# Structure of Benzotriazole in the Gas Phase: A UV Experimental Study

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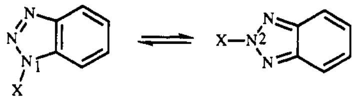
In a preceding paper,[1] we discussed the tautomerism of benzotriazole (1). A 6-31G//6-31G calculation of both taumers afforded that the 1H (**1a**) was 4.8 kcal mol$^{-1}$ more stable than the 2H (**1b**). This value was used to discuss the intrinsic basicity of the corresponding *N*-methyl derivatives, **2a** and **2b**. The only evidence available were two studies in the gas phase, one by photoelectron spectroscopy[2] and the other by mass spectrometry,[3] both concluding with the predominance of **1a**. An independent calculation,[4] 6-31G*//3-21G, found also that the 1H-tautomer was more stable by 2.7 kcal mol$^{-1}$.



**1a**: X = H
**2a**: X = $CH_3$

**1b**: X = H
**2b**: X = $CH_3$

Benzotriazole in the solid state (X-ray crystallography)[5,6] exists exclusively as the 1H-tautomer. This offers a unique possibility to settle an open controversy: when a crystal consisting of a single tautomer is vaporized at low partial pressure, does the resulting gas consist of the same tautomer or an equilibrium mixture?

The electronic spectroscopy of benzotriazole and its *N*-methyl derivatives in solution has been studied many times.[7-21] There is no ambiguity in the conclusion: in *all* solvents, the spectrum of benzotriazole is consistent with that expected of **1a**. Thus, in solution, even in apolar aprotic solvents, such as isooctane,[11] benzotriazole is predominantly in the 1H-form.

No report of the UV spectrum of benzotriazole in the gas-phase exists.[22] This may be due to its extremely low vapor pressure ($2 \times 10^{-5}$ Torr at 298 K, which corresponds to a $10^{-9}$ M concentration in the gas phase).[27] Using a CARY 5 spectrophotometer and a pair of thermostated cells (10 cm of optical path) we have recorded the spectra of benzotriazole (**1**), 1-methylbenzotriazole (**2a**), 2-methylbenzotriazole (**2b**), and benzimidazole (**3**) in the gas phase. Those corresponding to the first three compounds are represented in Figure 1.

An examination of Figure 1 reveals that the peaks which appear at 279, 273, and 268 nm in the UV spectrum of benzotriazole **1** at 80 °C correspond to the peaks of 2-methylbenzotriazole (**2b**) at 282, 275, and 269 nm; the peak at 279 nm in compound **1** appears more intense than the peak at 282 nm in compound **2b** because 1-methylbenzotriazole (**2a**) also absorbs at 282 nm. The peak at 251 nm and the shoulder at 247 nm of benzotriazole **1** corresponds to the peaks at 254 and 247 nm of 1-methylbenzotriazole (**2a**). The spectrum of benzotriazole **1** at 80 °C can be reproduced by adding the spectra of **2a** and **2b**, although the resulting envelope is slightly red-shifted due to the *N*-methyl groups.

Preliminary experimental evidence has been gathered on the following points: (1) the spectra of compounds **2a**, **2b**, and **3** (benzimidazole is much more volatile than benzotriazole, and only one tautomer is possible) do not change significantly in the 20–80 °C range of temperatures; (2) the spectra of the three benzotriazoles do not change when water or ethanol vapors are added; (3) the spectrum of benzotriazole **1** in methylcyclohexane dried over sodium wire is closely related to that of 1-methylbenzotriazole (**2a**) and is not sensitive to temperature changes.

From these results the following points appear: (1) There is an appreciable amount of 2H-benzotriazole in the vapor, thus the molecules of 1H-benzotriazole during the vaporization process (which requires the energy supply to destroy the crystal lattice) or after leaving the crystal are subjected to a tautomeric equilibrium to form **1b**. (2) The amount of 2H-benzotriazole can be estimated from the extinction coefficients of the *N*-methylbenzotriazoles **2a** and **2b** (roughly, the 2-methyl isomer has extinction coefficients twice those of the 1-methylbenzotriazole).[20] The proportion of 2H-tautomer **1b** is about 45% at 30 °C, about 35% at 50 °C, and about 25% at 80 °C. Thus, contrary to all available calculations, the 2H-tautomer is enthalpically more stable than the 1H-tautomer by about 3.8 kcal mol$^{-1}$. (3) The gas-phase experiments in which the evidence for the predominance of the 1H-tautomer **1a** was based are experiments at high temperature. For instance, in mass spectrometry,[3] the source was at 483 K, which roughly corresponds to only 10% of tautomer **1b**. (4) Katritzky reported that *N*-substituted benzotriazoles,[4,28] when equilibrated, are of nearly equal stability innonpolar solvents and in the gas phase. This result is

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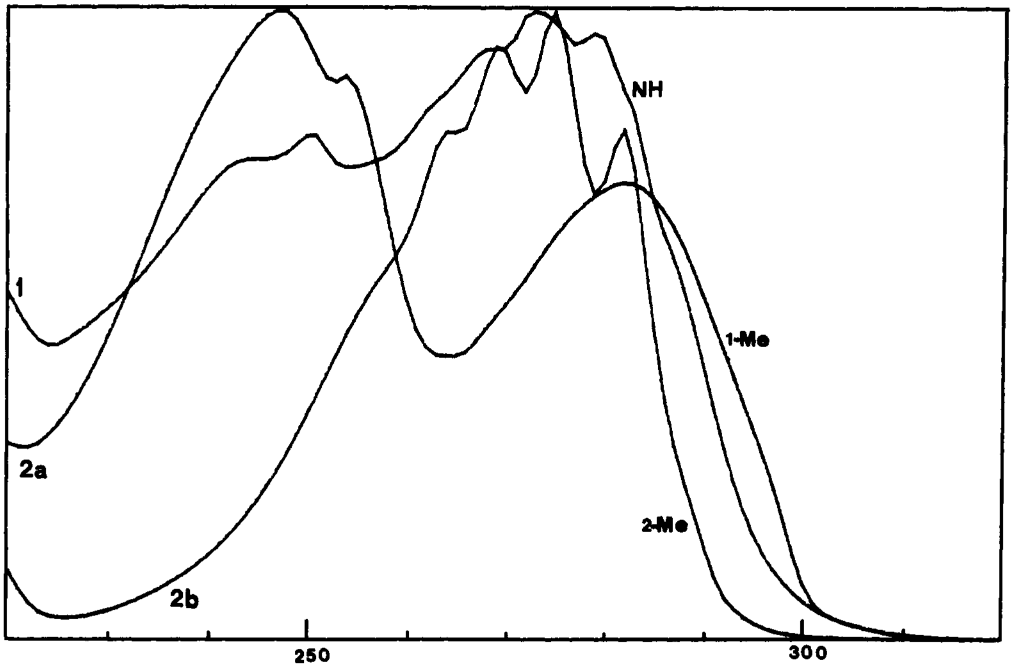

**Figure 1.** UV spectra of benzotriazole (1), 1-methylbenzotriazole (2a), and 2-methylbenzotriazole (2b).

now perfectly understandable. (5) The equilibrium **1a** ↔ **1b** is closely related to the problem of the aromaticity (benzene vs *o*-quinoid structures)[29] and to that of lone pair repulsions (in tautomer 1H).[30] It constitutes a bench case for theoretical studies, being a surprise that to have a correct estimation of the *relative* stability of benzotriazole tautomers it should be necessary to use basis sets of better quality than the 6-31G* and to take into account the contribution of electronic correlation.

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