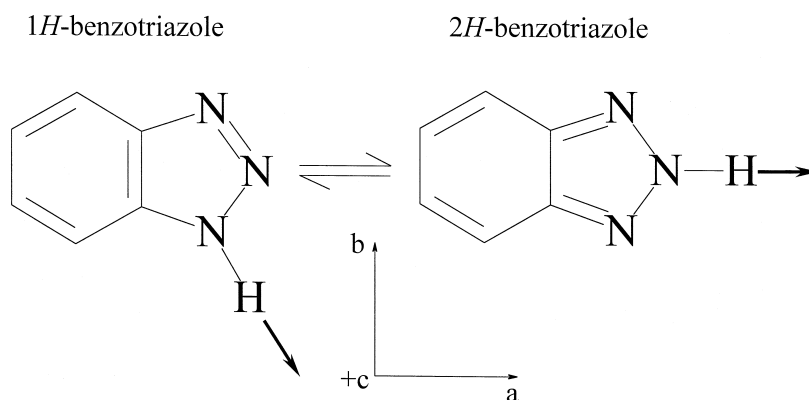


Fig. 1. Structures of 1*H*- and 2*H*-benzotriazole together with the displacement vectors for the N–H stretching vibration (indicated by arrows) for 1*H*- (a) and 2*H*-benzotriazole (b). The inset shows the in-plane inertial axes of 2*H*-BT. The inertial axis system of 1*H*-BT is only slightly rotated clockwise about the inertial *c*-axis of 2*H*-BT.

These apparently contradictory results for the gas phase experiments can be explained straightforwardly by the small dipole moment which prevents 2*H*-BT to be detected in the microwave experiments. The UV spectra of BT could be interpreted in terms of only one tautomer (2*H*-BT) absorbing in the observed spectral range. This might be due to a large spectral shift of the other tautomer or to a very small oscillator strength of the 1*H*-tautomer.

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 2*H*-BT are present in the gas phase at 90 °C [9,10]. Their calculations showed the 2*H*-tautomer to be 1330 cm^{-1} more stable than the 1*H*-tautomer. While HF calculations predict the 1*H*-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 [10]. At the MP2/6-31G(d,p) level of theory, the stabilization energy of 2*H*-BT is calculated to be 880 cm^{-1} .

The objective of this investigation is to elucidate the energetical order of the isolated benzotriazole tautomers and to evaluate their energy difference from the FTIR spectra of the N–H stretching vibration and from *ab initio* calculations.

2. Computational results

All *ab initio* calculations were performed using the Gaussian 94 program package [11]. The SCF

Table 1

Comparison of experimental and calculated rotational constants for 1*H*- and 2*H*-BT. The experimental rotational constants for the 1*H*-BT have been taken from the microwave results of Negri and Caminati [5] and for the 2*H*-tautomer from the rotationally resolved LIF-spectra of Berden et al. [7]

	1 <i>H</i> -BT						2 <i>H</i> -BT					
	A		B		C		A		B		C	
	MHz	%	MHz	%	MHz	%	MHz	%	MHz	%	MHz	%
Experiment	4008.166		1676.357		1182.201		3976.0		1699.2		1190.9	
B3LYP/6-311G(d,p)	4026.8	0.5	1675.8	−0.1	1183.3	0.1	3991.3	0.5	1700.8	−0.1	1192.6	0.1
MP2/6-311G(d,p)	3987.1	−0.5	1671.7	−0.3	1177.9	−0.4	3961.7	−0.5	1691.6	−0.3	1185.4	−0.4



Fig. 2. Relative ab initio stabilization energies of $1H$ - and $2H$ -BT for different methods (HF, B3LYP, BLYP, SVWN, MP2) and different basis sets. Up to the MP2 level the stabilization of $2H$ -BT relative to $1H$ -BT increases, while with increasing basis set the $1H$ -tautomer is favoured. The pure electronic stabilization energy ΔD_e is designated with $-$, the ZPE corrected value ΔD_0 with \diamond .

convergence criterion used for our calculations was 10^{-8} Hartree, while the convergence criterion for the gradient optimization of the molecular geometry was 1.5×10^{-5} Hartree/Bohr and 1.5×10^{-5} Hartree/degrees, respectively. The minimum energy structures for $1H$ - and $2H$ -BT were calculated at the HF and MP2 level and using different DFT functionals such as BLYP [12], B3LYP [13], BPW91 [14] and SVWN [15]. We used Pople's split valence basis

sets (4-31G(d), 6-31G(d,p), 6-311G(d,p)) as well as Dunning's basis sets of double and triple zeta quality [16]. The comparison of rotational constants obtained from the optimized geometries with the experimental ones from microwave ($1H$) and high resolution LIF spectroscopy ($2H$) can be regarded as a preliminary check. For the B3LYP/6-311G(d,p) and MP2/6-311G(d,p) structures deviations smaller than 0.5% are found as shown in Table 1. The electronic stabi-

Table 2

Absolute and relative ab initio stabilization energies of $1H$ - and $2H$ -BT obtained at different levels of theory with the 6-311G(d,p) basis set

	Absolute energies [au]		Relative energies: $1H$ - $2H$ [cm^{-1}]				
	$1H$ -BT	$2H$ -BT	ΔD_e	ΔZPE	ΔD_0	ΔH^\ominus	ΔG^\ominus
HF/6-311G(d,p)	-393.508441	-393.505022	-750	-243	-994	-964	-1008
B3LYP/6-311G(d,p)	-395.963528	-395.963858	72	-217	-145	-108	-315
BLYP/6-311G(d,p)	-395.839930	-395.840664	161	-230	-69	-28	-240
MP2/6-311G(d,p)	-394.841341	-394.845706	958	-214	744	788	567
HF/6-311G(d,p)//MP2/6-311G(d,p)	-393.425946	-393.420581	-1178				
MP4(SDQ)/6-311G(d,p)//MP2/6-311G(d,p)	-394.734878	-394.734153	-159				
CCSD/6-311G(d,p)//MP2/6-311G(d,p)	-394.734898	-394.734160	-162				
CCSD(T)/6-311G(d,p)//MP2/6-311G(d,p)	-394.797675	-394.797911	52				
B3LYP/6-311G(d,p)//MP2/6-311G(d,p)	-395.962713	-395.963052	74				

lization energy D_e is calculated as the difference between the absolute energies of the $1H$ - and $2H$ -tautomer.

The results of these calculations are compiled in Fig. 2. They can be summarized as follows: Fully optimized calculations at the Hartree–Fock level distinctly favor the $1H$ -tautomer by more than 1000 cm^{-1} above the $2H$ -tautomer, while calculations at MP2 level show the $2H$ -tautomer to be stabilized by approximately the same amount of energy. All density functionals which have been tested show an intermediate behavior with respect to the relative energies of $1H$ - and $2H$ -BT. Increasing the basis set for each method stabilizes the $1H$ -tautomer.

Using the optimized structures, the unscaled zero point energy (ZPE) contribution was calculated through normal mode analysis using analytical gradients. Scaling factors as proposed by Scott and Radom [17] change the relative energies of the tautomers only by a few wavenumbers and do not lead to a change in the relative stability of the tautomers. We find that nearly independent to the method and basis set, the ZPE energy of $1H$ -tautomer is about $230 \pm 20\text{ cm}^{-1}$ smaller than that of the $2H$ -tautomer, thus leading to a stabilization of the $1H$ -BT structure.

Because of the contradictory results of the ab initio calculations performed so far concerning the relative energies of the 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)). The results for the 6-311G(d,p) basis set are given in Table 2. The corresponding B3LYP energy has also been calculated for comparison with the optimized geometry in that table. It is obvious, that the coupled cluster energies resemble

the small energy gap between the two isomers as found by the DFT methods. But even these calculations did not lead to a final statement as the order in energy of $1H$ - and $2H$ -BT changes between CCSD where the $1H$ -tautomer is more stable by 162 cm^{-1} and CCSD(T) which favors $2H$ -BT by 52 cm^{-1} . However, inclusion of the zero point energy calculated at lower levels of theory, which has been found to be nearly independent of the method employed shows that the $1H$ -tautomer is the more stable one. We find a D_0 of approximately 430 and 180 cm^{-1} for CCSD and CCSD(T) respectively.

The harmonic frequencies of the N–H stretching vibrations have been calculated at various levels of theory. All results agree that the vibration of the $1H$ -tautomer is found at higher energy than for $2H$ -BT, cf. Table 3. We already reported that the MP2/6-311G(d,p) yield vibrational frequencies which are in very good agreement with the experimental frequencies of $2H$ -BT from our DF spectra [8]. Thus all calculated values are given unscaled and the ratio $\nu_{\text{calc}}/\nu_{\text{exp}}$ is presented instead.

3. Experimental results and discussion

The FTIR spectra of benzotriazole have been recorded using a commercial Perkin Elmer Paragon 1000 spectrometer. The sample was heated from 115°C up to 230°C in a homebuilt vacuum absorption cell with a sample path of 10 cm , which is sealed with NaCl windows. Heating of the absorption cell was performed by means of heating resistors, which are screwed directly to the window holders, in order to keep the windows at a slightly higher temperature than the cell to avoid condensation of the sample. Below 115°C the partial pressure of benzotriazole was too small to obtain reliable results. A spectral resolution of $\approx 1\text{ cm}^{-1}$ was achieved using a 4 mm Jacquinot aperture and a weak Norton-Beer apodization. Benzotriazole (98%, Janssen Chimica) has been used without further purification. The deuterated isotopomer was produced by stirring 5 g of benzotriazole with $10\text{ ml D}_2\text{O}$, evaporating the excess D_2O under reduced pressure and repeating this process for two times.

The FTIR spectrum of gaseous benzotriazole at a temperature of 400 K in the region of the N–H stretching vibration is shown in Fig. 3. Obviously the

Table 3

Experimental and calculated vibrational frequencies for the N–H stretch vibration of $1H$ -BT and $2H$ -BT and their deuterated isotopomers.

	Exp.	MP2	exp/calc	B3LYP	exp/calc
$1H$ -BT	3511	3681	0.954	3661	0.959
$2H$ -BT	3489	3649	0.956	3637	0.959
$1D$ -BT	2617	2706	0.967	2691	0.973
$2D$ -BT	2601	2684	0.969	2674	0.973

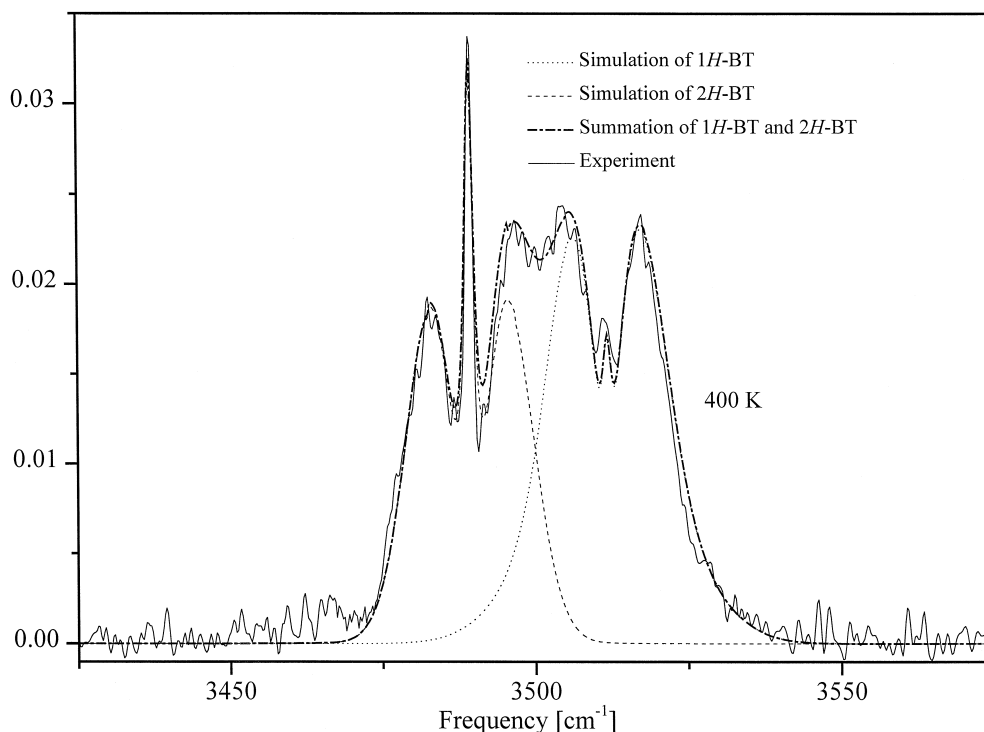


Fig. 3. FTIR spectrum of N–H stretching vibrations of benzotriazole in the gas phase at 400 K together with a simulation of the N–H stretch vibrations of both tautomers and their superposition.

overall contour is due to more than one single vibrational transition. In the following we will show that this band can be explained by partially overlapping N–H stretching vibrations of the two tautomers of benzotriazole. It is known that benzotriazole decomposes at higher temperatures, therefore it has to be shown at first that the observed spectral features are due to a two component mixture, namely the two isomers of benzotriazole

We determined the number of components which contribute to the N–H stretch vibration region by means of a factor analytical approach. The temperature series of our IR absorbance measurements can be represented by a $n_w \times n_T$ absorbance data matrix \mathbf{A} . Here n_w denotes the number of data points of the observed spectral region and n_T the number of spectra recorded at different temperatures. Under the assumption of Lambert-Beer's generalized law for unit path length this data matrix can be described by the matrix equation

$$\mathbf{A} = \mathbf{E}\mathbf{C} + \boldsymbol{\varepsilon} = \mathbf{A}^* + \boldsymbol{\varepsilon} \quad (1)$$

where \mathbf{E} is the $n_w \times n_c$ matrix of molar absorptivi-

ties of the n_c components which absorb in the chosen spectral range, \mathbf{C} is the $n_c \times n_T$ concentration matrix, $\boldsymbol{\varepsilon}$ is a $n_w \times n_T$ matrix of random measurement errors, and \mathbf{A}^* is the $n_w \times n_T$ matrix of absorbance data free of error. Basic matrix algebra shows that the rank of the idealized matrix \mathbf{A}^* is obtained from the equation

$$\begin{aligned} \text{rank}(\mathbf{A}^*) \\ = \min\{\text{rank}(\mathbf{E}), \text{rank}(\mathbf{C})\} \leq \min\{n_w, n_c, n_T\} \end{aligned} \quad (2)$$

Under the experimental conditions where $n_w > n_c$ and $n_T > n_c$, it can be shown that the rank of the matrix \mathbf{A}^* is equal to n_c provided that the spectrum of one of the individual components is not a linear combination of the other components and that the concentration of one or more species cannot be expressed as a linear combination of the other components for all experiments performed, [18,19]. The rank of the matrix \mathbf{A}^* can be calculated by an

eigenvalue-eigenvector decomposition of the covariance matrix $\mathbf{B}^* = \mathbf{A}^{*T}\mathbf{A}^*$. The symmetric $n_T \times n_T$ matrix \mathbf{B}^* with $\text{rank}(\mathbf{B}^*) = \text{rank}(\mathbf{A}^*)$ can be expressed in terms of $\text{rank}(\mathbf{B}^*)$ positive eigenvalues and eigenvectors as $\mathbf{B}^* = \mathbf{X}^T\mathbf{\Lambda}\mathbf{X}$ where \mathbf{X} is the orthogonal matrix of all eigenvectors and $\mathbf{\Lambda}$ is the diagonal matrix of eigenvalues. Thus the calculation of the number of nonzero eigenvalues of \mathbf{B}^* should provide the number of components n_c . However, because of experimental errors (e.g. noise), the corresponding rank of the experimental matrices \mathbf{A} and \mathbf{B} is $\min\{n_T, n_w\}$. Malinowski [20] showed that these extra eigenvalues are composed solely of experimental error and that the removal of this group of eigenvalues will lead to overall improvement of data reproduction. There exist different statistical criteria, to decide which of the eigenvalues belong to the primary group which contain some error embedded with the true factors and which of them belong to the second group. The first kind of criteria depends on a relatively precise knowledge of the experimental error, for example by estimating the standard deviation of all eigenvalues [19]. The second kind of criteria does not depend of this knowledge, for example the imbedded error function of Malinowski [21]. Most of these criteria are monotonic functions of the number n of included eigenvalues to the primary set and show a more or less strong change when the number of primary factors is reached. We used two different criteria which do not depend on the knowledge of measurement error and have the additional advantage to deliver an extreme functional value when the last eigenvalue of the primary group is included. These are Malinowski's indicator function IND [21] and Malinowski's F -test [22]. While the IND function is an empirical function and gives a minimum value at $n = \text{rank}(\mathbf{A})$, the F -test is based on a statistical reasoning. It compares the last significant eigenvalue to the mean of the eigenvalues of the secondary set. Table 4 shows the six eigenvalues and the value of the IND function as well as the value of Malinowski's F -ratio compared to the F -value at a 95% significance level with 1 and $n_T - n$ degrees of freedom, where n is the number of the first n eigenvalues included in the primary set. The IND function has a minimum value at $n = 2$, while the F -test fails for $n > 2$ and thus both tests show clearly that there are only two linear independent factors responsible for

Table 4

Eigenvalues of the covariance matrix \mathbf{B}^* and values of Malinowski's indicator function as well as Malinowski's F -test

n	Eigenvalues	IND $\times 10^5$	F -ratio	$F_{1, n_T - n}(95\%)$
1	33.627833	16.4883	2470.79	6.60789
2	0.059042	10.48	26.2161	7.70865
3	0.003529	16.778	1.93238	10.128
4	0.003412	28.401	3.30032	18.5128
5	0.001470	86.3834	2.45904	161.448
6	0.000598	—	—	—

the development of the N–H stretch region in the temperature region between 386 and 503 K. We attribute these components to the 1*H*- and the 2*H*-tautomer of BT.

The change in dipole moment for the N–H stretching mode of 2*H*-BT is orientated parallel to the inertial a -axis (cf. Fig. 1) so that only a -type rotational transitions will be allowed for this tautomer. In the case of 1*H*-BT a hybrid a/b -type rotational band is expected, since the projection of the change in dipole moment for the N–H stretching mode has components both onto the inertial a - and b -axes. Our ab initio calculations evaluate the angle between the N–H bond (which represents the vibrational coordinate quite well) and the a -inertial axis to be around 70° . Therefore the N–H stretching vibration of the 1*H*-tautomer will primarily show a b -type rotational contour together with smaller a -type participation. An angle of 70° would result in an a/b -ratio of 12:88. We therefore assign the lower frequency component of the band which has a pure a -type contour, as to be due to the N–H stretching vibration of 2*H*-BT and the higher frequency component, which is obviously an a/b -hybrid to the 1*H*-BT N–H stretching mode. This assignment agrees with the calculated vibrational frequencies from the normal mode analysis, see Table 3.

We have simulated the rovibrational band contours using a rigid rotor Hamiltonian in order to obtain the exact vibrational frequencies for both N–H stretching vibrations and the relative proportion of both bands. The ground state rotational constants used in our simulation were taken from microwave measurements [5] for the 1*H*-tautomer and from high resolution laser induced fluorescence spectroscopy [7] for the 2*H*-tautomer. The effects of changes in rotational constants on the rovibrational band con-

tion upon vibrational excitation are negligible in our experiment for both the $1H$ -tautomer and the $2H$ -tautomer. The spin statistical weights used for the simulation of $2H$ -BT are 78 for ee and eo levels and 66 for oe and oo levels, respectively. For $1H$ -BT the spin statistical weights are 1 for all rotational levels. The experimental spectrum was simulated using a one temperature model for the population of the ground state levels. Due to the relatively high temperatures which had to be applied because of the low vapor pressure of benzotriazole, a J quantum number up to 250 had to be used in the simulation together with ΔK selection rules up to ± 3 and a very small cutoff value for the intensity calculation. The resulting stick spectrum which consisted of up to 10^6 lines was convoluted with a Lorentzian line-shape of 50 GHz FWHM.

The contour of the $2H$ -tautomer could be simulated with a pure a -type band, while for the $1H$ -tautomer an a/b -hybrid with 75% b - and 25% a -character had to be assumed which yields an angle of 60° between the direction of change of the dipole moment with the inertial a -axis. This value differs considerably from the 70° as obtained from the ab

initio calculations showing that the change in the dipole moment is not parallel to the N–H bond coordinate. The dashed and dotted traces in Fig. 3 present the simulation of the rovibrational contour of the N–H stretching vibrations for $1H$ -BT and $2H$ -BT, together with the superposition of both tautomers for direct comparison with the experimental spectrum. Using the parameters described above, the rotational contours at six different temperatures have been simulated, with the intensity ratio of the two vibrational bands as only free parameter for the simulation. Fig. 4 shows the experimental spectra between 386 and 503 K. It is obvious that the amount of $1H$ -BT decreases with increasing temperature, while the amount of $2H$ -BT increases, what shows unambiguously that the $1H$ -tautomer is the more stable one.

A least square fit of the intensities of the N–H stretching vibration of both tautomers to the experimental spectra yielded the relative intensities of both bands at six different temperatures (Table 5). Utilizing van't Hoff's isochore, a plot of $\ln(I_1/I_2)$ versus $1/T$ should yield a straight line with the slope $\Delta H^\ominus/R$, irrespective of the oscillator strengths of

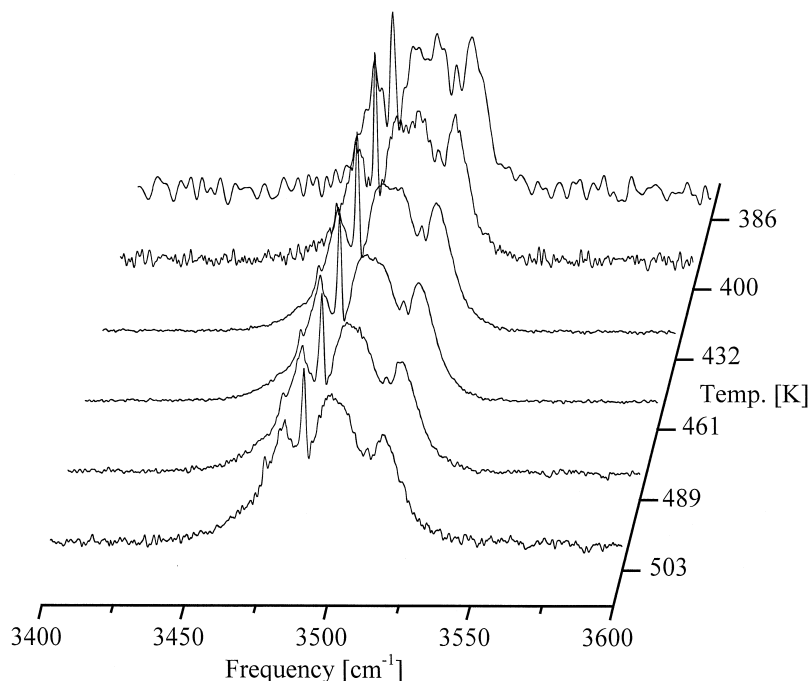


Fig. 4. FTIR spectra of N–H stretching vibrations of $1H$ - and $2H$ -benzotriazole in the gas phase at six different temperatures.

Table 5

Temperature dependence of the normalized IR intensities of 1*H*-BT and 2*H*-BT, obtained from a fit of the intensity ratio to the vibrational contour of the N–H stretching vibrations

Temperature [K]	Int.[1 <i>H</i> -BT]	Int.[2 <i>H</i> -BT]	T^{-1} [K $^{-1}$]
386	58.0	42.0	0.00259
400	56.9	43.1	0.00250
432	53.7	46.3	0.00231
461	51.9	48.1	0.00217
489	49.7	50.3	0.00204
503	49.3	50.7	0.00199

both tautomers, since each numerical factor, which takes into account a difference in oscillator strength between the two tautomers leads only to a shift parallel to the axis of ordinates. The same holds true for the different weights of the tautomers due to the fact that there exist two identical forms for the 1*H*-tautomer, and only one for 2*H*-BT. The linearity of the van't Hoff plot in the examined temperature range which is shown in Fig. 5 provides further evidence for the existence of a pure two component system without considerable decomposition at these temperatures. Evaluation of the slope yields a stabilization energy of the 1*H*- with respect to the 2*H*-

tautomer of 417 cm $^{-1}$ (5 kJ/mol). This value can be compared directly to the results of the ab initio calculations, presented above, keeping in mind that the calculations at highest level of theory, performed with the CCSD(T) method are single point calculations on MP2 optimized geometries, thus yielding no vibrational frequencies. Therefore neither ZPE corrections at this level of theory nor temperature corrections for the thermodynamic properties at higher temperatures could be performed. A rough estimation of the change in ΔH^\ominus between 298 and 450 K from ab initio calculations at the MP2 level of theory predicts a further stabilization of the 2*H*-tautomer of a few wavenumbers, which is well within the statistical error.

From the above presented analysis of the overall contour, the band centers of the N–H stretching vibrations of 2*H*-BT and 1*H*-BT could be determined to lie at 3489 and 3511 cm $^{-1}$, respectively. The corresponding values from the normal mode analysis on different levels of theory together with the ratios of experimental and theoretical frequencies together with the corresponding values for the deuterated isotopomers are presented in Table 3. The calculated vibrational frequencies in Table 3 are

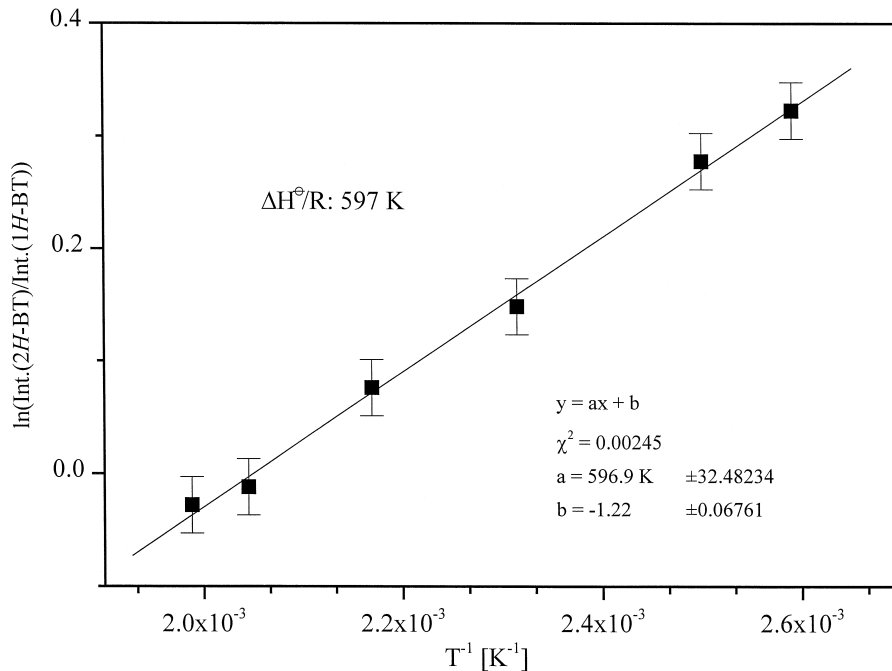


Fig. 5. Plot of $\ln\{\text{Int.}(1H\text{-BT})/\text{Int.}(2H\text{-BT})\}$ versus $1/T$ for six temperatures between 386 and 503 K.

unscaled, the ratio of experimental value to the calculated for the MP2 calculations is close to the recommended value [17] for the scaling factor for this method. This ratio is different for the deuterated (0.968) and the undeuterated species (0.955) which is a result of the very different reduced masses for this motion.

4. Conclusions

The N–H stretching vibration could be identified in the gas phase FT-IR spectrum for both *1H*- and *2H*-benzotriazole. The vibrational frequencies for the N–H stretching vibration of *2H*-BT could be determined experimentally to 3489 cm^{-1} , while the *1H*-tautomer has a slightly higher vibrational frequency of 3511 cm^{-1} in the gas phase. These values correspond well with the theoretical values which were obtained at the MP2 level of theory as well as with the B3LYP functional (cf. Table 3). From a rotational band contour analysis of the overlapping stretching vibrations the relative amount of each tautomer at six different temperatures could be determined. From this analysis the standard reaction enthalpy ΔH^\ominus , determined between 386 and 503 K, for the conversion of the *2H*-tautomer into the *1H*-tautomer was found to be $-417 \pm 25\text{ cm}^{-1}$, thus yielding the *1H*-tautomer the more stable one. The ab initio calculations of the relative stabilities and standard reaction enthalpies of the two tautomers yielded very different results, depending on the method used. Perturbation theory on the MP2 level with medium sized basis sets even leads to a reversed order of stability, while MP4, CCSD and CCSD(T) at least yield the correct energetic order. A good quantitative agreement with the experimental value could only be obtained on the highest level of theory and upon inclusion of zero point energy correction. Astonishingly all density functionals which have been tested to calculate the energy difference work pretty well and predict the *1H*-tautomer to be the more stable one. Also the vibrational frequencies could be predicted with nearly the same scaling factors to the experimental values compared to the much more CPU time demanding MP2 methods using the same basis sets.

Acknowledgements

We wish to thank Professor Kleinermanns for his steady interest in these investigations and helpful discussions and the Deutsche Forschungsgemeinschaft for financial support. W.R. would like to thank the Universitäts Rechenzentrum Düsseldorf and the Regionales Rechenzentrum der Universität zu Köln for the granted computer time.

References

- [1] P. Escande, J. Galigne, J. Lapasset, *Acta Cryst. B* 30 (1974) 1490.
- [2] A. Bigotto, A. Pandey, C. Zerbo, *Spect. Lett.* 29 (1996) 511.
- [3] G. Fischer, X. Cao, R. Purchase, *Chem. Phys. Lett.* 262 (1996) 689.
- [4] B. Velino, E. Canè, L. Gagliardi, A. Trombetti, W. Caminati, *J. Mol. Spectrosc.* 161 (1993) 136.
- [5] F. Negri, W. Caminati, *Chem. Phys. Lett.* 260 (1996) 119.
- [6] E. Jalviste, A. Treshchalov, *Chem. Phys.* 172 (1993) 325.
- [7] G. Berden, E. Jalviste, W.L. Meerts, *Chem. Phys. Lett.* 226 (1994) 305.
- [8] W. Roth, C. Jacoby, A. Westphal, M. Schmitt, *J. Phys. Chem. A* 102 (1998) 3048.
- [9] J. Catalán, P. Pérez, J. Elguero, *J. Org. Chem.* 58 (1993) 5276.
- [10] F. Tomás, J. Catalán, P. Pérez, J. Elguero, *J. Org. Chem.* 59 (1994) 2799.
- [11] M. Frisch, G. Trucks, H. Schlegel, P. Gill, B. Johnson, M. Robb, J. Cheeseman, T. Keith, G. Petersson, J. Montgomery, K. Raghavachari, M. Al-Laham, V. Zakrzewski, J. Ortiz, J. Foresman, J. Cioslowski, B. Stefanov, A. Nanayakkara, M. Challacombe, C. Peng, P. Ayala, W. Chen, M. Wong, J. Andres, E. Replogle, R. Gomperts, R. Martin, D. Fox, J. Binkley, D. Defrees, J. Baker, J. Stewart, M. Head-Gordon, C. Gonzalez, J. Pople, *Gaussian 94*, Revision B.3, 1994.
- [12] A. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [13] A. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [14] J. Perdew, Y. Wang, *Phys. Rev. B* 45 (1992) 13244.
- [15] S. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [16] R. Kendall, T. Dunning, *J. Chem. Phys.* 96 (1992) 6796.
- [17] A. Scott, L. Radom, *J. Phys. Chem.* 100 (1996) 16502.
- [18] J.J. Kankare, *Anal. Chem.* 42 (1970) 1322.
- [19] Z.H.Jr., A.A. El-Awady, *J. Phys. Chem.* 75 (1971) 2954.
- [20] E. Malinowski, *Anal. Chem.* 49 (1977) 606.
- [21] E. Malinowski, *Anal. Chem.* 49 (1977) 612.
- [22] E. Malinowski, *J. Chemom.* 3 (1988) 49.