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A MULTINUCLEAR NMR SPECTRAL STUDY OF PARENT AZOLES AND BENZAZOLES: EXPERIMENTAL RESULTS AND GIAO *AB INITIO* CALCULATIONS

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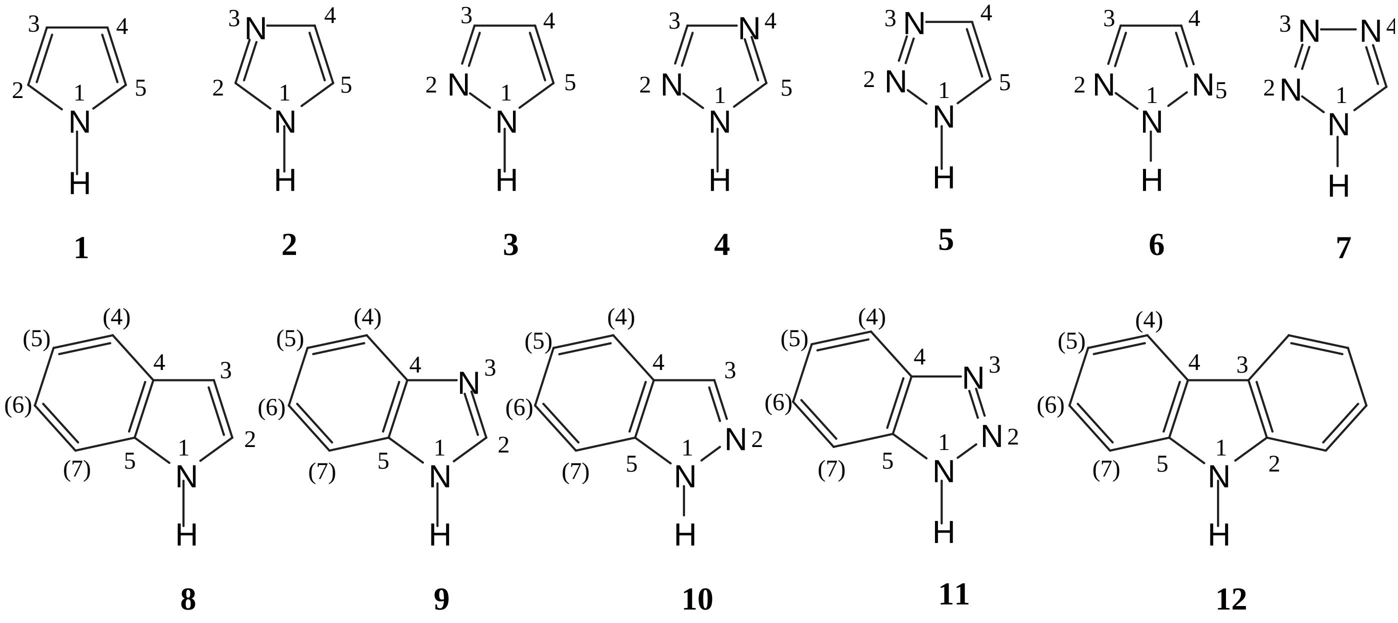
Abstract– The ^{13}C and ^{15}N chemical shifts of twelve azoles and benzazoles have been determined in the solid state at room temperature and in methanol solution at 178 K. The experimental values were compared with the absolute shieldings calculated at the GIAO/B3LYP/6-31G* level. These comparisons show that some signals, ^{13}C NMR but especially ^{15}N NMR, have to be corrected for hydrogen bonds present in certain solvents and in the solid state. The linear regressions are good enough to be used to predict some missing values.

INTRODUCTION

The NMR spectral properties of *N*-unsubstituted azoles and benzazoles are blurred by the annular tautomerism,[1] which averages the signals corresponding to tautomeric positions, those that permute by prototropy. There are several possibilities to overcome this difficulty: i) to use "fixed" (or "blocked") models, i.e. *N*-substituted derivatives;[1] ii) to block the tautomerism recording the spectra at low temperatures; iii) to block the tautomerism recording the spectra in the solid state, and iv) to carry out theoretical calculations on the isolated molecules. The first approach has the inconvenient that the substituent on the nitrogen, generally a methyl group, modifies the NMR spectral parameters in an unpredictable way (some authors have suggested other substituents that produce lesser effects).[2] The second approach requires conditions and solvents that are not standard; moreover, the tautomeric rate of some azoles is difficult to slow down. The third approach introduces solid-state effects that can be important. Finally, the fourth approach yield absolute shieldings corresponding to the monomer in the gas phase.

In this paper we have decided to combine approaches ii, iii and iv, together with average values reported in the literature,[3-5] in an attempt to determine the perturbations introduced by each method on the different nuclei, ^{13}C and ^{15}N (^{1}H chemical shifts are difficult to measure in the solid state). Of the seventeen possible azoles and benzazoles, five should be removed because the corresponding tautomers do not exist in the solid state: isoindole, 4*H*-1,2,4-triazole, 2*H*-tetrazole, 2*H*-indazole and 2*H*-benzotriazole. The remaining twelve compounds are gathered in Scheme 1, the X-Ray structure of all of them has been determined, only 1,2,3-triazole, when solid, is a 1:1 mixture of the two tautomers (**5** and **6**).[6,7]



Scheme 1

RESULTS AND DISCUSSION

In Table 1 we have collected the calculated relative shieldings and in Tables 2 and 3 the experimental values. We have adopted a numbering, which is not standard for 2*H*-1,2,3-triazole (**6**) and for compounds (**8-12**), but that allows the possibility to have, in the same column, the same type of atoms. In Table 1 we have added the conventional numbering between parentheses. We have illustrated in Scheme 2 the case of pyrazole (**3**).

Table 1. ^{13}C and ^{15}N Relative Shieldings (ppm) [GIAO/B3LYP/6-31G*] and Their Classical Numbering between Parentheses

Compd	N(1)	Position 2	Position 3	Position 4	Position 5	C(4)	C(5)	C(6)	C(7)
1	-232.60	107.86 C(2)	102.21 C(3)	102.21 C(4)	107.86 C(5)	-----	-----	-----	-----
2	-224.22	124.14 C(2)	-110.08 N(3)	122.53 C(4)	106.78 C(5)	-----	-----	-----	-----
3	-183.64	-75.22 N(2)	131.33 C(3)	99.52 C(4)	117.98 C(5)	-----	-----	-----	-----
4	-179.59	-86.74 N(2)	144.54 C(3)	-120.23 N(4)	132.63 C(5)	-----	-----	-----	-----
5	-153.69	-14.02 N(2)	-19.41 N(3)	125.05 C(4)	112.77 C(5)	-----	-----	-----	-----
6	-140.20 N(2)	-52.45 N(1)	126.60 C(4)	126.60 C(5)	-52.45 N(3)	-----	-----	-----	-----
7	-162.92	-15.54 N(2)	25.58 N(3)	-42.43 N(4)	131.73 C(5)	-----	-----	-----	-----
8	-250.84	114.97 C(2)	97.34 C(3)	121.06 C(3a)	126.11 C(7a)	114.34	113.70	115.63	103.11
9	-238.19	129.73 C(2)	-123.43 N(3)	135.96 C(3a)	124.90 C(7a)	115.64	115.54	116.96	102.76
10	-204.38	-63.10 N(2)	127.00 C(3)	117.99 C(3a)	130.90 C(7a)	114.47	114.33	119.71	101.72
11	-168.77	-0.28 N(2)	-26.96 N(3)	137.76 C(3a)	124.74 C(7a)	115.42	116.52	121.04	101.71
12	-263.97 N(9)	130.90 C(9a)	117.38 C(4a)	117.38 C(4b)	130.90 C(8a)	114.42 C(5)	113.16 C(6)	119.18 C(7)	102.73 C(8)

TMS	0.00	189.7	(^{13}C)
$MeNO_2$	0.00	-117.5	(^{15}N)

Table 2. ^{13}C and ^{15}N Chemical Shifts (ppm) from TMS and Nitromethane Internal

	Solid (CPMAS) at rt					Solution (average) DMSO at rt					Solution CD_3OD at 178 K[a]				
Compd	N(1)	2	3	4	5	N(1)	2	3	4	5	N(1)	2	3	4	5
1	Pyrrole is liquid at rt					-224.6	116.3	106.1	106.1	116.3	Pyrrole has not tautomerism.				
2	-210	136.3	-138	126.8	115.3	-167.6	135.0	-167.6	121.6	121.6	-216.3	136.8	-143.4	127.7	118.5
3[b]	-167.8	-90.5	138.7	107.0	128.8	-133.3	-133.3	133.7	104.8	133.7	-178.1	-100.2	140.0	106.3	130.0
4	-159.9	-89.6	148.5	-141.6	145.3	-126.6	-126.6	147.0	-137.5	147.0	-170.5	-100.2	151.9	-145.3	145.0
5/6	1,2,3-triazole is liquid at rt					-69.0	-75.9	-69.0	130.7	130.7	Unsuccessful				
7	-143.7	-28.0	2.4	-68.1	143.6	-98.7	-5.8	-5.8	-98.7	143.1	-150.6	n.o.[c]	n.o.[c]	-66.8	144.2
8	n.o.[c]	125.6	102.3	127.5	136.0	-245.5	123.7	101.8	127.0	134.8	Indole has not tautomerism.				
9	n.o.[c]	142.0	n.o.	142.9	135.8	-185	142.0	-185	138.1	138.1	-232.6	143.0	-153.5	143.0	134.4
10	-196.6	-77.5	134.3	123.6	140.3	-194.4	-65.6	133.4	122.8	139.9	No much sense (is only 1*H*)				
11	-157.6	-37.3	-56.4	142.3	132.6	-96.7	-7.5	-96.7	138.1	138.1	n.o.[c]	n.o.[c]	n.o.[c]	145.1	134.6
12	n.o.[c]	139.0	120.7	120.7	139.0	-264.1	140.5	119.2	119.2	140.5	Carbazole has not tautomerism.				

Table 2 (Cont.). ^{13}C and ^{15}N Chemical Shifts (ppm) from TMS and Nitromethane Internal

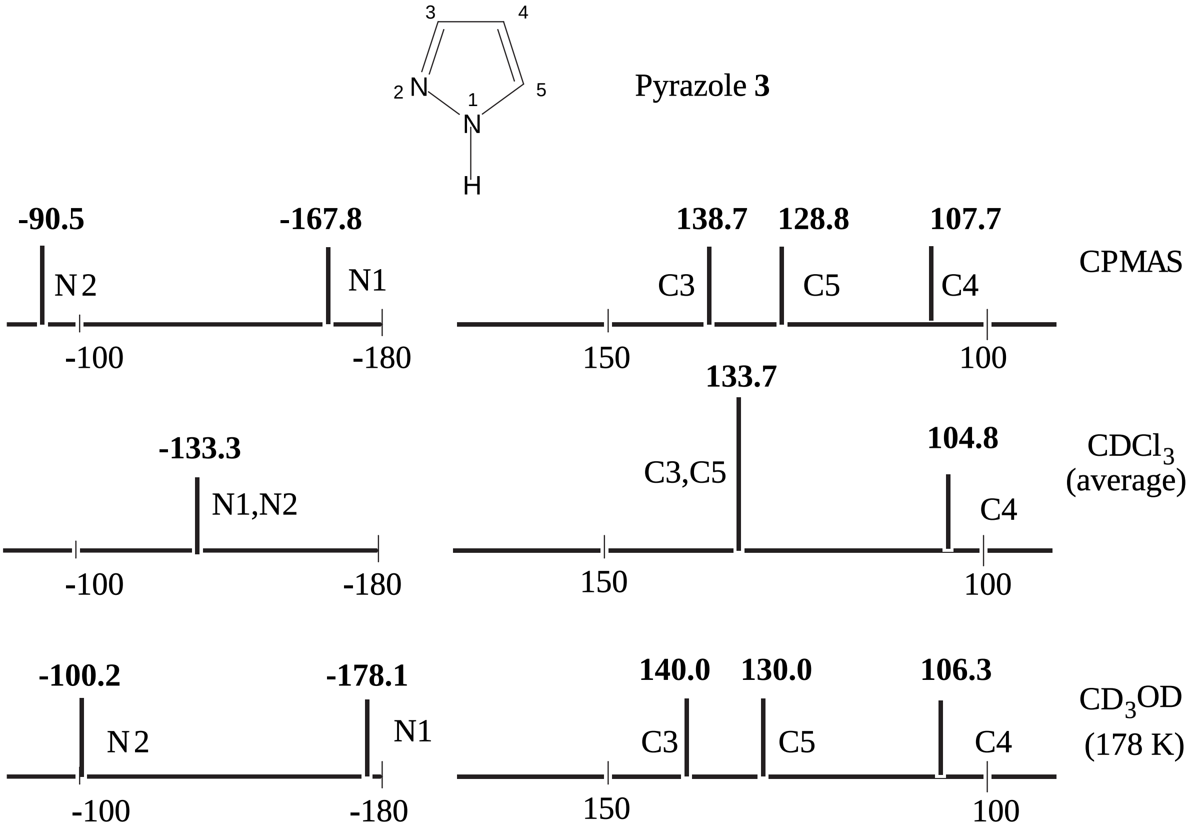
	Solid (CPMAS) at rt				Solution (average) DMSO at rt				Solution CD_3OD at 178 K [a]			
Compd	C(4)	C(5)	C(6)	C(7)	C(4)	C(5)	C(6)	C(7)	C(4)	C(5)	C(6)	C(7)
8	121.0 [d]	121.6 [d]	122.8	112.2	119.9	121.1	119.0	110.4	Indole has no tautomerism.			
9	120.4	121.2	123.0	112.8	115.5	121.6	121.6	115.5	119.7	123.9 [d]	124.7 [d]	113.7
10	122.0	122.0	126.5	111.7	120.4	120.1	125.8	110.0	No interesting (is only 1*H*)			
11	123.7	123.7	128.0	113.0	115.1	125.7	125.7	115.1	119.4	126.2	129.3	112.5
12	120.7	120.7	126.7	112.0	120.3	119.4	125.8	110.5	Carbazole has no tautomerism.			

[a] The tautomerism is blocked under these conditions. [b] The average values in solution are from $CDCl_3$. [c] Not observed. [d] Unassigned.

The choice of the B3LYP/6-31G* approach is based on two reasons. Firstly, GIAO (gauge including atomic orbitals) on geometries thus obtained gives, in general, acceptable results.[8-11] Secondly, the level of the basis set is low enough to allow the calculation of complex structures. This is important because our aim is to establish empirical equations between absolute shieldings and experimental chemical shifts that can be used for calculating the chemical shifts of more complex azoles. The calculations give directly absolute σ values; they have been converted into δ values through the calculated values of the references (Table 1). Since the references have very different structures to the azoles, it is in some cases preferable to compare σ and experimental δ and use the intercept of the linear regression as the σ value of the reference. The σ values for the references (TMS 189.7 ppm, nitromethane -117.5 ppm) correspond to the experimental values.[12]

Table 3. Some Solution ^{13}C and ^{15}N Chemical Shifts (ppm) from TMS and Nitromethane Internal

Compd	N(1)	2	3	4	5	Conditions
1	-232.0	---	---	---	---	CD_3OD at rt
3	-172.1	-79.0	138.4	104.2	127.9	DMSO at rt (blocked)
7	-105.5	-10.8	-10.8	-105.5	144.3	CD_3OD at rt (average)
8	-253.1	---	---	---	---	CD_3OD at rt
11	---	---	---	138.5	138.5	CD_3OD at rt (average)
12	-269.7	---	---	---	---	CD_3OD at rt (average)
13	-172.8	-87.3	152.4	-139.4	145.7	CD_3OD at rt
13	-171.2	-82.1	151.3	-127.8	144.4	DMSO at rt
Compd	C(4)	C(5)	C(6)	C(7)		
11	115.9	127.4	127.4	115.9		CD_3OD at rt (average)



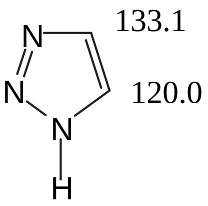
Scheme 2

The experimental data are reported in Table 2 and some supplementary values in Table 3. The data of Table 2 concerning the solid state and solution in methanol at low temperature have been determined in the present work as well as all the data of Table 3. On the other hand the average values corresponding to DMSO at room temperature are from the literature: **1** ^{13}C,[13] ^{15}N;[5] **2** ^{13}C,[14] ^{15}N;[5] **3** ^{13}C (in $CDCl_3$),[3] ^{15}N;[5] **4** ^{13}C (this work) ^{15}N;[5] **5**/**6** ^{13}C (this work, very close values are reported),[15] ^{15}N;[5] **7** ^{13}C (this work) ^{15}N;[5] **8** ^{13}C,[13] ^{15}N;[5] **9** ^{13}C (this work, very close values are reported),[16] ^{15}N;[5] **10** ^{13}C,[4] ^{15}N;[5] **11** ^{13}C,[17] ^{15}N;[5] **12** ^{13}C,[18] ^{15}N.[18] Note that both in the solid state and in methanol at low temperatures some signals were not found although we tried in different conditions. Compound (**13**) (1-methyl-1,2,4-triazole, Table 3) was used to assign the signals of 1*H*-1,2,4-triazole (**4**).

We dispose now of two series of d values, experimental (Table 2) and calculated (Table 1) that can be treated statistically. First we have approached the ^{13}C chemical shifts mixing the data obtained in methanol at 178 K with those obtained in DMSO at room temperature for compounds that exists in one tautomeric form: **1**, **8**, **10** and **12**. That is, we have assumed that solvent effects are negligible in a first approximation (Eq. [1]).

$$d^{13}C_{exp\text{-}sol} = (1.064 \pm 0.003)\ d^{13}C_{calc},\ n = 45,\ r^2 = 1.000 \qquad [1]$$

The range of experimental values is 46 ppm (calculated, 47 ppm) and the worse points are imidazole C5 (exp.: 118.5 ppm, fitted 113.6 ppm) and carbazole C3 (C4a) (exp.: 119.2 ppm, fitted 124.9 ppm). In the case of 1,2,3-triazole we have been unable to slow down sufficiently the tautomeric rate and consequently to determine the chemical shifts of tautomers (**5**) and (**6**) experimentally. Using the relative shieldings of Table 1, Equation [1] predicts for 1,2,3-triazole tautomers:



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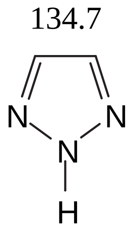

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Then we tried to separate the solvents, using a dummy variable **d_1** (0 for methanol and 1 for DMSO) and the model improves a little (the chemical shifts in DMSO are 1.5 ppm lower on average compared to those in methanol). An examination of the residuals shows that carbon atoms between N(1)-H and another N atom deviate significantly: C2 of **2** and **9** and C5 of **4** and **7**. Using another dummy variable **d_2** (1 for these situations, 0 for all the remaining signals), eq. [2] is obtained:

$$d^{13}C_{exp\text{-}sol} = (1.066 \pm 0.004)\ d^{13}C_{calc} - (1.1 \pm 0.7)\ \mathbf{d_2} + (3.4 \pm 1.2)\ \mathbf{d_1},\ n = 45,\ r^2 = 1.000 \qquad [2]$$

We assign the deshielding of 3.4 ppm on average observed on these four carbon signals to association, through the nitrogen atoms (either N-H···DMSO or CD_3OD···N), of the azoles with the solvent.

Solid state values are also related to calculated ones but here the correlation is not so good. For once, the intercept is now significant (probably meaning that solid TMS should appear at about 9 ppm from TMS in solution, but remember that TMS melts at -99 °C):

$$d^{13}C_{exp\text{-}solid} = (9 \pm 4) + (0.991 \pm 0.035)\ d^{13}C_{calc},\ n = 43,\ r^2 = 0.952 \qquad [3]$$

Here also the four above discussed carbons (C2 of **2** and **9** and C5 of **4** and **7)** deviate significantly. Using the dummy variable, eq. [4] is obtained:

$$d^{13}C_{\text{exp-solid}} = (14\pm3) + (0.941\pm0.028)\ d^{13}C_{\text{calc}} + (5.7\pm1.0)\ \mathbf{d_1},\ n = 43,\ r^2 = 0.973 \qquad [4]$$

In this case, the deshielding effect is larger because it is due not to the average stochastic hydrogen bonds with the solvents but to the permanent N-H···N associations present in all the solid azoles (save **1**, **8** and **12**). Note that the four carbons are between the donor N-H group and the acceptor N atom (hydrogen bond in 1,2,4-triazoles involved N-4).[19]

Table 4. Relationships between Experimental and Calculated ^{15}N Chemical Shifts

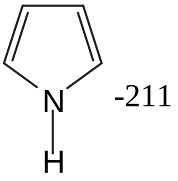
y	x	Intercept	Slope	n	r^2	Eq.
DMSO	$d^{15}N_{calc}$	None	(0.975±0.01)	7	0.999	[5]
CD_3OD	$d^{15}N_{calc}$	-(35±8)	(0.840±0.05)	14	0.965	[6]
CD_3OD^a	$d^{15}N_{calc}$	-(18±6)	(0.911±0.04)	14	0.983	[7]
CPMAS	$d^{15}N_{calc}$	-(25±5)	(0.813±0.04)	16	0.970	[8]
CPMAS^b	$d^{15}N_{calc}$	-(23±3)	(0.808±0.03)	16	0.986	[9]
CPMAS	DMSO	-(19±6)	(0.894±0.04)	4	0.996	[10]
CPMAS	CD_3OD	None	(0.953±0.009)	9	0.999	[11]
CD_3OD	DMSO	-(25±5)	(0.923±0.02)	5	0.998	[12]

[a] The experimental values of N3 of **2**, N4 of **4** and N3 of **9** have been corrected by + 18 ppm.
[b] The experimental values of N3 of **2** and N4 of **4** have been corrected by + 20 ppm.

We will now examine the ^{15}N NMR results. First, note that the range of calculated values is much larger for ^{15}N, 290 ppm, than for ^{13}C, 47 ppm. We have collected in Table 4 the different equations [5 to 12], necessary for the discussion. In several cases, the intercept is significant; leaving aside eq. [6], the intercept is about 20-25 ppm, indicating that nitromethane in solid state or in methanol should be corrected by this amount. This does not mean to say that these effects will be observed with the reference alone (nitromethane is only shifted 2 ppm in methanol),[20] but that this solvent affect differently the reference and the azoles.

In a similar way and with a similar explanation, some nitrogen atoms (see Table 4, eqs. [7] and [9]) have to be corrected by an important effect, 18-20 ppm, to fit the calculated values in methanol or in solid state. Otherwise, the three experimental and the calculated results are mutually consistent, but some slopes are far from being 1, a result not entirely satisfactory.

The equations of Table 4 can be used to make some predictions. For instance, in the solid state, the following ^{15}N chemical shifts are expected (the chemical shift of the N-3 of benzimidazole takes into account the 20 ppm correction of Eq. [9]):



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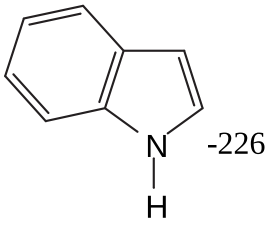

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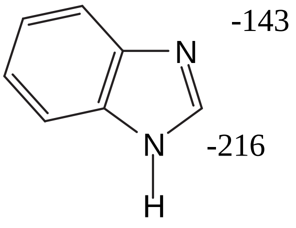

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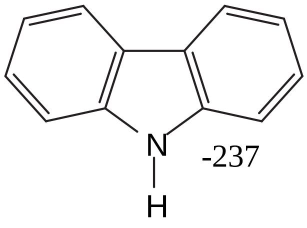

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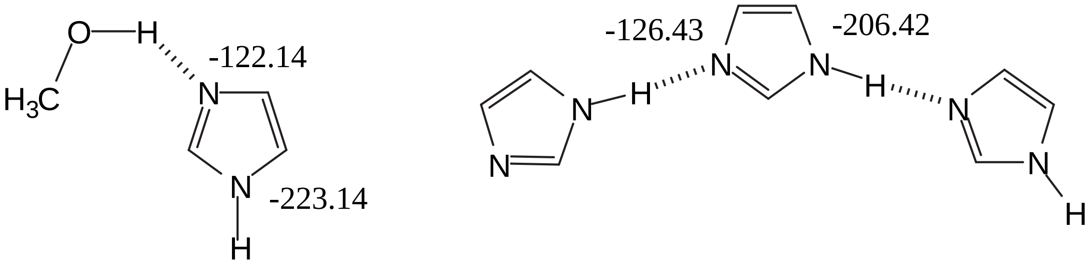
We wanted to know if the large effects observed on ^{15}N for some signals (Table 4) could be explained on theoretical grounds. For this we selected imidazole (**2**) and imagine two situations (Scheme 2): one to simulate methanol-d_4 and the other, the solid state (the central imidazole). The GIAO/B3LYP/6-31G* calculated chemical shifts (reported to nitromethane) are given on Scheme 2.



Scheme 2

Compared with the values of Table 1 for imidazole (**2**), methanol does not affect N1 (+1.08 ppm) but produces a large, low frequency shift, on N3 (-12.06 ppm). This effect is comparable with that observed for pyridine in methanol (-24.9 ppm),[21] but much weaker than that observed for 1-methylimidazole on protonation (-95 ppm).[22] In any case it provides an explanation for the 18 ppm effect reported in Table 4. The imidazole trimer used to model the catemer, shows that both nitrogen atoms are strongly affected but in opposite directions: N1 (+17.80 ppm) and N3 (-16.35 ppm).

Therefore, the correction applied on eq. [9] of Table 4 which affects only pyridine-like nitrogens should be extended to the pyrrole-like nitrogens, but only if there is another nitrogen atom in the molecule. That is, pyrrole, indole and carbazole that cannot form N-H···N bonds should not be corrected. With this is mind and knowing that the acceptor nitrogen is N4 in 1,2,4-triazole and tetrazole and N3 in benzotriazole, eq. [13] was found.

$$d^{15}N_{\text{exp-solid}} = -(14\pm3) + (0.929\pm0.05)\, d^{15}N_{\text{calc}} - (14\pm5)\ \text{acceptor N} + (15\pm8)\ \text{donor N-H}$$

$$n = 16,\ r^2 = 0.992 \qquad [13]$$

CONCLUSIONS

A series of analytical works rely on the use of ^{13}C and ^{15}N NMR data of parent azoles and benzazoles in the solid state. For instance, several papers are based on estimated values of pyrrole (**1**), imidazole (**2**), indole (**8**) and carbazole (**12**).[23-25] The collection of data here reported should prove useful for these studies. Moreover, the values obtained in CD_3OD at low temperature could be used for future tautomeric studies of *C*-substituted derivatives. Finally, thanks to the GIAO calculations, a clearer image of the structure of azoles in the solid state emerges.

EXPERIMENTAL

All compounds are commercial products except 1-methyl-1,2,4-triazole (**13**) prepared according to reference 26.

^{13}C and ^{15}N NMR spectroscopy

^{13}C (100.62 MHz) and ^{15}N NMR (40.56 MHz) spectra in solution were obtained using a Bruker DRX 400 instrument (corresponding to 9.4 T). Variable temperature ^{1}H, ^{13}C and ^{15}N NMR experiments were recorded on the same spectrometer using CD_3OD as solvent. 2D Inverse proton detected heteronuclear shift correlation spectra, HMBC, HMQC, were obtained using the standard pulse sequence.[27] Solid state ^{13}C (50.32 MHz) and ^{15}N (20.28 MHz) CPMAS NMR spectra have been obtained on a Bruker AC-200 spectrometer at 298 K using a 7 mm BRUKER DAB 7 probehead that achieves rotational frequencies of about 3.5-4.5 kHz. Samples were carefully packed in ZrO_2 rotors and the standard CPMAS pulse sequence was employed. Chemical shifts (δ) in ppm are referred to Me_4Si and $^{15}NH_4Cl$ [these were converted to nitromethane using the relationship: d ^{15}N (nitromethane) = d ^{15}N (ammonium chloride) – 338.1 ppm].

Computational details

All the calculations were carried out using the programs implemented in Gaussian 98.[28]

ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

1. J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, *The Tautomerism of Heterocycles*, Academic Press, New York, 1976.
2. E. Gonzalez, R. Faure, E.-J. Vincent, M. Espada, and J. Elguero, *Org. Magn. Reson.*, 1979, **12**, 587.
3. M. Begtrup, G. Boyer, P. Cabildo, R. M. Claramunt, J. Elguero, J. I. García, C. Toiron, and P. Vedsø, *Magn. Reson. Chem.*, 1993, **31**, 107.
4. J. Elguero, A. Fruchier, E. M. Tjiou, and S. Trofimenko, *Chem. Heterocycl. Comp.*, 1995, 1006.
5. R. M. Claramunt, D. Sanz, C. López, J. A. Jiménez, M. L. Jimeno, J. Elguero, and A. Fruchier, *Magn. Reson. Chem.*, 1997, **35**, 35.
6. V. I. Minkin, A. D. Garnovskii, J. Elguero, A. R. Katritzky, and O. V. Denisko, *Adv. Heterocycl. Chem.*, 2000, **76**, 157.
7. R. Goddard, O. Heinemann, and C. Krüger, *Acta Crystallogr., Sect. C*, 1997, **53**, 1846.
8. R. Lazaro, P. Bouchet, R. Solé, I. Alkorta, and J. Elguero, *Mod. Chem.*, 1999, **136**, 531.
9. I. Alkorta, J. Elguero, B. Donnadieu, M. Etienne, J. Jaffart, D. Schagen, and H.-H. Limbach, *New J. Chem.*, 1999, **23**, 1231.
10. J. Eloranta, J. Hu, R. Suontamo, E. Kolehmainen, and J. Knuutinen, *Magn. Reson. Chem.*, 2000, **38**, 987.

11. R. P. Corbally, L. N. Mehta, J. Parrick, and E. L. Short, *Magn. Reson. Chem.*, 2000, **38**, 1034.
12. I. Alkorta and J. Elguero, *Struct. Chem.*, 1998, **9**, 187.
13. D. J. Chadwick, in *Comprehensive Heterocyclic Chemistry*, Pergamon Press, Oxford, 1984, Vol. 4, p. 171 and 173.
14. K. G. R. Pachler, R. Pachter, and P. L. Wessels, *Org. Magn. Reson.*, 1981, **17**, 278.
15. H. Wamhoff, in *Comprehensive Heterocyclic Chemistry*, ed. by A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, Vol. 5, p. 681.
16. R. Benassi, R. Grandi, U. M. Pagnoni, and F. Taddei, *Magn. Reson. Chem.*, 1986, **24**, 415.
17. R. Faure, E.-J. Vincent, and J. Elguero, *Heterocycles*, 1983, **20**, 1713.
18. G. B. Jones and B. J. Chapman, in *Comprehensive Heterocyclic Chemistry II*, ed. by A. R. Katrizky, C. W. Rees, and E. F. V. Scriven, Pergamon Press, Oxford, 1996, **2**, 20 and 21.
19. C. Foces-Foces, I. Alkorta, and J. Elguero, *Acta Crystallogr.*, *Sect. B*, 2000, **56**, 1018.
20. M. Witanowski, L. Stefaniak, S. Szymánski, and H. Januszewski, *J. Magn. Reson.*, 1977, **28**, 217.
21. W. von Philipsborn and R. Müller, *Angew. Chem.*, *Int. Ed. Engl.*, 1986, **25**, 383.
22. R. M. Claramunt, D. Sanz, G. Boyer, J. Catalán, J. L. G. de Paz, and J. Elguero, *Magn. Reson. Chem.*, 1983, **31**, 791.
23. H. Knicker and H.-D. Lüdemann, *Org. Geochem.*, 1995, **23**, 329.
24. M. S. Solum, R. J. Pugmire, D. M. Grant, S. R. Kelemen, M. L. Gorbaty, and R. A. Wind, *Energy Fuels*, 1997, **11**, 491.
25. J. Zhang, J. Zhai, F. Zhao, and T. Tao, *Anal. Chim. Acta*, 1999, **378**, 177.
26. R. Jacquier, M.-L. Roumestant, and P. Viallefont, *Bull. Soc. Chim. Fr.*, 1967, 2630.
27. S. Braun, H.-O. Kalinowski, and S. Berger, *150 and More Basic NMR Experiments*, Wiley-VCH, 1998.
28. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.