The tautomeric equilibrium of benzotriazole: New evidence from the jet-cooled rotational spectrum and first principles calculations

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The tautomeric equilibrium of benzotriazole: new evidence from the jet-cooled rotational spectrum and *first principles* calculations

Fabrizia Negri, Walther Caminati

Dipartimento di Chimica "G. Ciamician", Via F. Selmi, 2 Università di Bologna, I-40126 Bologna, Italy

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Abstract

The microwave spectrum of jet-cooled benzotriazole is presented and, similarly to the room temperature spectrum, it is shown to be due to the 1H-tautomer. With the help of ab initio quantum chemical calculations of the electronic excitation energies and relative stability of the two tautomers, we show that the microwave results do not disagree with the conclusions of the recent rotational analysis of the 0–0 fluorescence band in jet-cooled molecular beams, which was attributed to the 2H-species.

1. Introduction

Benzotriazole (BTZ) belongs to the family of heterocycles characterized by a six-membered ring fused to a five-membered ring and is well known as an excellent corrosion inhibitor of copper [1]. Similarly to purine, the most important member of the family, benzotriazole exists in two tautomeric forms 1H- and 2H- (see Fig. 1). The elucidation of the relative stability of the two tautomers has been the subject of several theoretical [2–5] and experimental [5–10] studies. Early ab initio calculations at the Hartree–Fock (HF) level combined with various basis sets [2,3] pointed to a considerable stability of the 1H-tautomer, in agreement with experimental evidence that the 1H-species dominates the solid state phase [11] and is responsible for the observed microwave spectrum of the vapor [6].

Conversely, the gas phase UV absorption spectrum was interpreted as being due to both tautomers in equilibrium [4,8] and the 2H-tautomer was shown

to be responsible for the 34918 cm^{-1} emission observed in jet-cooled molecular beams [9,10]. To account for the lack of detection of the 1H-tautomer, it was suggested that either the population of the latter species was negligible in the free jet experimental conditions, or its fluorescence was much weaker than that of the 2H-tautomer.

Indeed, at variance with the HF results, recent ab initio calculations performed with Møller–Plesset perturbation theory up to second order (MP2) indicated an opposite direction of the tautomeric equilibrium, with the 2H-tautomer more stable than the 1H-species by ≈ 2.5 kcal/mol [4]. A similar energy difference implies, for instance at 160°C, that the population of the less stable 1H-tautomer is $\approx 10\%$ of the 2H-form, and will decrease at lower temperatures. Beside the population, another important observable for the success of a microwave measurement is the magnitude of the dipole moment. Unfortunately, the latter has been measured only for the 1H-tautomer ($\mu_a = 2.9$ D, $\mu_b = 3.20$ D [6]). How-

ever, the dipole moment of the 2H-tautomer is predicted, on the basis of ab initio calculations, to be six to ten times smaller than that of the 1H-tautomer [3,4]. Despite the unfavorable dipole moment, it might be anticipated that, thanks to its larger population, the free-jet microwave spectrum of the 2H-species should be easily detectable.

Prompted by these results, we have undertaken a microwave study in the free jet. Although the aforementioned rotational analysis of the 0–0 fluorescence band [10] showed evidence of the 2H-tautomer alone, our experimental data show unquestionably that the microwave spectrum is due to the 1H-tautomer.

2. Experimental

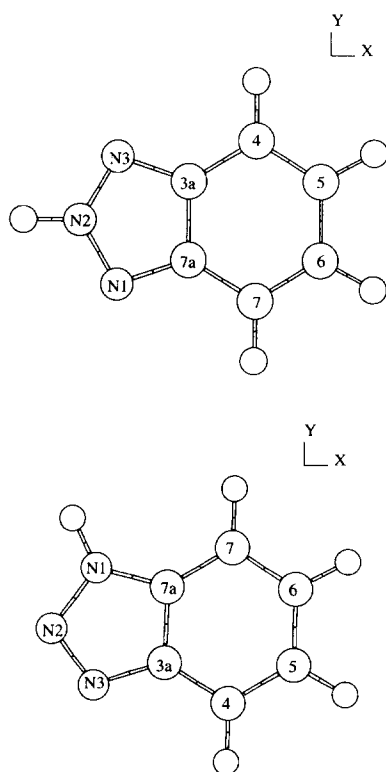A sample of BTZ was purchased from Aldrich and used without further purification. It is a crys-

Fig. 1. Atom numbering of 2H-benzotriazole (top) and 1H-benzotriazole (bottom).

Table 1

Frequencies of free-jet measured rotational transitions of BTZ (MHz)

$J'(K_a', K_c') \leftarrow J''(K_a'', K_c'')$	ν (MHz)
8(8)–7(7) [a]	61562.96
9(4, 6)–8(1, 7)	61839.26
12(6, 7)–11(5, 6)	62470.74
12(6, 6)–11(5, 7)	62733.15
13(5, 8)–12(4, 9)	62211.11
20(5, 16)–19(4, 15)	61449.82
20(5, 15)–9(5, 14)	61920.37
20(6, 14)–19(6, 13)	61791.48
21(5, 17)–20(4, 16)	62653.52
21(7, 15)–20(7, 14)	62294.44
21(8, 14)–20(8, 13)	62055.56
21(8, 13)–20(8, 12)	62240.93
21(9, 13)–20(9, 12)	61692.59
21(9, 12)–20(9, 11)	61709.82
21(11)–20(11)	61203.70
22(4, 18)–21(5, 17)	61853.33
23(3, 20)–22(3, 19)	62779.07
23(3, 20)–22(4, 19)	62703.70
23(4, 20)–22(3, 19)	62818.89
23(4, 20)–22(4, 19)	62743.52
23(13)–23(12) [a]	63289.63
24(13)–24(12) [a]	63110.74
25(13)–25(12) [a]	62906.48

[a] Asymmetry degenerate K_a transition doublets.

talline white solid melting at 98°C. To obtain a suitable concentration of the sample in the carrier gas it was necessary to warm it up. The heating device and the details of the free-jet spectrometer are described elsewhere [12]. In the present experiment the sample seeded in argon at a stagnation pressure of ≈ 10 kPa at 120°C was expanded to about 0.05 Pa through a 0.35 mm diameter nozzle.

3. Rotational spectrum

Based on the rotational constants of Ref. [6] several μ_a-R-type, μ_b-R and Q-type transitions of the 1H-tautomer have been easily identified and then measured in the 61200–63300 MHz frequency range. The list of frequencies is given in Table 1. The spectroscopic constants obtained when treating these experimental frequencies combined with those of Ref. [6], with a quartic Watson Hamiltonian [13], are reported in Table 2 (A reduction, I^r representation).

Table 2
Spectroscopic constants of BTZ

A(MHz)	4008.166(4) [a]
B(MHz)	1676.357(2)
C(MHz)	1182.201(2)
Δ_J(Hz)	34(2)
Δ_{JK}(Hz)	71(14)
Δ_K(Hz)	266(19)
δ_J(Hz)	16(2)
δ_K(Hz)	50(24)
N [b]	114
σ(MHz)	0.13

[a] Errors in parentheses are expressed in units of the last digit.
[b] Number of transitions in the fit.

A slight improvement is obtained with respect to the set reported in Ref. [6]. We also searched carefully for the spectrum of the 2H-tautomer, by using the relatively precise rotational constants of Ref. [10], but we were not able to observe rotational transitions of the more symmetric tautomer. Thus, both at room temperature and in supersonic expansion conditions, only the rotational spectrum of the 1H-tautomer has been observed. Since we did not observe the 2H-tautomer it is difficult to estimate quantitatively the abundance of the 1H-species in the tautomeric mixture. Nevertheless, we can get some qualitative information on the abundance of the observed species by comparing the intensities of the BTZ spectrum with the corresponding rotational transitions of the predominant N(9)H tautomer of purine, recently observed with the same free-jet spectrometer [14]. This comparison is appropriate since the two molecules have almost the same inertial parameters. In spite of the fact that the dipole moment of purine is expected to be slightly larger than that of BTZ, both μ_a- and μ_b-type transitions of BTZ were about twice as intense as those of purine. Thus, we can confidently state that the population of 1H-BTZ not only cannot be marginal at equilibrium, but it can be estimated to

Table 3
Equilibrium bond lengths (Å) of the 1H- and 2H-tautomers of benzotriazole

	HF/6-31G* [a]	MP2/6-31G** [a]	DFT-BLYP/6-31G* [b]
2H-benzotriazole			
N_1N_2	1.296	1.333	1.346
N_3C_{3a}	1.325	1.368	1.369
$C_{3a}C_{7a}$	1.408	1.422	1.443
$C_{3a}C_4$	1.424	1.407	1.421
C_4C_5	1.351	1.383	1.390
C_5C_6	1.441	1.420	1.435
N_2H_2	0.995	1.010	1.020
C_4H_4	1.078	1.081	1.092
C_5H_5	1.075	1.082	1.094
1H-benzotriazole			
N_1N_2	1.332	1.362	1.392
N_2N_3	1.253	1.321	1.310
N_3C_{3a}	1.375	1.375	1.394
$C_{3a}C_{7a}$	1.384	1.412	1.425
$C_{7a}N_1$	1.355	1.362	1.375
$C_{3a}C_4$	1.399	1.407	1.413
C_4C_5	1.369	1.369	1.397
C_5C_6	1.414	1.418	1.425
C_6C_7	1.370	1.386	1.399
N_1H_1	0.993	1.009	1.018
C_4H_4	1.074	1.082	1.092
C_5H_5	1.074	1.082	1.093
C_6H_6	1.075	1.082	1.094
C_7H_7	1.075	1.082	1.093

[a] From Ref. [4].
[b] This work; for 2H-benzotriazole, energy $= -395.737422380$ E_h, for 1H-benzotriazole, energy $= -395.736830387$ E_h.

be at least as abundant as the 2H-tautomer, to account for our experimental observations.

4. Computational results and discussion

The result of the free-jet microwave study is of considerable interest since it poses serious restrictions to the relative population of the two tautomers. Indeed, our experimental data can be interpreted only by assuming a much less pronounced predominance of the 2H-tautomer population than predicted from the energy difference computed at the MP2 level of theory [4]. On the other hand, if the population of the 1H-tautomer is not negligible compared to the 2H-tautomer, the results of the free-jet fluorescence study [10] have to be re-examined to state the consistency with the microwave results presented here.

To assist the interpretation of the spectroscopic experimental data we have performed quantum chemical calculations of the relative stability of the two BTZ tautomers. The most recent calculations to date [4] include correlation energy contributions up to second order (MP2), and should be regarded as superior compared to early HF estimates [2,3]. There are, however, indications [15] that the evaluation of the relative energies of tautomers is sensitive to the amount of correlation energy introduced in the calculations, and that MP2 estimates can lead to misleading results. As a consequence, it has been suggested [15] that reliable energy estimates are obtained only when perturbative corrections up to fourth order are employed. As an alternative to the expensive MP4 calculations we have explored the performance of the much cheaper density functional theory (DFT)

which has become a strongly competitive and reliable computational tool over the last few years.

To estimate the stabilities of the two tautomers we employed the gradient corrected BLYP functional [16,17] and the 6-31G* basis set. There is evidence that the method is more reliable than MP2 for predicting relative stabilities [18,19], and inaccuracies smaller than 1 kcal/mol have been reported [18]. In addition to the stability calculations we have also computed the transition energies and dipole moments of the low-lying $\pi\pi^*$ electronic excitations of the two tautomers, by employing the configuration interaction with single excitations (CIS) method. All the calculations were performed with the Gaussian94 suite of programs [20].

The equilibrium structures and energies of the two tautomers of BTZ are presented in Table 3. It is seen that the DFT-BLYP/6-31G* geometries are much closer to the MP2 results than to the HF results. Nevertheless, the predicted energy difference between the two tautomers is drastically reduced compared to the MP2 results [4] (see Table 4). It amounts to 0.37 kcal/mol in favour of the 2H-tautomer, and becomes 0.33 kcal/mol in favour of the 1H-tautomer if the zero-point energy correction is introduced. Even by accepting an error of the order of 1 kcal/mol [18], the present results point to a much more similar stability of the two tautomers than predicted by the MP2 results. Such a small energy difference has a considerable effect on the population of the 1H-tautomer in the vapor, but also in free jets. In fact, in the latter condition, the populations are frozen at the temperature prior to expansion and equilibration does not occur because of the high energy barrier that separates the two tautomers [21]. Thus, in the jet, the

Table 4
Energies (hartree) and energy differences $\Delta E = E_{2H} - E_{1H}$ (kcal/mol) of benzotriazole tautomers

Method	1H-benzotriazole	2H-benzotriazole	ΔE [a]
HF/3-21G [b]	−391.19777	−391.18898	+5.51
HF/6-31G [b]	−393.24173	−393.23401	+4.84
HF/6-31G* [c]	−393.42213	−393.41843	+2.32
HF/6-31G** [c]	−393.43350	−393.42959	+2.45 (3.16)
MP2/6-31G** [c]	−394.71201	−394.71604	−2.53
DFT-BLYP/6-31G* [d]	−395.73742	−395.73683	−0.37 (0.33)

[a] Energy difference inclusive of zero-point energy correction in parentheses.
[b] From Ref. [2].   [c] From Ref. [4].   [d] This work.

population of each tautomer is that of the vapor prior to expansion (120°C with the present experimental apparatus) and, by assuming a computed energy difference of 0.33 kcal/mol, the amount of 1H-tautomer is estimated to be $\approx 75\%$. By recalling that the dipole moment of the 1H-tautomer is predicted to be about ten times larger than that of the 2H-tautomer [4], the intensities of rotational lines corresponding to the more symmetric tautomer are expected to be at least a hundred times smaller than those of the 1H-tautomer and will be hidden under the noise of the microwave spectrum.

In this sense, the predictions of DFT-BLYP/6-31G* calculations appear to be more consistent with the observation of the 1H-tautomer in the microwave spectra than the MP2 results. It is important, however, to examine whether our experimental and computational results are also consistent with the conclusions of the rotational analysis of the 0–0 fluorescence band in free jets [10]. To this end we present, in Table 5, the vertical electronic excitation energies of the lowest two excited states, which are of $\pi\pi^*$ nature, of each BTZ tautomer along with transition dipole moments and oscillator strengths. The excitation energies were computed at two different reference structures for each tautomer, namely the HF/6-31G* and DFT-BLYP/6-31G* geometries. The overestimate of the excitation energies of Table 5, compared to the experimental data, is a normal feature of the CIS method [22] that, due to the inclusion of a selected number of excitations (only singles), accounts for a fraction of the correlation energy. Nevertheless, in our experience the transition dipole moments, which are of peculiar interest in the following discussion, are reliably predicted by the method [22]. Two additional comments to Table 5

are in order. First, the $S_0 \leftrightarrow S_1$ oscillator strength of the 2H-tautomer is twice as strong as that of the 1H-tautomer. Second, the excitation energy of the 1H-tautomer is computed to be larger than that of the 2H-tautomer. More importantly, the latter result is independent of the geometrical structure chosen to compute the transition energies. Thus, the $S_0 - S_1$ energy difference is always computed to be larger for the 1H-tautomer. As expected, the same holds for the 0–0 excitation energy, which is computed to be 43219 cm^{-1} for the 2H-tautomer and 46507 cm^{-1} for the 1H-species. The fact that the oscillator strength of the $S_0 \leftrightarrow S_1$ transition of the 1H-tautomer is predicted to be half of that of the 2H-tautomer implies that the former, which we have just indicated to be more populated, should also be observed in electronic spectroscopic studies. However, its larger computed transition energy suggests that the origin of its fluorescence and absorption spectra should be located in an energy range that was not explored experimentally in Ref. [10], where the fluorescence spectrum was obtained by exciting the 34918 cm^{-1} band. Emission at this excitation wavelength originates only from the 2H-tautomer, whilst the 1H-tautomer, which absorbs at higher wavenumbers, cannot contribute to it. Thus, the rotational structure of the band studied in Ref. [10] does indeed belong to the 2H-tautomer, and corresponds to a pure *short-axis* transition, as confirmed by the results of Table 5. Accordingly, the assignment proposed in Ref. [7] for the 34920 cm^{-1} band of the gas phase absorption spectrum should also be reconsidered, and reassigned to the origin of the 2H-tautomer [23].

In conclusion, we have shown that the microwave spectrum of jet cooled benzotriazole is due to the 1H-tautomer. From the combined results of DFT-

Table 5
Vertical excitation energies, transition dipole moments (M_x, M_y) and oscillator strengths (f) of the lowest two excited states of 1H- and 2H-benzotriazole computed with the CIS method and the 6-31G* basis set

			E(eV) [a]	M_x [a]	M_y [a]	f [a]	E(eV) [b]	M_x [b]	M_y [b]	f [b]
2H-benzotriazole	1B$_2$	S$_1$	5.79	–	1.23	0.22	5.33	–	1.29	0.22
	2A$_1$	S$_2$	6.33	1.14	–	0.20	5.80	1.15	–	0.19
1H-benzotriazole	2A'	S$_1$	6.06	0.69	0.50	0.11	5.68	0.82	0.45	0.12
	3A'	S$_2$	6.23	0.52	0.67	0.11	5.88	0.56	0.81	0.14

[a] HF/6-31G* geometry employed for the CIS calculation.
[b] DFT-BLYP/6-31G* geometry employed for the CIS calculation.

BLYP/6-31G* energy calculations, which indicate similar stability for the two tautomers, and the experimental microwave studies, which reveal only the 1H-tautomer, it is suggested that the population of the latter in the experimental free-jet conditions cannot be less than 50%. The about ten times larger dipole moment of the 1H-tautomer accounts for its detection in the microwave experiments whilst the excitation region chosen in the fluorescence studies [10], is responsible for the detection of the 2H-species. Since the computed excitation energies indicate that the 0–0 transition of the 1H-tautomer is located ≈ 3000 cm^{-1} above the 2H-origin, it is suggested that possible evidence of the 1H-tautomer fluorescence might be obtained by extending the study of the fluorescence excitation and single vibronic level fluorescence spectra [9] to higher excitation energies.

Acknowledgement

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