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An experimental (NMR) and theoretical (GIAO) study of the tautomerism of benzotriazole in solution

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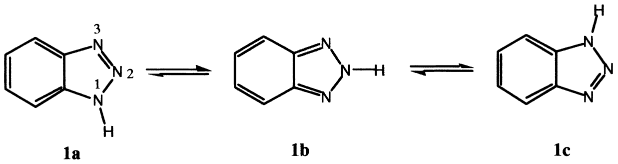
Abstract—The ^1H, ^{13}C and ^{15}N chemical shifts of benzotriazole and its adducts with acetone have been measured. Using dynamic ^{13}C NMR spectroscopy in the $+30/-90$°C range, the barrier to prototropy in benzotriazole has been determined (10.8 kcal mol^{-1} at 294 K). The thermodynamic parameters corresponding to the equilibria between benzotriazole and its two acetone adducts have been measured. GIAO calculations (B3LYP/6-311++G**) have been carried out on 1*H*-benzotriazole tautomer: they provide a sound basis for signal assignment of all the nuclei. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The most interesting cases of annular tautomerism are those balanced, that is, where both tautomers have similar energies. This is the case of 1,2,3-triazole[1] and of benzotriazole **1**. This last compound can exist in three tautomeric forms, **1a**–**c**, two of them being degenerated in the absence of isotopic labeling (Scheme 1).



Scheme 1.

The situation is well summarized in lit.[1] (references till 1998): in the gas phase at 0 K the most stable tautomer is the 2*H*, **1b**, but in the solid state and in solution, the only observed tautomer is the 1*H*, **1a** (or 3*H*, **1c**). In the gas phase, the population of the 1*H*-tautomer increases with temperature.[2,3] More recent work confirms these findings.[4–6]

All this concerns the thermodynamic part of the problem, but what about the kinetic aspects? Assuming that only **1a** and **1c** are present in solution, what information do we have about the proton transfer between N-1 and N-3? For instance, it has been established that the proton transfer in azoles, even between adjacent nitrogen atoms, is not an intramolecular process but an intermolecular one usually requiring several solvent molecules.[7]

The information about proton transfer in benzotriazole is scarce. Actually, the only relevant publication is an older one by Nesmeyanov et al.[8] using ^1H NMR spectroscopy. Working in anhydrous THF and under argon atmosphere, the AA′BB′ system of the four aromatic protons (0°C) becomes an ABCD system at −100°C. The NH signal becomes narrower on cooling, values for the line width ν being 56 Hz at 56°C and 2 Hz at −100°C. The authors have used a modified Arrhenius equation [$\log \nu = \log \nu_0 - (E_a/4.57T)$] to calculate an E_a=2.4 kcal mol^{-1}.[8,9]

In what concerns ^{13}C or ^{15}N NMR spectroscopy in solution, there was no report on slowing down the exchange rate and transforming the average spectrum of C_{2v} symmetry of **1a**/**1c** into the actual C_s symmetry of **1a**. In the case of ^{15}N NMR, only two signals were reported, one for N-2 and the other for N-1/N-3.[10] This was so until a paper by Elsevier et al.[11] where the ^{14}N NMR spectra of benzotriazole in supercritical CO_2/acetone and in benzene were described. We have adapted a figure of that publication to estimate the ^{14}N chemical shifts (not reported). These chemical shifts are referred to (almost) pure nitromethane (ca. 5% of $CDCl_3$).[11] We measured from Fig. 1, −15, −43 and −177 ppm in CO_2/acetone and 0, −27, −67* (N_2 gas) and −168 ppm in benzene.

2. Results and discussion

The assignment of the three nitrogen atoms is not correct,[10,12]

Keywords: benzotriazole; tautomerism; NMR; GIAO.

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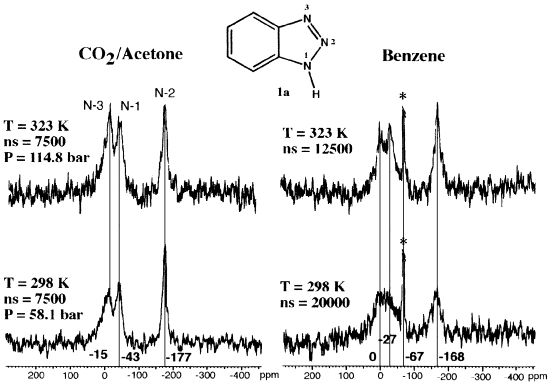


Figure 1. ^{14}N NMR chemical shifts of **1** obtained in CO_2/acetone (left) and benzene (right), adapted from Fig. 2 of lit.[11]

the correct one is −15 (N-2), −43 (N-3) and −177 ppm (N-1) in CO_2/acetone and 0 (N-2), −27 (N-3) and −168 ppm (N-1) in benzene. The most important result of Elsevier[11] is that the prototropic exchange is blocked or, at least, slow in CO_2/acetone solution both in the liquid (298 K) and supercritical states (323 K). It is relatively better resolved at 323 K, although Elsevier concludes that the τ_c values of the ^{14}N resonances are similar. Taking into account that the coalescence should affect N-1 (−177 ppm) and N-3 (−43 ppm), then the broadening of the signal at −15 ppm (N-2) is not due to a decrease in the prototropic rate. There is a supplementary complication, since it is known from 1969 that NH-azoles add reversibly to acetone to yield N–$(CH_3)_2$OH adducts.[13,14] These adducts can be observed by ^{1}H and ^{13}C NMR but not directly by ^{15}N NMR.

Katritzky et al.[15] have studied, by ^{1}H and ^{13}C NMR spectroscopy, the behavior of equimolar mixtures of benzotriazole and carbonyl compounds in benzene and reported that in the case of acetone the addition products are not observed (K<0.001). Some of us have described the formation of adducts **2a** and **2b** in pure acetone at −40°C.[16] The 1-substituted adducts are more abundant than the 2-substituted ones.[15] Nobody has reported the evolution of the total amount and the proportion of azole–acetone adducts with temperature, although it is known that they are only observed at low temperatures.[13,14] Those corresponding to benzotriazole are reported in a review where their ^{13}C chemical shifts are given in Fig. 2.[16]

In the related topic of N-(aminomethyl)benzotriazole derivatives,[17–19] the following conclusions have been reached: (i) between −50 and +40°C, there is no significant change in the isomer distribution (**a**/**b** ratio); (ii) polar solvents increase the population of the 1-substituted isomer **a**; (iii) isomers interconvert with barriers of the order of $\Delta G^{\ddagger}$=15–18 kcal mol^{-1} by dissociation into benzotriazolate anion and iminium cation.

In any case, the phenomenon of slow prototropy was also observed by Elsevier in benzene and here, clearly, ^{14}N signals become narrower on heating, fact that the authors assigned to a reduction of the linewidths by a decrease of the viscosity of the solvent, according to the Stokes–Einstein–Debye model.[11]

2.1. Proton and carbon-13 NMR study

The assignment of the signals was straightforward considering the large number of publications dealing with the ^{13}C NMR spectroscopy of benzotriazoles,[8,15,16] in particular the ^{13}C NMR spectrum obtained for **1a** in the solid state, where no prototropy intervenes.[20] The results are reported in Tables 1 and 2. The assignments of the protons have been ascertained by a TOCSY experiment with selective irradiation at 8.2 ppm.

We decided first to study by ^{1}H and ^{13}C NMR spectroscopy the behavior of benzotriazole in acetone-d_6 at different temperatures. We wanted to calculate the equilibria **1**⇌**2** and **2a**⇌**2b** as well the kinetic aspects of the interconversion **1a**⇌**1c** (the amount of **1b** is negligible). We have recorded eleven ^{1}H and ^{13}C NMR spectra between +30 and −90°C. The ^{13}C experimental spectra were subject to a deconvolution program that yields the percentages of free benzotriazole **1** and its two adducts **2a** and **2b**. We have defined K_{12} as [**1**]/[**2a**+**2b**] and K_{2a2b} as [**2a**]/[**2b**]. The results are reported in Table 3. Regressions yield the thermodynamic data: ΔH^0_{12}=2.2 kcal mol^{-1}, ΔS^0_{12}=

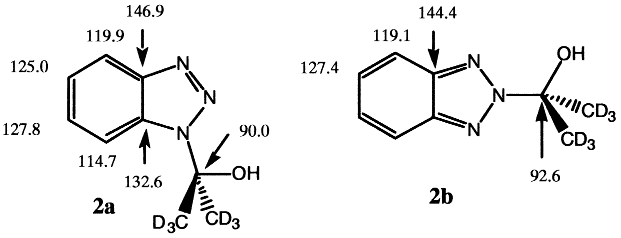


Figure 2. ^{13}C chemical shifts of acetone adducts.

Table 1. ^{1}H NMR chemical (δ ppm) shifts in acetone-d_6

Comp.	Temperature (°C)	H4	H5	H6	H7
1a/1c	+21.4	8.00	7.44	7.44	8.00
2a	+21.4	8.20	7.36	7.47	8.06
1a	−85.0	8.11	7.48	7.48	8.05
2a	−85.0	8.28	7.45	7.56	8.11

Table 2. ^{13}C NMR chemical shifts

Comp.	State	T (°C)	C4	C5	C6	C7	C3a	C7a	N–R
1a/1c	DMSO-d_6^a	25	115.1	125.7	125.7	115.1	139.2	139.2	–
1[a]	Solid[a]	25	115.5	123.4	123.4	110.7	144.2	132.7	–
1a/1c	Acetone-d_6	25	115.2	126.0	126.0	115.2	139.3	139.3	–
1a	Acetone-d_6	−83.7	118.9	124.8	128.0	111.8	144.5	133.5	–
2a	Acetone-d_6	−83.7	119.3	124.8	127.5	114.4	146.2	132.2	89.8
2b	Acetone-d_6	−83.7	118.7	127.1	127.1	118.7	143.9	143.9	92.6

[a] Lit.[20]

Table 3. Populations of **1a**, **2a** and **2b** and rates of the interconversion **1a**$\rightleftharpoons$**1c**

T (°C)	*T* (K)	% **1**	% **2a**	% **2b**	*k* (s^{-1})	ln *k*
−90.0	183.15	70.2	24.6	5.2	140	4.942
−85.0	188.15	73.7	21.5	4.8	230	5.438
−80.0	193.15	76.0	19.5	4.5	480	6.174
−70.0	203.15	81.5	15.3	3.2	980	6.888
−59.7	213.45	84.6	12.8	2.6	2,200	7.696
−40.0	233.15	89.0	9.2	1.8	6,800	8.825
−20.0	253.15	91.7	6.9	1.4	14,500	9.582
0.0	273.15	94.5	4.5	1.0	34,500	10.449
10.0	283.15	95.2	4.0	0.8	50,000	10.820
21.4	294.55	96.9	2.5	0.6	60,000	11.002
30.0	303.15	96.5	2.95	0.55	72,500	11.191

-13.8 cal mol^{-1} K^{-1} ($r^2=0.998$) and $\Delta H^0_{\mathbf{2a2b}}=0.08$ kcal mol^{-1}, $\Delta S^0_{\mathbf{2a2b}}=-3.5$ cal mol^{-1} K^{-1} ($r^2=0.97$). Therefore, (i) the equilibrium is shifted towards the adducts (**2a**+**2b**) when the temperature decreases and (ii) the composition of the mixture of adducts (**2a**/**2b**) is very insensitive to temperature, both observations being in agreement with results on *N*-(aminomethyl)benzotriazole derivatives.[17–19] The closest example with carbonyl compounds was reported by Katritzky[15] and concerns an equimolar mixture of **1** and cyclohexanone in benzene where they measured $K_{\mathbf{2a2b}}=2.9$ (in our case $K_{\mathbf{2a2b}}$ at 21.4° is 4.7).

When discussing $K_{\mathbf{2a2b}}$, it is necessary to consider that there is a twofold probability of obtaining **2a** than **2b**, due to the equivalence of N-1 and N-3 atoms. Therefore, on pure statistical grounds, $K_{\mathbf{2a2b}}$ should be equal to 2 (66–33%). Since we have measured a value of 4.7, there is an extra stabilization of **2a** over **2b**, that could be intrinsic (but this seems improbable because **1b** is more stable than **1a** in the gas phase at 0 K) or due to a solvent effect. According to the previous discussion, polar solvents should favor **2a**.

At low temperatures, for instance at −85°C, we observe two additional signals, one narrow at 106.83 ppm and another large, probably a septuplet, at 28.14 ppm (clearly a CD_3–X–CD_3 group). We will try to identify these peaks in the part concerning the GIAO calculations.

Turning now to the kinetic aspect of the equilibrium **1a**$\rightleftharpoons$**1c**, we have calculated the rates by visual comparison between the eleven ^{13}C NMR experimental spectra and those obtained with different rates using the program gNMR. The results are reported on Table 3.

A treatment of these data using the Eyring's equation leads to $\Delta G^{\ddagger}_{294}=10.8$ kcal mol^{-1}, $\Delta H^{\ddagger}=5.1\pm0.2$ kcal mol^{-1} and a $\Delta S^{\ddagger}=-19\pm1$ cal mol^{-1} K^{-1} ($r^2=0.989$). The use of the Arrhenius equation leads to the following values: $E_a=5.7\pm0.2$ kcal mol^{-1} and $\log A=20.9\pm0.3$ ($r^2=0.994$). This barrier is higher than that reported by Nesmeyanov, $E_a=2.4$ kcal mol^{-1}.[8,9] An examination of the residuals of these models show that they are not random because there is a small but clear curvature in the plots. Therefore, we decided to use another model: $\ln k_{exp} = \ln k_0 + E/RT + C/R \ln T$.[21] This model led to $\ln k_0=117\pm18$, $E=12.5\pm1.3$ kcal mol^{-1} and $C=29.4\pm5.6$ ($r^2=0.999$). This points out to a more complex mechanism for the **1a**$\rightleftharpoons$**1c** equilibrium, maybe involving tautomer **1b** or the adducts **2a** and **2b**. We have summarized in Table 4 other prototropic barriers measured for azoles.

An examination of Table 4 shows that Nesmeyanov's value is probably underestimated. Minkin[1] has pointed out that large and negative values of $\Delta S^{\ddagger}$ correspond to complex mechanisms rather than to the simple ionization reaction facilitated by the solvent. The participation of **1b** in the transfer mechanism cannot be excluded but intramolecular 1,2-shifts of protons in azoles are energetically prohibited.[7]

2.2. Nitrogen-15 results

A natural abundance ^{15}N NMR experiment has been performed at 50.7 MHz in benzene where **1** is very insoluble, but after 48 h no signal was detected. We conclude that the ^{14}N NMR spectrum of Fig. 1 must have been obtained with a very diluted solution, which is probably relevant for slowing down the prototropic

Table 4. Activation barriers in kcal mol^{-1}

Azole	Solvent	E_a[a]	$\Delta G^{\ddagger}$[b]	Method	Lit.
Benzotriazole	THF	2.4	–	^1H NMR	8,9
Benzotriazole	Acetone	5.7	10.8	^{13}C NMR	This work
Benzotriazole	$CHCl_3$	–	11.0[c]	^{15}N NMR	1,22
1,2,3-Triazole	CH_2Cl_2	–	11.7	^1H NMR	1,7
1,2,4-Triazole	HMPA	–	14.7	^1H NMR	1,9
1,2,4-Triazole	DME	–	15.5	^1H NMR	1
1,2,4-Triazole	CH_2Cl_2	–	13.5	^1H NMR	1
Pyrazole	HMPA	–	15	^1H NMR	1
Pyrazole	Ether/THF	–	11	^{13}C NMR	1
Pyrazole	DMSO	–	14.8	^{13}C NMR	1
4-Nitropyrazole	Acetone	–	10	^1H NMR	9
3,5-Dimethyl-4-nitropyrazole	Acetone	–	9.5	^1H NMR	9
4-Trimethylsilylpyrazole	CH_3OH	–	11.9	^1H NMR	7
3(5)-Methylpyrazole	CH_3OH	–	10	^{13}C NMR	7
2-Chlorobenzimidazole	THF	4.25	10.9	^1H NMR	9

[a] Arrhenius equation ($\log k = \log A - E_a/4.57T$).
[b] Eyring equation ($\log k/T = 10.32 + \Delta S^{\ddagger}/4.57 - \Delta H^{\ddagger}/4.57T$).
[c] Using ^{15}N line-widths between+35 and +47°C.[22]

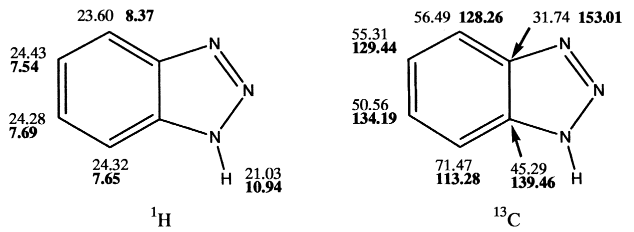


Figure 3. Calculated absolute shieldings (σ ppm) ^{1}H and ^{13}C NMR chemical shifts (δ ppm bold).

tautomerism. Our sample of benzotriazole in benzene shows, at room temperature, ^{13}C NMR signals (100.6 MHz: 115.1 ppm broad, C4+C7; 125.7 ppm, C5+C6, and 139.0 ppm very broad, C3a+C7a) consistent with a slow prototropic exchange.

2.3. GIAO theoretical studies

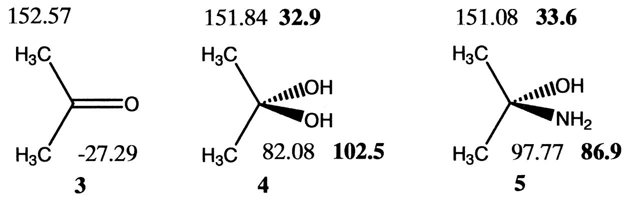
We carried out GIAO/B3LYP/6-311++G** calculations on tautomer **1a**. The usual approach[23] is to correlate directly calculated absolute shieldings σ and experimental chemical shifts δ, using or not the reference (TMS for ^{1}H and ^{13}C and pure MeNO$_2$ for ^{15}N). In this paper we will use the calculated shieldings (at the same level) of TMS (^{1}H 31.97 ppm, ^{13}C 184.75 ppm)[24] and simply subtract them from the calculated values. For ^{15}N, due to the fact that the difference between MeNO$_2$ pure liquid (δ=0.000 by definition) and MeNO$_2$ gas is unknown, we will use an indirect approach.

2.3.1. ^{1}H NMR. We have represented graphically, the absolute shieldings and the chemical shifts (in bold) of benzotriazole **1a** (see Fig. 3). It is difficult to compare the calculated ^{1}H chemical shifts with the experimental ones reported in Table 1. On one hand, solvent effects are important in ^{1}H NMR, on the other, even at −83.7°C, the ^{1}H NMR spectrum is still very broad and the assignment of Table 1 only tentative. Nevertheless, the calculated value of 7.65 ppm for H7 does not seem reasonable.

2.3.2. ^{13}C NMR. Between the values determined at −83.7°C (Table 2) and the calculated $\delta\,^{13}$C values (including TMS), there is the following relationship, Eq. (1):

$$\delta^{13}\mathrm{C}_{\mathrm{exp}} = (0.954 \pm 0.007)\delta^{13}\mathrm{C}_{\mathrm{calc}}, \qquad n = 7, \quad r^2 = 1.000 \tag{1}$$

The worse points correspond to C4 and C7 signals: a reasonable explanation is that acetone hydrogen-bonded to N-1 of **1a** to form an N1–H···O=C complex that perturbates these carbon atoms chemical shifts.



3 **4** **5**

Figure 4. Calculated absolute shieldings (σ ppm) and ^{13}C NMR chemical shifts (δ ppm bold).

We have proposed that the two unexplained signals at 106.83 ppm (narrow) and at 28.14 ppm (broad septuplet) could correspond to the acetone hydrate (2,2-propanediol). We have calculated at the same level three compounds: acetone (**3**), 2,2-propanediol (**4**) and 2-amino-2-propanol (**5**) (as a model of adducts) and reported the result in Fig. 4.

If we put together our present calculations for benzotriazole (**1a**) and acetone (**3**) with those we previously reported for simple compounds,[24] the following equation is obtained:

$$\delta^{13}\mathrm{C}_{\mathrm{Exp}} = (1.000 \pm 0.009)\delta^{13}\mathrm{C}_{\mathrm{Calc}}, \qquad n = 19, \quad r^2 = 0.999 \tag{2}$$

This equation predicts for 2,2-propanediol (**4**) and 2-amino-2-propanol (**5**) the chemical shifts reported in Fig. 4. The 86.9 ppm value of **5** is close to that at 89.8 ppm of **2a** but those of **4** do not correspond to the unexplained signals at 106.8 and 28.1 ppm (even taking into account the isotope effect between acetone, 30.7 ppm, and perdeuteroacetone, 29.8 ppm). A spectrum of acetone-d_6 at −85°C containing a drop of water does not show any supplementary signals.

2.3.3. ^{15}N NMR. Both Stefaniak et al.[12] and ourselves[25] have used the GIAO approach to calculate the absolute shieldings of the three nitrogen atoms of **1a**. They have used a base [3s,3p,1d/3s,1p] that is close to HF/STO-3G** basis set and the X-ray geometry of benzotriazole; as we will see, their relative values are good but the reference, nitromethane, has not be included. We have used previously, a DFT approach, B3LYP/6-31G*, that allows to include nitromethane.[25] Now we have increased the level of the basis set up to B3LYP/6-311++G** and calculated the three nitrogen atoms of benzotriazole, the reference, ammonia and the dinitrogen molecule, whose experimental ^{15}N chemical shift is known (−75.2 ppm).[26] All the results are reported in Table 5.

On comparing the three theoretical methods, we found:

$$\sigma\mathrm{HF/STO\text{-}3G^{**}} = (1.30 \pm 0.03)\sigma\mathrm{B3LYP/6\text{-}311{+}{+}G^{**}}, \qquad n = 3, \quad r^2 = 0.999 \tag{3}$$

$$\sigma\mathrm{B3LYP/6\text{-}31G^{*}} = (23 \pm 2) + (0.90 \pm 0.01)\sigma\mathrm{B3LYP/6\text{-}311{+}{+}G^{**}}, \qquad n = 6, \quad r^2 = 0.999 \tag{4}$$

The calculated σ values obtained using the STO-3G* base are proportional to those obtained using the largest one (no intercept) but this base is unable to reproduce the value of nitromethane (estimated experimental absolute shielding in the gas phase −143 ppm),[23] moreover, the slope is far from 1. The two other bases are related but using nitromethane as a test, the 6-31G* yields a value of −117.75 ppm while the 6-311++G** affords −154.43 much closer to the estimated experimental value. Therefore, in the following discussion we will limit ourselves to the results obtained at B3LYP/6-311++G** level. It is not possible to compare

Table 5. ^{15}N absolute shieldings (σ) and experimental chemical shifts (δ values), both in ppm

N	CPMAS	CO_2/acetone	Benzene	HF/STO-3G**	B3LYP/6-31G*	B3LYP/6-311++G**
Lit.	10,12	Fig. 1	Fig. 1	12	20	This work
N-1	−157.6	−177.0	−168.0	37.3	51.02	25.06
N-2	−11.8	−15.0	0.0	−209.3	−117.47	−158.34
N-3	−56.4	−43.0	−27.0	−164.6	−90.79	−130.25
	Experimental (σ values)		Calculated (σ values)			
	Gas phase	Benzene solution[11]	B3LYP/6-31G*	B3LYP/6-311++G**		
N_2 gas	−75.3[a]	−67.0	−55.79[b]	−79.81		
CH_3NO_2 gas	−143[c]	–	−117.75	−154.43		
NH_3 gas	264.5[c]	–	254.97[b]	259.37		

[a] Lit.[26]

[b] This work.

[c] Lit.[23]

directly the calculated value of nitromethane (−154.43 ppm, supposedly in the gas phase) with the value used as reference (δ=0.000 for the pure liquid). It is necessary to correct the −154.43 ppm value by the effect obtained for $MeNO_2$ in cyclohexane extrapolated at infinite dilution (−9.05 ppm),[27] that is $\sigma\,^{15}N=-163.48$ ppm.

$$\delta\text{CPMAS} = -(140 \pm 10) - (0.79 \pm 0.08)\sigma\text{B3LYP/6-311} + +\text{G}^{**}, \quad (5)$$

$$n = 5,\ \ r^2 = 0.968$$

$$\delta\text{CO}_2/\text{acetone} = -(155 \pm 6) - (0.90 \pm 0.04)\sigma\text{B3LYP/6311} + +\text{G}^{**}, \quad (6)$$

$$n = 4,\ \ r^2 = 0.995$$

$$\delta\text{Benzene} = -(143 \pm 3) = -(0.90 \pm 0.02)\sigma\text{B3LYP/6-311} + +\text{G}^{**}, \quad (7)$$

$$n = 5,\ \ r^2 = 0.998$$

In this case we have only five points (the three of benzotriazole **1a** plus N_2 gas and nitromethane) but a range of about 420 ppm, note that the all intercepts are close to the absolute shielding of nitromethane, −143 ppm.[23] Between CO_2/acetone and benzene, there is a shift of 12 ppm (the slopes are the same). In the case of CPMAS, the signal of N-3 deviates significantly. If one removes it, then Eq. (6) is found:

$$\delta\text{CPMAS} = -(138 \pm 3) - (0.82 \pm 0.03)\sigma\text{B3LYP/6-311} + +\text{G}^{**}, \quad (8)$$

$$n = 4,\ \ r^2 = 0.998$$

This equation predicts −26.3 ppm for N-3, that is, +30 ppm from the experimental value of −56.4 ppm (Table 4). We have already noted that in azoles, the N–H···N hydrogen bond (HB) network present in the solid state (benzotriazole crystallizes forming an N(1)–H···N(3) HB chain)[28] strongly modifies the signal of the N atom that accepts the HB.[25]

3. Conclusions

The main conclusions of the work presented here are:

(i) We have determined the activation barrier for the proton transfer of benzotriazole in acetone solution using a wide range of temperatures (between +30 and −90°C). Although the value of the barrier agrees with that determined by Wofford, Forkey and Russell in chloroform,[22] their small range (+35 to +47°C) makes our value more reliable. Moreover, we were able to determine, for the first time, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this process.

(ii) The accuracy of our measurements allows to find that a more complex kinetic expression is necessary to explain the measured rates. This has never been previously found for any of the compounds of Table 4.

(iii) We have measured the effect of the temperature on the equilibrium between benzotriazole and its two acetone adducts, thus obtaining all the thermodynamic parameters for the three equilibria.

(iv) GIAO calculations have been analyzed and their successes and failures reported. For instance, the abnormal value of H-7 in ^1H NMR, the excellent result obtained with the ^{13}C NMR data, and the difficulties inherent to nitromethane as a bulk reference in ^{15}N NMR.

(v) The comparison between calculated absolute shieldings and solid state ^{15}N CPMAS chemical shifts has been used to identify the N-3 atom as the site of a hydrogen bond.

4. Experimental

The NMR study has been carried out in a Varian Unity 500 spectrometer working at 499.9 MHz (^1H), 125.7 MHz (^{13}C) and 50.7 MHz (^{15}N). For the first two nuclei an inverse H-X detection probe equipped with gradients has been used. The sample (5 mg) was dissolved in 0.6 mL of perdeuterated acetone. Eleven spectra were recorded at +30.0, +21.4, +10.0, 0.0, −20.0, −40.0, −59.7, −70.0, −80.0, −85.0 and −90.0°C, in this order. It is important to go from rt to low temperatures, otherwise, a rapid cooling of the solution makes the addition to acetone very slow and the percentages of adducts do not correspond to equilibrium mixtures. All the ^{13}C NMR spectra (110–150 ppm region) were submitted to deconvolution because many signals overlap, mainly at the higher temperatures. The calculation of the full shape of the ^{13}C NMR spectrum line was performed with the use of the gNMR v 4.0 program.[29] Activation parameters of the dynamic process were determined from the Eyring plot of the determined rate constants against the temperature (in K). Calibration of the thermostabilization system was performed by the registration of ^{1}H NMR spectra of methanol.

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