

Influence of Lone Pair Repulsion vs Resonance Energy on the Relative Stabilities of Molecular Structures: A Theoretical Approach to the Equilibrium between 1*H*- and 2*H*-Benzotriazole Tautomers

Francisco Tomás,[†] Javier Catalán,^{*‡} Pilar Pérez,[‡] and José Elguero[§]

Departamento de Química Física, Facultad de Ciencias, Universidad de Valencia, E-46100 Burjassot, Spain, Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain, and Instituto de Química Médica, CSIC, E-28006 Madrid, Spain

Received December 29, 1993*

The experimental conclusion that the tautomerism of benzotriazole is shifted toward the 2*H* tautomer in the gas phase ($\Delta E_{1H \rightarrow 2H} = \sim -4$ kcal mol⁻¹) can only be reproduced theoretically if electron correlation is introduced during the geometry optimization (MP2-6-31G**). The geometries obtained at this level yield excellent rotational constants, and the associated charges explain the different vectorial components of the experimental dipole moment, a result that 6-31G** geometries cannot afford. Receipt spectroscopic data obtained for benzotriazole in the gas phase, interpreted assuming that the major tautomer is the 1*H*-benzotriazole, were reanalyzed to show that they can be explained considering a mixture of both tautomers and its dependence with temperature.

We have recently reported the UV spectra of benzotriazole in the gas phase at three temperatures.¹ The unexpected result we obtained was that the 2*H* tautomer is about 4 kcal mol⁻¹ more stable than the 1*H*-tautomer in apparent contradiction with all previous evidence, both experimental and theoretical.^{2,3} The problem of the stabilities of these tautomers is related to such fundamental problems as the aromaticity of heterocycles⁴ and the importance of lone pair repulsion.⁵ The value of $\Delta E_{1H \rightarrow 2H}$ (-4 kcal mol⁻¹) should result of the balance between an exothermic contribution due to the adjacent lone pairs of the 1*H* tautomer and an endothermic contribution due to the larger resonance stabilization of tautomer 1*H* (benzenoid) with regard to tautomer 2*H* (quinonoid).

The aim of the present paper is 2-fold: first, to find a theoretical method able to describe correctly the equilibrium of benzotriazole in the gas phase, and second, to discuss three recent publications in which the interpretation of experimental results in the gas phase was based on the presence of the 1*H* tautomer.⁶⁻⁸ Incidentally, the tautomeric structure of benzotriazole in the first excited state will also be examined.

These three previous papers,⁶⁻⁸ discussed the results assuming that the tautomer responsible for the experimental observations is the 1*H*. Thus, Cané, Trombetti, and Velino,⁶ using a sample of benzotriazole in the gas

phase at 140 °C, analyzed the rotational band contour of the 0-0 component of the S₀ → S₁ transition and concluded its π-π* nature. Jalviste and Treshchalov⁷ reported the spectroscopy of jet-cooled benzotriazole. Finally, Velino, Cané, *et al.*⁸ described the microwave spectra of benzotriazole at 90 °C and conclude that the isomer present at that temperature was the 1*H*.

Experimental Section

Materials. Benzotriazole was kindly supplied as a pure sample by Dr. C. Turrión, and it is identical to the sample studied in ref 9. 1-Methyl- and 2-methylbenzotriazole are identical with those described in ref 3.

Measurements. Fluorescence spectra at 70 °C, corrected for instrumental sensitivity, were measured with a SLM 48000S spectrofluorometer using a cooled wide-band RF housing for the R298 photomultiplier tube. Using a CARY 5 spectrophotometer and a pair of thermostated cells (10 cm of optical path) we recorded the UV spectra of benzotriazole, 1-methylbenzotriazole, and 2-methylbenzotriazole in the gas phase at 90 °C.

Theoretical Calculations. All computations were carried out using a standard version of the GAUSSIAN 92 program.¹⁰ The geometry has been fully optimized with the only restriction of assuming planarity with the following basis sets: 6-31G*, 6-31G**, and MP2-6-31G**. The optimization was stopped when internal coordinates changed less than 0.001au. Electron correlation was introduced at the MP2 level over the 6-31G**-optimized geometry, and zero point energy (ZPE) correlation was carried out over that geometry. Finally, a full optimization has been carried out at MP2-6-31G** level considering the significance of correlation energy in this case.

[†] Universidad de Valencia.

[‡] Universidad Autónoma de Madrid.

[§] Instituto de Química Médica.

* Abstract published in *Advance ACS Abstracts*, April 1, 1994.

(1) Catalán, J.; Pérez, P.; Elguero, J. *J. Org. Chem.* **1993**, *58*, 5276.

(2) Katritzky, A. R.; Yannakopoulou, K.; Anders, E.; Stevens, J.; Szafran, M. *J. Org. Chem.* **1990**, *55*, 5683.

(3) Tomás, F.; Abboud, J.-L. M.; Laynez, J.; Notario, R.; Santos, L.; Nilsson, S. O.; Catalán, J.; Elguero, J. *J. Am. Chem. Soc.* **1989**, *111*, 7348.

(4) (a) Cook, M.; Katritzky, A. R.; Linda, P. Aromaticity of Heterocycles. *Adv. Heterocycl. Chem.* **1974**, *17*, 255. (b) Katritzky, A. R.; Bacynski, P.; Musumarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7.

(5) Taft, R. W.; Anvia, F.; Taagepera, M.; Catalán, J.; Elguero, J. *J. Am. Chem. Soc.* **1986**, *108*, 3237.

(6) Cané, E.; Trombetti, A.; Velino, B. *J. Mol. Spectrosc.* **1993**, *158*, 399.

(7) Jalviste, E.; Treshchalov, A. *Chem. Phys.* **1993**, *172*, 325.

(8) Velino, B.; Cané, E.; Gagliardi, L.; Trombetti, A.; Caminati, W. *J. Mol. Spectrosc.* **1993**, *161*, 136.

(9) Jiménez, P.; Roux, M. V.; Turrión, C.; Gomis, F. *J. Chem. Thermodyn.* **1987**, *19*, 985.

(10) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92, Revision C, Gaussian Inc., Pittsburgh, PA, 1992.

(11) Catalán, J.; Sánchez-Cabezudo, M.; de Paz, J. L. G.; Elguero, J.; Taft, R. W.; Anvia, F. *J. Comput. Chem.* **1989**, *10*, 426.

(12) Cox, J. R.; Woodcock, S.; Hillier, I. H.; Vincent, M. A. *J. Phys. Chem.* **1990**, *94*, 5499.

(13) Törnkvist, C.; Bergman, J.; Liedberg, B. *J. Phys. Chem.* **1991**, *95*, 3123.

Table 1. Energies (in Hartrees)^a and Differences in Energy (in kcal mol⁻¹) of Benzotriazole and 1,2,3-Triazole Tautomers

basis set	1 <i>H</i> -benzotriazole	2 <i>H</i> -benzotriazole	difference
3-21G	-391.197 77	-391.188 98	+5.51 ²
6-31G	-393.241 73	-393.234 01	+4.84 ³
6-31G*/3-21G	-393.417 70	-393.413 38	+2.71 ²
6-31G*	-393.422 13	-393.418 43	+2.32
6-31G**	-393.433 50	-393.429 59	+2.45
6-31G** + ZPE	-393.318 91	-393.313 88	+3.16
MP2//6-31G**	-394.705 22	-394.707 59	-1.49
MP2-6-31G**	-394.712 01	-394.716 04	-2.53

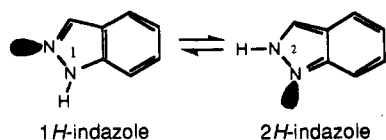
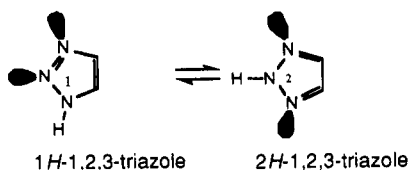
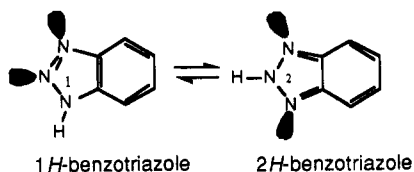
basis set	1 <i>H</i> -	2 <i>H</i> -	difference ^b
	1,2,3-triazole	1,2,3-triazole	
3-21G	-239.392 66	-239.399 00	-3.94 ^{11,12}
6-31G	-240.638 95	-240.645 16	-3.93 ^{8,11}
6-31G*/6-31G	-240.767 32	-240.774 86	-4.73 ^{3,11}
6-31G**/3-21G	-240.7719	-240.7793	-4.68 ¹²
6-31G**/6-31G*	-240.775 29	-240.782 80	-4.71 ¹¹
6-31G**			-4.93 ^c
MP2-6-31G*	-241.538	-241.546	-5.0 ¹³
MP2+6-31G**/3-21G + ZPE	-241.5615	-241.5674	-3.55 ¹²

^a 1 hartree/particle = 627.509 59 kcal mol⁻¹. ^b $\Delta E_{1H \rightarrow 2H}$. ^c Anders, F. Personal communication.³

Results and Discussion

Calculations. Relative Stabilities. We have reported in Table 1 the energies for both tautomers (in hartrees) and the differences in energies (in kcal mol⁻¹) for benzotriazole and for 1,2,3-triazole for a series of basis sets.

The data reported in Table 1 show four important things: (i) for benzotriazole, the introduction of electron correlation is necessary to establish the correct sign of the difference in energies between both tautomers; (ii) the complete optimization of the geometry at the MP2-6-31G** level yields a value of $\Delta E_{1H \rightarrow 2H}$ (-2.5 kcal mol⁻¹) closer to the experimental result (~-4 kcal mol⁻¹) than an MP2 calculation on the 6-31G** optimized geometry, MP2/6-31G** ($\Delta E_{1H \rightarrow 2H} = -1.5$ kcal mol⁻¹); (iii) this problem is characteristic of benzotriazole since $\Delta E_{1H \rightarrow 2H}$ in 1,2,3-triazole is rather insensitive to the introduction of electron correlation; and (iv) a zero-point energy calculation at the 6-31G** level favors the 1*H* tautomer by 0.6 kcal mol⁻¹.



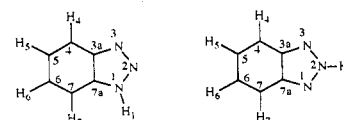
Since the system of lone pairs is identical in both heterocycles, observation iii points out the difficulty

Table 2. Geometries of 1*H*- and 2*H*-Benzotriazole Tautomers

1 <i>H</i> -benzotriazole	6-31G	6-31G*	6-31G**	MP2-6-31G**	exptl ^c
Bond Lengths (Å)					
N ₁ N ₂	1.359	1.332	1.332	1.362	1.346
N ₂ N ₃	1.269	1.253	1.253	1.321	1.310
N ₃ C _{3a}	1.389	1.375	1.375	1.375	1.377
C _{3a} C _{7a}	1.389	1.384	1.383	1.412	1.389
C _{7a} N ₁	1.363	1.355	1.355	1.362	1.366
C _{3a} C ₄	1.395	1.399	1.399	1.407	1.408
C ₄ C ₅	1.374	1.369	1.369	1.369	1.368
C ₅ C ₆	1.414	1.414	1.414	1.418	1.405
C ₆ C ₇	1.375	1.370	1.370	1.386	1.367
N ₁ H ₁	0.987	0.993	0.992	1.009	
C ₄ H ₄	1.072	1.074	1.074	1.082	
C ₅ H ₅	1.072	1.074	1.075	1.082	
C ₆ H ₆	1.073	1.075	1.076	1.082	
C ₇ H ₇	1.071	1.075	1.075	1.082	
Bond Angles (deg)					
C _{7a} N ₁ N ₂	110.18	110.51	110.44	111.69	110.3
N ₁ N ₂ N ₃	109.07	109.82	109.85	108.03	108.8
N ₂ N ₃ C _{3a}	109.04	108.57	108.57	108.04	108.2
N ₃ C _{3a} C _{7a}	107.86	108.12	108.11	109.38	108.4
C _{3a} C _{7a} N ₁	103.85	102.98	103.02	102.86	104.2
C _{7a} C _{3a} C ₄	121.24	121.02	121.04	120.48	120.9
C _{3a} C ₄ C ₅	117.36	117.24	117.22	117.12	116.2
C ₄ C ₅ C ₆	121.08	121.20	121.21	121.76	122.2
C ₅ C ₆ C ₇	121.92	122.16	122.17	122.05	122.6
C ₆ C ₇ C _{7a}	118.58	116.11	116.09	115.98	115.3
C _{7a} N ₁ H ₁	130.35	130.42	130.34	129.83	
C _{3a} C ₄ H ₄	120.80	120.72	120.74	120.60	
C ₄ C ₅ H ₅	119.87	119.97	119.96	119.57	
C ₅ C ₆ H ₆	118.96	118.68	118.67	118.86	
C ₆ C ₇ H ₇	119.74	121.69	121.68	121.63	

2 <i>H</i> -benzotriazole	6-31G	6-31G*	6-31G**	MP2-6-31G**
Bond Lengths (Å)				
N ₁ N ₂	1.320	1.296	1.297	1.333
N ₂ C _{3a}	1.333	1.325	1.324	1.368
C _{3a} C _{7a}	1.415	1.408	1.408	1.422
C _{3a} C ₄	1.419	1.424	1.424	1.407
C ₄ C ₅	1.356	1.351	1.350	1.383
C ₅ C ₆	1.438	1.441	1.441	1.420
N ₂ H ₂	0.989	0.995	0.994	1.010
C ₄ H ₄	1.069	1.078	1.074	1.081
C ₅ H ₅	1.072	1.075	1.075	1.082
Bond Angles (deg)				
C _{7a} N ₁ N ₂	103.03	102.92	102.97	101.04
N ₁ N ₂ N ₃	116.45	118.21	118.12	120.04
N ₂ C _{3a} C _{7a}	106.14	107.96	107.96	108.93
C _{3a} C ₄ C ₅	116.96	118.79	116.76	116.66
C ₄ C ₅ C ₆	122.08	122.13	122.15	121.99
N ₁ N ₂ H ₂	121.77	120.89	120.93	119.98
C _{3a} C ₄ H ₄	120.65	120.85	120.88	121.22
C ₄ C ₅ H ₅	119.88	119.80	119.77	119.29

^a Data from refs 15 and 16. Average from four independent molecules in one cell. Numbering of the atoms



in conveniently describing the quinonoid system of 2*H*-benzotriazole; a similar problem was encountered in the case of 2*H*- and 2-methylindazole.¹⁴

Geometries. We have gathered in Table 2 the geometries calculated using the following basis sets 6-31G, 6-31G*, 6-31G** and MP2-6-31G** for 1*H*-benzotriazole

(14) Catalán, J.; Del Valle, J. C.; Claramunt, R. M.; Boyer, G.; Laynez, J.; Gómez, J.; Jiménez, P.; Tomás, F.; Elguero, J. Manuscript in preparation.

Table 3. Rotational Constants for Benzotriazole (in MHz)

method	1H-benzotriazole			2H-benzotriazole		
	A	B	C	A	B	C
6-31G	4080.75	1685.73	1192.94	4035.54	1710.93	1201.52
6-31G*	4106.68	1702.53	1203.56	4058.59	1727.66	1211.81
6-31G**	4106.39	1703.06	1203.80	4058.40	1727.99	1211.96
MP2-6-31G**	3989.95	1673.66	1179.04	3962.68	1694.65	1187.01
MW ⁸	4008.171(5)	1676.359(2)	1182.200(2)			

Table 4. Dipole Moments (D)

method	1H-benzotriazole				2H-benzotriazole			
	μ_A	μ_B	μ_C	$ \mu $	μ_A	μ_B	μ_C	$ \mu $
6-31G	3.17	3.40	0	4.65	-0.77	0	0	0.77
6-31G*	2.50	3.23	0	4.09	-0.30	0	0	0.30
6-31G**	2.50	3.23	0	4.08	-0.31	0	0	0.31
MP2-6-31G**	2.65	3.31	0	4.24	-0.38	0	0	0.38
MW ⁸	2.9(2)	3.20(5)	0	4.3(4)				

and 2H-benzotriazole as well as the X-ray structure of 1H-benzotriazole (the only tautomer existing in the solid state).

Unfortunately, "plausible r_0 structures" described by Velino, Cané, *et al.*⁸ cannot be used for comparison since they are not experimental MW geometries but simply our 6-31G-optimized geometry³ after scaling. Using the averaged X-ray geometry (four independent molecules in the unit cell) as a model it can be noted that only the geometry obtained when the optimization including electron correlation (MP2-6-31G**) is able to adequately reproduce N₁-N₂ and N₂-N₃ bond lengths in 1H-benzotriazole. Optimized geometries without taking into account the effect of the correlation lead to significantly shorter N-N bond lengths.

The clearest proof of the goodness of the MP2-6-31G** geometries was provided by the rotational constants (Table 3). The ones calculated at this level are in excellent agreement with those determined by MW for 1H-benzotriazole,⁸ the deviations for rotational constants A, B, and C being as small as 0.45%, 0.16%, and 0.26%. These percentages considerably increase using the 6-31G** geometry (2.5%, 1.6%, and 1.8%). We feel that the MP2-6-31G** geometry (Table 2) and rotational constants (Table 3) of 2H-benzotriazole could be useful to identify the rotational spectra of this tautomer.

Dipole Moments. The dipole moments are collected in Table 4. Note that the scalar value but mainly the vectorial components, determined by microwave spectroscopy, are well reproduced only at the MP2-6-31G** level.

Spectroscopic Results. The assignment, by rotational band contour analysis, of the S₀ → S₁ electronic absorption spectrum of benzotriazole as $\pi^*-\pi$ of the 1H tautomer⁶ is consistent with our results since these experiments were carried out at 140 °C where this tautomer should be present in large amounts (more than 80%).

Velino *et al.*⁸ described the microwave spectra of benzotriazole at 90 °C and conclude that the tautomer present in these conditions is the 1H. They have determined its rotational constants (Table 3) and its dipole moment (Table 4). We have represented in Figure 1 the UV spectra of benzotriazole, 1-methylbenzotriazole, and 2-methylbenzotriazole at this temperature. It is clear, from these spectra, that there is a mixture of both tautomers in an approximately 80/20 ratio. The probable reason why they have not detected the ~20% of the 2H tautomer is easy to understand considering the corresponding dipole

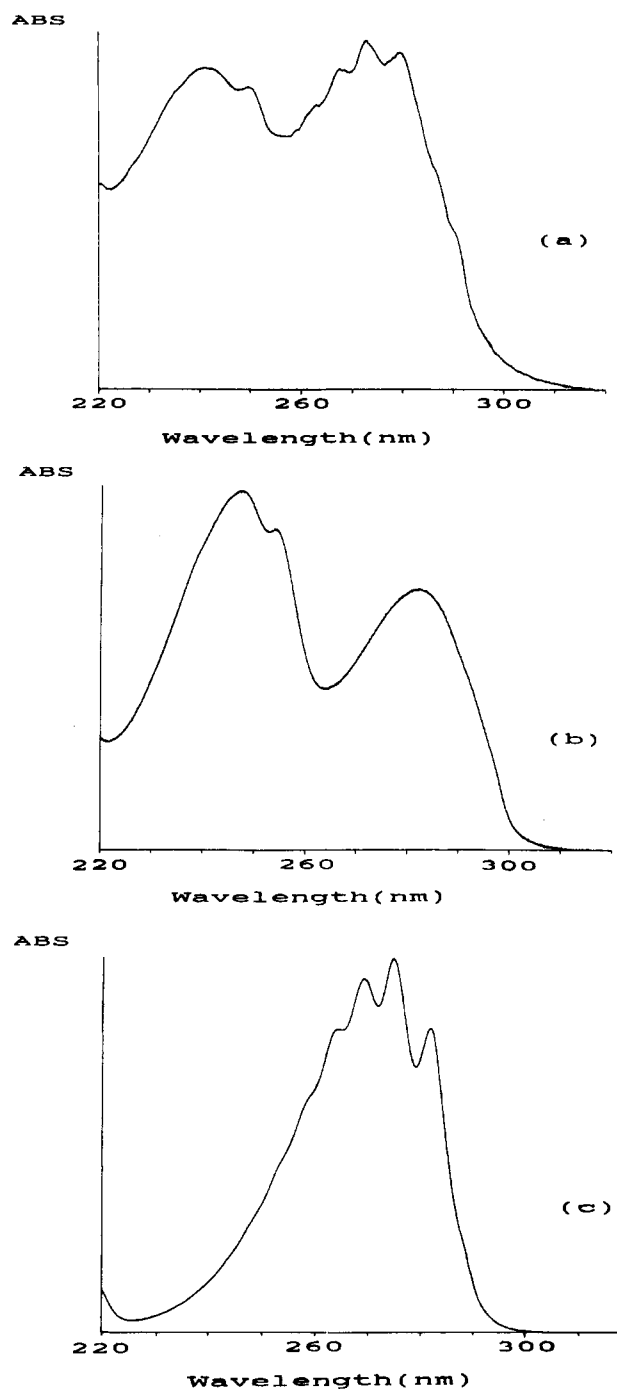


Figure 1. UV spectra in the gas phase at 90 °C of (a) benzotriazole, (b) 1-methylbenzotriazole, and (c) 2-methylbenzotriazole.

moments (4.2 and 0.4 D, Table 4). Since the MW signals are proportional to the square of the dipole moment, the signals of the 1H-tautomer should be almost 500 times more intense than those of the 2H-tautomer. A similar problem occurred with the microwave study of 1,2,3-triazole, when initially only the 1H tautomer was observed

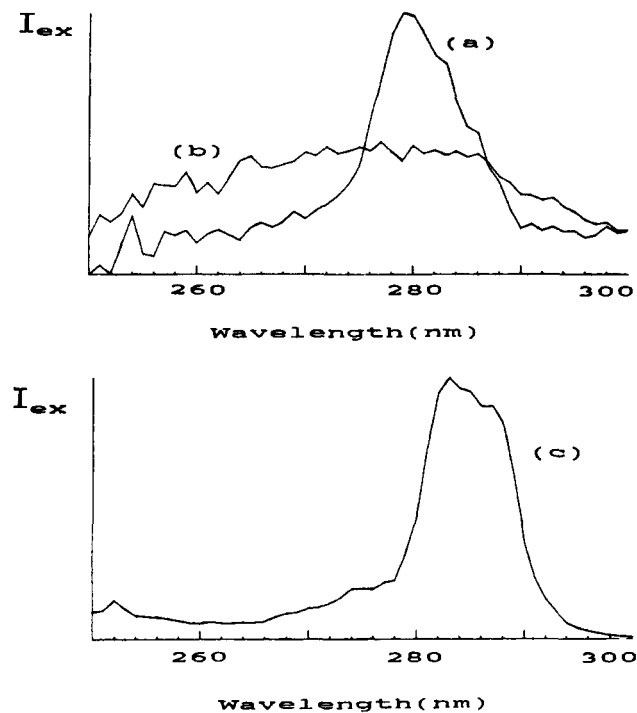


Figure 2. Fluorescence excitation spectra in the gas phase at 70 °C of (a) benzotriazole; (b) 1-methylbenzotriazole, and (c) 2-methylbenzotriazole.

($\mu = 4.38$ D) although it was present in much smaller amount than the *2H* tautomer ($\mu = 0.22$ D).^{3,12,13}

Jalviste and Treshchalov recently reported the fluorescence excitation and emission spectra of jet-cooled benzotriazole.⁷ Their main conclusion is that the tautomers present in the ground (S_0) and the first excited states (S_1) are different, which should imply an excited-state proton transfer taking place in times shorter than a few ns at very low temperatures, a few K. These authors describe an interesting feature of the excitation spectrum of benzotriazole: above 1200 cm^{-1} , with regard to the 0–0 band, only a weak and broadened band appears due to a rapid intensity decline. In Figure 2a we present the fluorescence excitation spectrum of benzotriazole in the gas phase at 70 °C: a rapid decline of intensity in the zone described by Jalviste and Treshchalov⁷ is observed. Moreover, the excitation spectrum of 2-methylbenzotriazole (Figure 2c) shows the same behavior at slightly longer wavelengths which is consistent with the absorption spectrum (see Figure 1). The excitation spectrum of 1-methylbenzotriazole does not show this phenomenon (Figure 2b). The fluorescence emission spectra, in the gas phase at 70 °C, for benzotriazole and 2-methylbenzotriazole are reported in Figure 3. A reasonable conclusion of these spectra is that the tautomer present in the free-jet experiments as well as that responsible for the fluorescence emission at room temperature is the *2H*.

The free-jet experiments can be rationalized as follows. Solid benzotriazole was heated at 160 °C and the resulting vapor mixed with Ar carrier gas. Under these conditions, the gas should be composed predominantly of *1H* tautomer

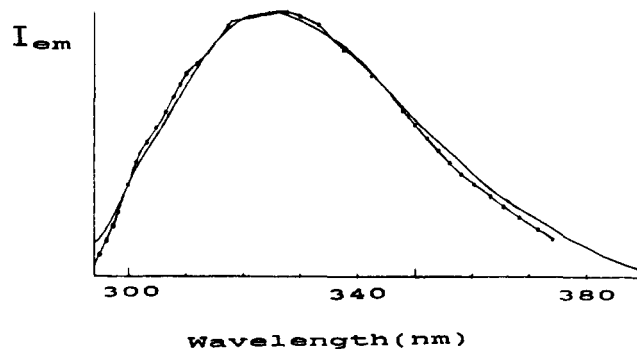


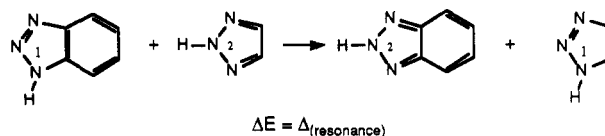
Figure 3. Fluorescence emission spectra in the gas phase at 70 °C of benzotriazole (---) and 2-methylbenzotriazole (—).

(more than 90%). Then, the gas expansion lowers the temperature to a few K which results in a complete shift of the equilibrium toward the *2H* tautomer.

Conclusions

The intrinsically most stable tautomer of benzotriazole is the *2H* and the origin of the difference in stability with regard to the *1H* results in a balance between the lone pair repulsion ($6.5 \text{ kcal mol}^{-1}$)⁵ which favors the *2H* tautomer and the aromaticity which favors the *1H* tautomer. The last term is not present in 1,2,3-triazole, and for this reason the *2H* tautomer is much favored while the first term is not present in indazole and consequently the *1H* tautomer is much more stable than the quinonoid *2H*-indazole.

The resonance contribution can be estimated from the following isodesmic process:



The best theoretical data available for the differences in energy between *1H* and *2H* tautomers (Table 1) are $-2.5 \text{ kcal mol}^{-1}$ for benzotriazole (MP2-6-31G**) and $-5.0 \text{ kcal mol}^{-1}$ for 1,2,3-triazole (MP2-6-31G*). Thus, the stabilization of *1H*-benzotriazole with regard to *2H*-benzotriazole, $\Delta(\text{resonance})$, is $2.5 \text{ kcal mol}^{-1}$. This result is in agreement with the value of $2.3 \text{ kcal mol}^{-1}$ for the resonance stabilization of *1H*-indazole with regard to *2H*-indazole.¹⁴

The reason why *1H*-benzotriazole is the dominant tautomer in condensed media, solid state,^{15,16} or solution¹⁷ is probably related to its high dipole moment which favors interactions with itself (solid) or with the solvent (solution).

Acknowledgment. We gratefully acknowledge the CICYT of Spain for financial support (Project No. PB90-0226-C02-01).

(15) Escande, A.; Galigné, J. L.; Lapasset, J. *Acta Crystallogr.* 1974, B30, 1490.

(16) Escande, A.; Lapasset, J.; Faure, R.; Vincent, E. J.; Elguero, J. *Tetrahedron* 1974, 30, 2930 (Erratum, 1975, 31, 2).

(17) Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda, P. *The Tautomerism of Heterocycles*; Academic: New York, 1976.