The Molecular Structure of 2-Methylbenzotriazole (2MeBzTr) in Connection with the X-Ray Structure of $2MeBzTr.HBF_4.H_2O$

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The fluoroborate of 1*H*-2-methylbenzotriazolium monohydrate crystallizes in the Pbca space group [$Z = 8$, $a = 16.734(3)$, $b = 19.153(9)$, $c = 6.937(1)$ Å]. The hydrogen bond network between the three molecules, 2MeBzTr, HBF_4 and H_2O, corresponds to a situation intermediate between the fluoroborate of a protonated benzotriazole ($BF4^-.2MeBzTrH^+$) and a neutral benzotriazole hydrogen-bonded to fluoroboric acid (HBF_4,2MeBzTr). The behaviour of the title compound in solution is also intermediate between these two extreme situations. Thus, the present compound is one of the rare examples of a proton solvated only by very weak hydrogen bond acceptors.

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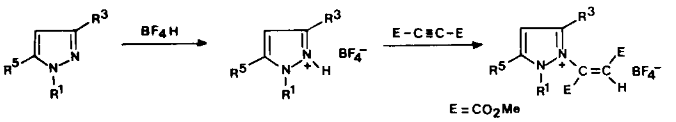
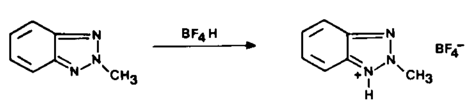
For some time, we have been working on the synthesis, reactivity and spectroscopic properties of vinyl azolium salts [1-4]. These compounds can be prepared, in a two step procedure, from *N*-substituted azoles; as an example, the case of pyrazoles is represented in Scheme 1.

Scheme 1



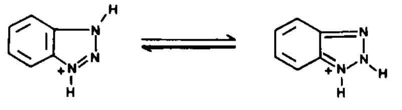
This reaction can be extended to other azoles such as indazoles, benzimidazoles and triazoles [5] and, rather unexpectedly, also to 2-methylbenzotriazole **1**.



1 2

This compound is such a weak base that its pK_a cannot be measured. From theoretical calculations and experimental evidence [6] it was established that the tautomeric equilibrium constant between the two possible cations of benzotriazole, the 1,3-diH$^+$, **3**, and the 1,2-diH$^+$, **4** (Scheme 2), is about $K_T = 10^{-11}$.

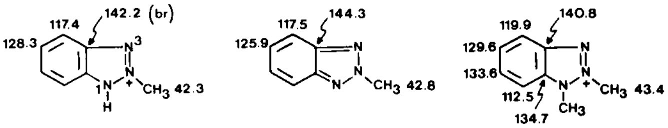
Scheme 2



3 4

When the ^{13}C-nmr spectrum of the salt **2** was recorded in deuteriochloroform, the signal corresponding to carbons C3a and C7a was very broad (Scheme 3). This broadening could result from a slow exchange of the proton between N1 and N3, as occurs in benzimidazoles.

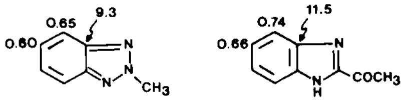
Scheme 3



2 1[7] 5[8]

However, the chemical shifts of compound **2** correspond roughly to a 50:50 mixture of structures **1** and **5**, *i.e.* they are intermediate between a neutral and a 1,2-cationic form. The T_1 relaxation times (in s) have been measured for compound **2** in trifluoroacetic acid (Scheme 4). They are very similar to those of 2-acetylbenzimidazole in the same solvent [9]. In both cases, they correspond to a fast prototropic exchange.

Scheme 4



In summary, compound **2** behaves in solution like a partially protonated 2-methylbenzotriazole.

Table 2 shows the geometrical parameters for 2-MeBzTr.$HBF_4.H_2O$ with the numbering system displayed in Figure 1 [10]. As expected, the 2-MeBzTr group is planar with average and maximum deviations of 0.007 and 0.019 Å, respectively [11]. The crystal structure shows no significant differences in the bond lengths and angles between the atoms of both sides of a hypothetical line joining the N2 atom and the mid-point of the C3-C4 bond.

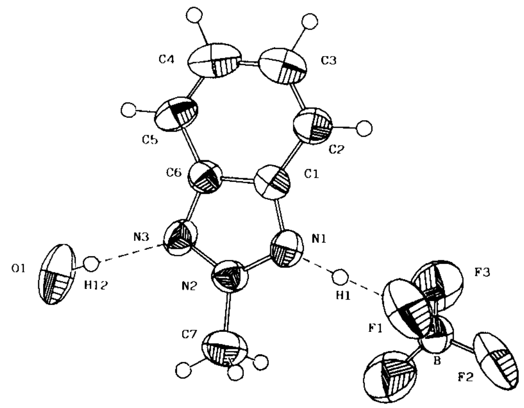


Figure 1. ORTEP (14) drawing of compound **2**.

Table 1

Crystal and Refinement Data for Compound **2**

formula	$C_7N_3H_8 \cdot H_2O \cdot BF_4$
crystal system	Orthorhombic
space group	Pbca
a, Å	16.734 (3)
b, Å	19.153 (9)
c, Å	6.937 (1)
V, Å^3	2223 (1)
Z	8
F(000)	976
ρ (calcd), g cm^{-3}	1.43
temp, °C	22
μ, cm^{-1}	1.34
cryst dimens, mm	0.10 x 0.20 x 0.40
diffractometer	Enraf-Nonuis CAD4
radiation	graphite-monochromated MoKα (λ = 0.71069 Å)
scan technique	ω/2θ
data collected	(0,0,0) to (19,22,8)
rflns collected	1992
unique data	1942
unique data (I) ≥2σ (I)	623
R (int), %	0.76
std rflns	3/42 rflns
decay	≤2% variation
R_F, %	6.0
Rw_F, %	5.6
average shift/error	0.07

Table 2

Bond Lengths (Å) and Bond Angles (°)

E.s.d.'s are Given in Parentheses

C(1) - C(2)	1.40(1)	N(1) - N(2)	1.31(1)
- C(6)	1.39(1)	N(2) - N(3)	1.31(1)
- N(1)	1.35(1)	B - F(1)	1.48(2)
C(2) - C(3)	1.35(1)	- F(2)	1.32(2)
C(3) - C(4)	1.42(2)	- F(3)	1.34(2)
C(4) - C(5)	1.36(2)	- F(4)	1.36(2)
C(5) - C(6)	1.41(1)	N(1) - H(1)	1.22(9)
C(6) - N(3)	1.34(1)	O(1) - H(11)	0.91(9)
C(7) - N(2)	1.47(1)	- H(12)	0.82(9)
C(6)-C(1)-N(1)	108.1(8)	F(2)-B -F(3)	113(1)
C(2) -N(1)	130.9(9)	F(1)- -F(4)	106.4(9)
- -C(6)	121.9(9)	- -F(3)	109(1)
C(1)-C(2)-C(3)	116.2(9)	- -F(2)	109(1)
C(2)-C(3)-C(4)	122.4(9)	C(1)-N(1)-N(2)	102.9(8)
C(3)-C(4)-C(5)	122(1)	H(1)- -C(1)	131(4)
C(4)-C(5)-C(6)	116(1)	H(1)- -N(2)	127(5)
C(1)-C(6)-C(5)	121.4(9)	C(7)-N(2)-N(1)	121.1(8)
C(5)- -N(3)	130.0(9)	N(1)- -N(3)	117.5(8)
C(1)-C(6)-C(5)	108.6(8)	C(7)- -N(3)	121.4(8)
F(3)-B -F(4)	106(1)	C(6)-N(3)-N(2)	102.9(8)
F(2)- -F(4)	114(1)	H(11)-O(1)-H(12)	127(9)

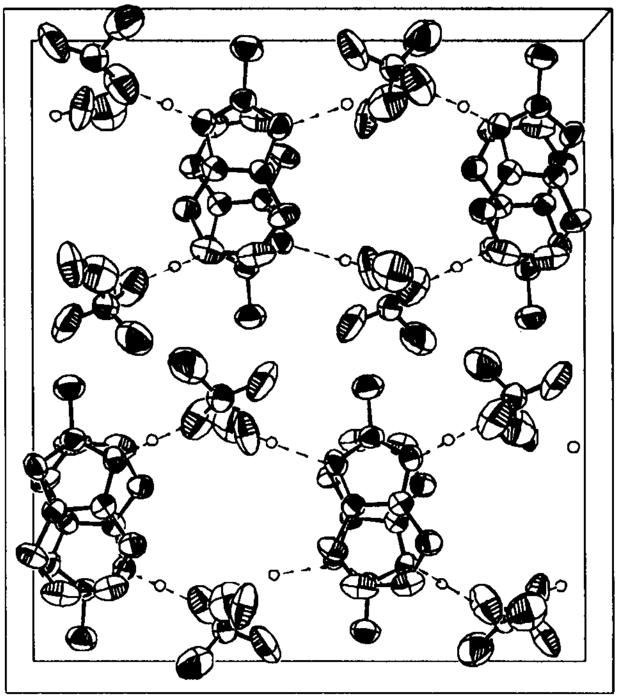


Figure 2. View along the c axis of the unit cell in compound **2**.

In our previous work [6], we have found that theoretically calculated geometries (fully optimized at the 6-31G level) accurately reproduced the experimental geometries of benzotriazole derivatives, when available. This was the case for 1*H*-benzotriazole **6**, 2*H*-benzotriazole **7**, benzotriazole anion and 1,3-di*H*$^+$-benzotriazolium cation **3**. No experimental geometry is known related to 1,2-di*H*$^+$-benzotriazolium cation **4**. In Table 4, the experimental geometry here determined for compound **2** is compared with the calculated geometry of cation **4**. As we have already pointed out, it is immediately apparent that the experimental geometry is near C_{2v} whereas the calculated one for **4** is clearly "assymetric" (C_S). In fact, the experimental geometry closely ressembles that of 2*H*-benzotriazole **7**, *i.e.* it is like a 2-methylbenzotriazole molecule **1** solvated by water and fluoroboric acid ($H_2O\cdots$2MeBzTr$\cdots HBF_4$) (Figure 2).

Table 3

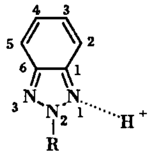
Hydrogen-bond Distances (Å) and Angles (°)
E.s.d.'s are in Parentheses

X-H...Y	X...Y	X-H	H...Y	X-H...Y
O1-H11...F3′	2.81(1)	0.91(9)	1.91(9)	176(9)
O1-H12...N3″	2.83(1)	0.82(9)	2.03(3)	163(9)
N1-H1 ...F1	2.64(1)	1.22(9)	1.44(9)	170(8)

Symmetry code: (′) x,y,z+1; (″) 1/2+x,y,1/2-z

Table 4

Comparison of Experimental and Calculated
Geometries of 2*H*-Benzotriazole



	Experimental [a] **2**	1,2-H+ **4**	Neutral 2H **7**
N(1)-N(2)	1.31	1.348	1.321
N(2)-N(3)	1.31	1.282	
N(1)-C(1)	1.35	1.349	1.334
N(3)-C(6)	1.34	1.343	
C(1)-C(6)	1.39	1.413	1.415
C(1)-C(2)	1.40	1.401	1.420
C(5)-C(6)	1.41	1.413	
C(3)-C(4)	1.42	1.430	1.439
C(4)-C(5)	1.36	1.359	1.356
C(2)-C(3)	1.35	1.368	
N(1)-N(2)-N(3)	117.5	112.5	116.4
N(2)-N(3)-C(6)	102.9	106.9	103.6
N(2)-N(1)-C(1)	102.9	107.1	
C(1)-C(6)-N(3)	108.6	108.5	108.1
C(6)-C(1)-N(1)	104.9	104.9	

[a] Selected distances (Å) and angles (°) from Table 2.

Another way to discuss if the structure of compound **2** corresponds to a solvated 2-MeBzTr **1** or to a salt of benzotriazolium is to examine the hydrogen bonds. The N1-H1 and H1-F1 distances, 1.22(9) and 1.44(9) Å, respectively, suggest an intermediate situation between that of the neutral 2-MeBzTr and its cationic form. The distance B-F1, 1.48(2) Å, is larger than the remaining three B-F distances and shows a stronger F$\cdots$H interaction than is usual for such hydrogen bonds.

The water molecule connects the 2-MeBzTr and the BF_4 groups through the N3....H12 and F3....H11 hydrogen bonds. Although these bonds are weaker than the F1....H1 interaction, as is shown by the corresponding distances (Table 3), they can contribute to "symmetrize" the 2-methylbenzotriazole molecule.

In the case of 1*H*-benzotriazole **6** (pK_a = 1.6 [12]), the resulting cation **3** shows "normal" hydrogen bonds. Thus, the ratio of the N-H bond length over the N$\cdots$X distance is 0.37 for 1,3-diH^+-benzotriazolium dihydrogen phosphate [13] and 0.32 for the corresponding hydrogen sulfate [14]. For 1-phenyl-3,5-dimethylpyrazole (pK_a = 2.3 [12]), its perchlorate (proton on the pyrazole ring) and its oxalate (proton on the oxalic acid) show ratios of 0.36 and 0.37, respectively [15]. The very low basicity of 2-methylbenzotriazole leads to a situation where the proton occupies an intermediate position (ratio: 0.85).

The literature results on hydrogen bonds (HBs) show that two extreme situations are normally found: i) two strong acceptors lead to geometries where the proton is nearly equidistant to both heteroatoms X$\cdots$H$\cdots$Y; ii) a weak and a strong acceptor lead to unsymmetrical HBs, X-H$\cdots\cdots$Y. The structure of 2MeBzTr.$HBF_4.H_2O$ is one of the rare examples of two weak HB acceptors, which results in a quasi symmetrical situation X$\cdots\cdots$H$\cdots\cdots$Y, but, in this case, with a long X$\cdots$Y distance (N1$\cdots$F1 = 2.64 Å).

EXPERIMENTAL

The melting point is uncorrected. The ir spectrum was recorded on a Perkin-Elmer 781 spectrophotometer. The ^1H-nmr spectrum was recorded both at 60 MHz (Varian T-60) and at 300 MHz (Varian VXR-300S), while the ^{13}C-nmr spectrum was recorded on a Varian FT-80 spectrometer. In all cases, tetramethylsilane was used as internal standard.

Synthesis of 2-methylbenzotriazolium Tetrafluoroborate.

To a solution of 2-methylbenzotriazole (10 mmoles) in ethanol (20 ml), 2.7 g of 32% aqueous tetrafluoroboric acid was added and the mixture stirred for 1 hour at room temperature. After removing the solvent under vacuum, 2-methylbenzotriazolium tetrafluoroborate was obtained in 96%, mp 126-128° (ethyl acetate); ir (potassium bromide): 3700-2800 (N-H), 1200-950 cm^{-1} (B-F).

Anal. Calcd. for $C_7H_8N_3BF_4 \cdot H_2O$: C, 35.18; H, 4.22; N, 17.58. Found: C, 35.56; H, 4.18; N, 17.63.

The ^1H-nmr (deuteriochloroform): 4.67 (s, 3H, N-CH_3), 7.55 (m, 2H, H5 and H6), 7.97 ppm (m, 2H, H4 and H7). At 60 MHz, aromatic protons appear like an AA'BB' system with the multiplet corresponding to protons H4 and H7 slightly broad. Increasing the frequency up to 300 MHz produces a considerable broadening of all the AA'BB' signals, which results in the loss of the fine coupling structure; ^{13}C-nmr (deuteriochloroform): 43.3 (N-CH_3), 117.6 (C4 and C7), 128.2 (C5 and C6), 142.2 ppm (very broad, C3a and C7a). The T_1 values of 2-methylbenzotriazole in trifluoroacetic acid were determined in the Varian VXR-300S apparatus using the inversion recovery technique.

Crystallography.

A summary of the fundamental crystal data is given in Table 1. The crystal was silicon grease coated, introduced into a glass capillary and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflexions. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms were taken from the International Tables for X-Ray Crystallography [16]. The structure was solved by MULTAN [17] and Fourier methods. An empirical absorption correction [18] was applied at the end of the isotropic refinement. A difference synthesis calculated with those reflexions with sin θ/λ = 0.5 Å showed all H atoms as the highest peaks of the map. A final refinement was undertaken with fixed isotropic factors and coordinates for all H atoms, except H1, H11 and H12, whose coordinates were refined. Most of the calculations were carried out with the X-Ray 80 system [19].

Acknowledgements.

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REFERENCES AND NOTES

[1] A de la Hoz, E. Diez-Barra, M. C. Pardo, J. P. Declercq, G. Germain, M. van Meerssche and J. Elguero, *Tetrahedron*, **39**, 2193 (1983).

[2] A. de la Hoz, C. Pardo and J. Elguero, *Tetrahedron Letters*, **26**, 3869 (1985).

[3] J. Elguero, A. de la Hoz and C. Pardo, *Croatica Chem. Acta*, **59**, 153 (1986).

[4] A. de la Hoz, M. C. Pardo, J. Elguero and A. Fruchier, *Magn. Reson. Chem.*, **27**, 603 (1989).

[5] M. M. Ramos Gallego, Ph.D. Thesis, Madrid, 1992.

[6] F. Tomás, J. L. M. Abboud, J. Laynez, R. Notario, L. Santos, S. O. Nilsson, J. Catalán, R. M. Claramunt and J. Elguero, *J. Am. Chem. Soc.*, **111**, 7348 (1989).

[7] M. Begtrup, J. Elguero, R. Faure, P. Camps, C. Estopá, A. Fruchier, C. Marzin and J. de Mendoza, *Magn. Reson. Chem.*, **26**, 134 (1988).

[8] J. P. Fayet, M. C. Vertut, A. Fruchier, E. M. Tjiou and J. Elguero, *Org. Magn. Reson.*, **11**, 234 (1978).

[9] L. Vander Elst, Y. Van Haverbeke, A. Maquestiau and R. N. Muller, *Magn. Reson. Chem.*, **25**, 16 (1987).

[10] C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.

[11] M. Nardelli, A. Musatti, P. Domiano and G. D. Andreetti, *Ric. Sci. Part 2, Sez. A*, **8**, 807 (1965).

[12] J. Catalán, J. L. M. Abboud and J. Elguero, *Adv. Heterocyclic Chem.*, **41**, 187 (1987).

[13] J. Emsley, N. M. Reza, H. M. Dawes and M. B. Hirsthouse, *J. Chem. Soc., Chem. Commun.*, 1458 (1985).

[14] F. Giordano, *Acta Crystallogr.*, **B36**, 2458 (1980).

[15] J. Zukerman-Schpector, E. E. Castellano, G. Oliva, A. C. Massabni and A. D. Pinto, *Can. J. Chem.*, **62**, 725 (1984).

[16] International Tables for X-Ray Crystallography, Vol **IV**, Kynoch Press, Birmingham, 1974, pp 72-98.

[17] P. Main, L. Lessinger, M. M. Woolfson, G. Germain and J. P. Declercq. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of York, England and Louvain, Belgium.

[18] N. Walker and D. Stuart, *Acta Crystallogr.*, **A39**, 158 (1983).

[19] J. M. Stewart, The XRAY80 System, Computer Science Center, University of Maryland, College Park, 1985.