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Reference Data Review

Substituent effects on the ^{15}N NMR Parameters of Azoles

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The ^{15}N chemical shifts and a large collection of coupling constants pertaining to azoles have been gathered from the literature. To complete this collection and to check some anomalies, the spectra of 14 compounds in several solvents were recorded again and 31 compounds were studied for the first time; in all, data for 420 compounds (pyrroles, imidazoles, pyrazoles, triazoles, tetrazoles, indoles, benzimidazoles, indazoles, benzotriazoles and carbazoles) are reported. Additive models are used to discuss the substituent chemical shifts.

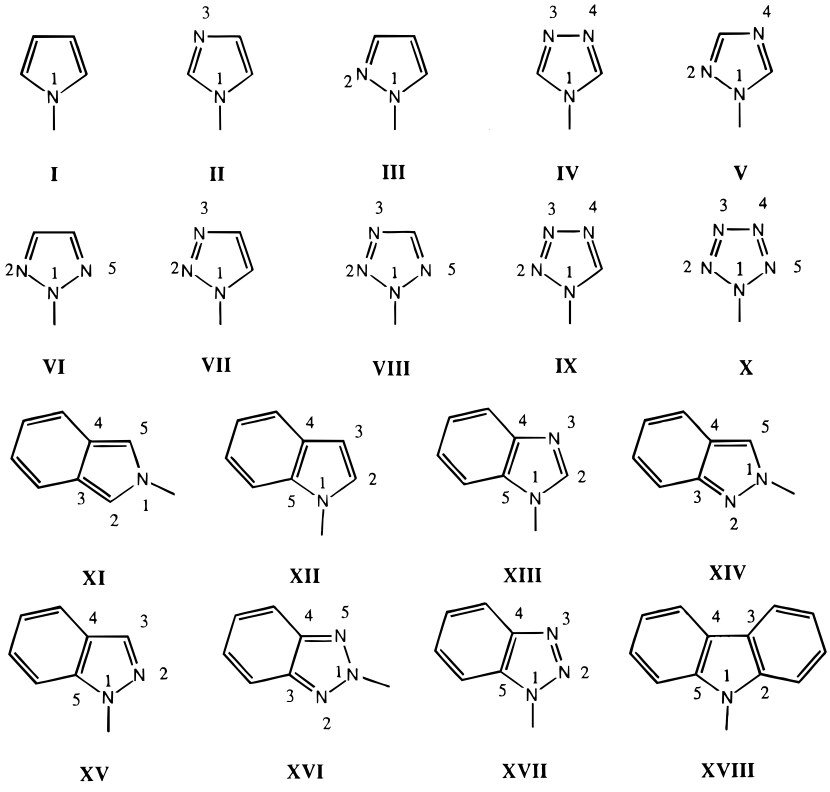
KEY WORDS ^{15}N NMR; azoles; benzazoles; additive models; substituent chemical shifts

INTRODUCTION

The information available concerning the ^{15}N NMR spectroscopy of azoles is considerable; some of this information is collected annual reports in.[1–4] Other useful reviews are those of Gil and von Philipsborn on the effect of electron lone-pairs on nuclear spin–spin coupling constants which contain several examples of azoles,[5] and that of von Philipsborn and Müller[6] on ^{15}N NMR spectroscopy. Finally, two general books on ^{15}N NMR spectroscopy report many examples of azoles and should be consulted for general information.[7,8] Here, we have collected all data concerning compounds derived from the eighteen systems **I–X** (azoles) and **XI–XVIII** (benzazoles), completed with some unpublished results.

The numbering of the nitrogen atoms is not the conventional one in azoles; the reason is that we intend to discuss the ^{15}N chemical shifts with empirical models and, for this purpose, it is necessary for equivalent nitrogen atoms to have the same number. For instance, the pyrrole-like *N*-substituted atom will always be N-1.

The data are collected in Tables 1–18, corresponding to pyrroles **I** (Table 1), imidazoles **II** (Table 2), pyrazoles **III** (Table 3), 1,3,4-triazoles **IV** (4*H*-1,2,4-triazoles, Table 4), 1,2,4-triazoles **V** (1*H*-1,2,4-triazoles, Table 5), 1,2,5-triazoles **VI** (2*H*-1,2,3-triazoles, Table 6), 1,2,3-triazoles **VII** (1*H*-1,2,3-triazoles, Table 7), 1,2,3,5-tetrazoles **VIII** (2*H*-1,2,3,4-tetrazoles, Table 8), 1,2,3,4-tetrazoles **IX** (1*H*-1,2,3,4-tetrazoles, Table 9), pentazoles **X** (Table 10), isoindoles **XI** (Table 11), indoles **XII** (Table 12), benzimidazoles **XIII** (Table 13), 2*H*-indazoles **XIV** (Table 14), indazoles **XV** (1*H*-indazoles, Table 15), 2*H*-benzotriazoles **XVI** (Table 16), benzotriazoles **XVII** (1*H*-benzotriazoles, Table 17) and 9*H*-carbazoles **XVIII** (Table 18). In the tables, the order of seniority is that of the *N*-substituent: $^{1}H > {}^{11}B > {}^{13}C > {}^{14}N > {}^{16}O > {}^{31}P > {}^{32}S$; inside the most abundant class, that of N—C compounds, the order is: CH_3 > alkyl > benzyl > functional alkyl > aryl > CN > acyl > ester > amide. The classification system is similar to that which we used in our reviews on the ^{13}C NMR spectroscopy of



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Reference Data Review

Table 1. Nitrogen-15 chemical shifts and some coupling constants of pyrrole derivatives I

No.	Compound	Solvent	N-1	Substituents	Ref.
1	Pyrrole	Neat	−231.4	—	1
	Pyrrole[b]	Acetone	−229	—	16
	Pyrrole	Acetone	−229.6	—	1
			^2J(N1C3) = 3.9	—	17
	Pyrrole[a]	$CDCl_3$	−232.7	—	18
			^1J(N1H1) = −96.53	—	19
			^2J(N1H2) = −4.52, ^3J(N1H3) = −5.39	—	20
	Pyrrole	DMSO	−222.3	—	1
	Pyrrole	DMSO	−224.6	—	18
	Pyrrole	DMSO	−226.1	—	21
	Pyrrole	DMSO	−226.1	—	22
	Pyrrole	CCl_4	−236.4	—	1
			^2J(N1H2) = 4.5, ^3J(N1H3) = 5.4	—	23
	Pyrrole[a]	C_6D_6	^1J(N1H1) = −96.40	—	24
			^2J(N1H2) = ^2J(N1H5) = −4.55		
			^3J(N1H3) = ^3J(N1H4) = −5.36		
	Pyrrole[a]	Nematic phase	^1J(N1H1) = −96.48	—	25
			^2J(N1H2) = ^2J(N1H5) = −4.55		
2	2,5-Di-*tert*-butyl[a]	CCl_4	^1J(N1H1) = 91.5	—	26
			^3J(N1H3) = ^3J(N1H4) = 5.2		
3	2-Formyl	Acetone	−228.7	—	19
			^1J(N1H1) = 98		
			^3J(N1H3) = 4.15, ^3J(N1H4) = 5.00,		
			^2J(N1H5) = 4.05		
4	2-Acetyl	Acetone	−225.4	—	19
			^1J(N1H1) = 98		
			^3J(N1H3) = 4.60, ^3J(N1H4) = 5.10,		
			^2J(N1H5) = 4.00		
	2-Acetyl	Acetone	−227.9	—	This work
5	2-Methoxycarbonyl	Acetone	−224.1	—	19
			^1J(N1H1) = 98		
			^3J(N1H3) = 4.31, ^3J(N1H4) = 4.95,		
			^2J(N1H5) = 4.10		
6	2-Nitro	Acetone	−227[b]	NO_2: −23.1	16
	2-Nitro	Acetone	−229[b]	—	19
	2-Nitro[a]	Not reported	^3J(H3NO_2) = 0.3, ^4J(H4NO_2) = 0.8		27
			^4J(H5NO_2) = 0.85		
7	3-Nitro	Acetone	—	NO_2: −13.5	16
	3-Nitro[b]	Acetone	−225	—	19
	3-Nitro[a]	not reported	^3J(H2NO_2) = −0.2		27
			^4J(H5NO_2) = 0.8		
8	2,4-Dinitro[b]	Acetone	−227	α-NO_2: −25.7	16
				β-NO_2: −18.3	
	2,4-Dinitro[a]	not reported	^3J(H3-2NO_2) = 0.4, ^3J(H3-4NO_2) = 0.45		27
			^3J(H5-4NO_2) = 0.9, ^4J(H5-2NO_2) = 0.95		
9	2,5-Dinitro[b]	Acetone	−236	NO_2: −25.5	16
10	2-Methoxycarbonyl-4-nitro	Acetone	−222.0	—	19
			^1J(N1H1) = 100 (at −20 °C)		
			^3J(N1H3) = 5.05, ^2J(N1H5) = 3.45		
11	2-Methoxycarbonyl-5-nitro	Acetone	−229.4	—	19
			^1J(N1H1) = 101 (at −20 °C)		
			^3J(N1H3) = 3.05, ^3J(N1H4) = 3.63		
12	1-Methyl	$CDCl_3$	−230.9	—	18
	1-Methyl	DMSO	−230.2	—	18
	1-Methyl	DMSO	−230.1	—	28
	1-Methyl	DMSO	−230.1	—	29
	1-Methyl[b]	Neat	−231.4	—	2,3
	1-Methyl[b]	Acetone	−230	—	16
	1-Methyl[b]	Acetone	−231.6	—	2,3

Table 1. *Continued*

No.	Compound	Solvent	N-1	Substituents	Ref.
13	1-Methyl-2-nitro[b]	Acetone	−228	NO_2: −22.5	16
14	1-Methyl-2,4-dinitro[b]	Acetone	−225	—	16
15	1-Methyl-2-B$(NMe_2)_2$[b]	Neat	−230	—	30
16	1-Methyl-2-B$(C_2H_5)_2$[b]	Neat	−214	—	30
17	1-$CH_2CH(CH_3)_2$	DMSO	−223.9	—	31
18	1-$CH_2C(CH_3)_3$	DMSO	−223.1	—	31
19	1-Vinyl[b]	Neat	−206.5	—	2,3
	1-Vinyl[b]	Acetone	−205.6	—	2,3
20	1-Vinyl-2-methyl[b]	Neat	−208.5	—	2,3
	1-Vinyl-2-methyl[b]	Acetone	−207.5	—	2,3
21	1-Vinyl-2,3-tetramethylene[b]	Neat	−216.9	—	2,3
	1-Vinyl-2,3-tetramethylene[b]	Acetone	−212.9	—	2,3
22	1-Phenyl[b]	Neat	−202	—	32
	1-Phenyl	DMSO	−205.8	—	33
23	1-Acetyl	$CDCl_3$	−183.8	—	34
24	1-Amino	DMSO	−209.8	NH_2: −306.4	29
25	1-B$(Me)_2$[b]	$(C_2H_5)_2O$	−186	—	32
	1-B$(Me)_2$	$CDCl_3$	−187	—	35
	1-B$(Me)_2$	C_6D_6	−190	—	35
26	[B(pyrrol-1-yl)]$_2$	$CDCl_3$	−207	—	35
27	1-Dimethylgallyl[b]	Neat	−221	—	32
28	1-Trimethylstannyl	$CDCl_3$	−216.2	—	36
	1-Trimethylstannyl[b]	Neat	−222	—	32
29	1-Trimethylsilyl	C_6D_6	−216.0	—	36
	1-Trimethylsilyl[b]	Neat	−221	—	32
30	1-Trimethylplumbyl	C_6D_6	−206.7	—	36
	1-Trimethylplumbyl[b]	Neat	−215	—	32
31	1-Trimethylphosphinyl	C_6D_6	−219.3	—	36
	1-Trimethylphosphinyl[b]	Neat	−227	—	32

[a] Coupling constants from ^1H NMR spectroscopy.
[b] From ^{14}N NMR spectroscopy.

azoles.[9–11] Aza derivatives (e.g. carbolines and purines) are not considered within the scope of this review. For coupling constants, when the sign is not given they correspond to absolute values. The solvents are reported in a simplified way, e.g. $CHCl_3$ and $CDCl_3$, acetone and [$^2H_6$]acetone and DMSO and [$^2H_6$]DMSO are not differentiated. In some instances, the authors use $Cr(acac)_3$; we have not reported this information in the tables since we have verified that in the case of [$^{15}N_2$]-1-benzylpyrazole (**156**) in $CDCl_3$ the chemical shifts of N-1 and N-2 are not modified by adding the relaxation reagent.

The problem of the interconversion of the different standards for relating ^{15}N chemical shifts is both trivial and complicated. In this review all our chemical shifts are reported to an external sample of pure nitromethane (ext. CH_3NO_2), although in our solid-state CP/MAS studies we used a saturated $^{15}NH_4Cl$ solution in D_2O. The equations that we used to transform data from other sources are given below (ignoring concentration effects since concentration is often not reported):

From 1 M $^{15}NO_3H$
to saturated $^{15}NH_4Cl$ in D_2O:
$(349.1 - \delta NO_3H)$ ppm (1)

From saturated $^{15}NH_4Cl$ in: D_2O
to ext. CH_3NO_2:
$(\delta^{15}NH_4Cl$ in $D_2O - 355.3)$ ppm (2)

From 1 M $^{15}NO_3H$ to
ext. CH_3NO_2: $(-\delta NO_3H - 6.2)$ ppm (3)

From CH_3NO_2 in DMSO
to ext. CH_3NO_2: +2.0 ppm (4)

From CH_3NO_2 in $CHCl_3$
to ext. CH_3NO_2: −3.8 ppm (5)

From CH_3NO_2 in acetone
to ext. CH_3NO_2: −0.8 ppm (6)

From NH_3 (liq.)
to ext. CH_3NO_2: −380.2 ppm (7)

From 6 M $^{15}NH_4NO_3$ in 2 N HNO_3
to ext. CH_3NO_2: −358.2 ppm (8)

From 5 M $^{15}NH_4NO_3$ in 2 N HNO_3
to ext. CH_3NO_2: −359.0 ppm (9)

From solid $^{15}NH_4Cl$
to ext. CH_3NO_2: $(338.1 - \delta NH_4Cl)$ ppm (10)

From $^{15}NO_3^-$ Na^+ (or K^+)
to ext. CH_3NO_2: −3.6 ppm (11)

These values are in some cases identical with[12] or slightly different from[13] the values reported in the literature. For instance, the nitrogen atoms of pyrazole itself appear at 128.5 (average) in the original paper (reference, 1 M $^{15}NO_3D$),[14] and subsequently it was quoted as −134.7 ppm (reference, external CH_3NO_2).[15] In Table 1 in Ref. 54 (see Table 3) the same result is quoted as 220.6 (reference, sat. $^{15}NH_4Cl/D_2O$). Owing to problems related with references, the chemical shifts of Ref. 62 have to be corrected by $\Delta\delta = +21.6$ ppm (A. Gasco and R. Fruttero, personal communication).

In addition to this problem of so many references, there is the additional problem of the sign. In older publications, the chemical shifts of azoles with regard to external neat nitro-

Table 2. Nitrogen-15 chemical shifts and some coupling constants of imidazole derivatives II

No.	Compound	Solvent	N-1	N-3	Substituents	Ref.
32	Imidazole	$CHCl_3$	−172.6	−172.6	—	37
	Imidazole	$CDCl_3$	−170.7	−170.7	—	18
	Imidazole	$CDCl_3$	−172.4	−172.4	—	15
	Imidazole[c]	DMSO	−167	−167	—	16
	Imidazole	DMSO	−167.6	−167.6	—	18
	Imidazole	DMSO	−169.0	−169.0	—	15
	Imidazole[a,b]	H_2O	−177.2	−177.2	—	38
			^2J(N1N3) = 1.1, ^1J(N1C2) = ^1J(N3C2) = 6.9			39
			^1J(N1C5) = ^1J(N3C4) = 5.9,			
			^2J(N1C4) = ^2J(N3C5) = 0.9			
			^2J(N1H2) = ^2J(N3H2) = 9.6,			
			^2J(N1H5) = ^2J(N3H4) = 7.2			
			^3J(N1H4) = ^3J(N3H5) = 2.5			
	Imidazole	H_2O	−177.2	−177.2	—	37
	Imidazole	$CHCl_3$ + TFA	−178.6	−178.6	—	37
	Imidazole	TFA	−182.4	−182.4	—	37
	Imidazole	$CHCl_3$ + AcOH	−172.6	−172.6	—	37
	Imidazole	$O{=}P(OMe)_3$	−214	—	—	40
	Imidazole	Solid	−210	−138	—	41
33	2-Methyl	$CDCl_3$	−174.2	−174.2	—	15
	2-Methyl	DMSO	−171.6	−171.6	—	15
34	4-Methyl	$CHCl_3$	−173.2	−179.5	—	37
	4-Methyl	$CDCl_3$	−172.8	−167.0	—	15
	4-Methyl	$CHCl_3$ + TFA	−167.7	−173.2	—	37
	4-Methyl	DMSO	−172.8	−163.9	—	15
	4-Methyl	H_2O	−170.6	−179.9	—	37
	4-Methyl	TFA	−213.2	−209.0	—	15
35	4-$CH_2CH_2NH_2$	H_2O	−200.9	−152.2	—	42
36	4-Carboxylic acid	H_2O	−161.8	−186.2	—	38
37	4-CH_2CO_2H	H_2O	−209.8	−205.6	—	42
38	4-$CH_2CH_2CO_2H$	H_2O	−204.5	−208.2	—	42
39	4-$CH{=}CHCO_2H$ (*cis*)	H_2O	−208.2	−198.8	—	42
40	4-$CH{=}CHCO_2H$ (*trans*)	H_2O	−205.8	−202.6	—	42
41	2-Amino-4,5-dicyano	DMSO–CH_3OH	−201.8	−201.8	NH_2: −326.6; CN: −111.8	43
42	4-Nitro[c]	DMSO	−202	—	NO_2: −16	16
	4-Nitro	DMSO-acetone	−205.6	−128.9	NO_2: −17.4	15
43	4,5-Dinitro[c]	Acetone	−158	−158	NO_2: −28	16
44	2-Methyl-4-nitro[c]	DMSO	−203	—	NO_2: −16	15
	2-Methyl-4-nitro	DMSO	−205.8	−133.2	NO_2: −17.0	15
45	2-Methyl-4,5-dinitro[c]	Acetone	−202	−160	NO_2: −27	16
46	4-$CH_2CH(CO_2H)NH_2$ (histidine)	H_2O	−204.1	−150.8	—	44
	4-$CH_2CH(CO_2H)NH_2$ (histidine)	C_2H_5OH (−55 °C)	−217.0	−135.3	—	44
			^1J(N1H1) = 96			

Table 2. *Continued*

No.	Compound	Solvent	N-1	N-3	Substituents	Ref.
47	1-Methyl	Cyclohexane	−221.9	−117.6	—	45
	1-Methyl[a,b]	$CHCl_3$	^2J(N1N3) = 1.1, ^1J(N1C2) = 12.2, ^1J(N1C5) = 13.4 ^1J(N1Me) = 10.6, ^2J(N1C4) = 4.8, ^1J(N3C2) = 1.9, ^1J(N3C4) = 0.9, ^2J(N3C5) < 0.5 ^2J(N1H2) = 7.6, ^3J(N1H4) = 3.5, ^2J(N1H5) = 5.5, ^2J(N1Me) = 1.6 ^2J(N3H2) = 10.8, ^2J(N3H4) = 9.0, ^3J(N3H5) = 1.7			39
	1-Methyl	$CDCl_3$	−219.5	−124.3	—	18
	1-Methyl	$CDCl_3$	−221.7	−124.1	—	15
	1-Methyl	C_6H_6	−221.9	−117.6	—	37
	1-Methyl	DMSO	−218.0	−119.5	—	18
	1-Methyl	DMSO	−219.2	−119.1	—	15
			^2J(N3H4) = 9.0, ^2J(N1H2) = 8.1, ^2J(N1H5) = 4.7 ^3J(N3H5) = 1.7, ^3J(N1H4) = 3.4, ^2J(N1Me) = 1.6			
	1-Methyl	DMSO	−218.5	−118.1	—	28
	1-Methyl	DMSO	−218.5	−118.1	—	29
	1-Methyl	CH_3OH	−218.7	−134.0	—	45
	1-Methyl	CH_3OH	−218.7	−134.0	—	37
	1-Methyl	H_2O	−217.7	−134.7	—	45
	1-Methyl	H_2O	−217.7	−134.7	—	37
	1-Methyl	$CHCl_3$ + TFA	−220.2	−134.0	—	37
	1-Methyl	$CHCl_3$ + AcOH	−219.2	−140.4	—	37
	1-Methyl	H_2O (pH 11–13)	−216.2	−135.2	—	39
	1-Methyl	TFA	−209.3	−213.0	—	46
			^1J(N3H3) = 103.3			
48	1,2-Dimethyl	$CDCl_3$	−225.0	−127.3	—	15
	1,2-Dimethyl	DMSO	−223.2	−121.5	—	15
			^2J(N3H4) = 10.0, ^3J(N3H5) = 1.0			
49	1-Methyl-4-$CH_2CH(CO_2H)NH_2$	H_2O	−218.0	−135.3	—	44
50	1-Methyl-5-$CH_2CH(CO_2H)NH_2$	DMSO	−217.0	−122.2	—	44
	1-Methyl-5-$CH_2CH(CO_2H)NH_2$	H_2O	−216.5	−140.7	—	44
51	1-Methyl-4-nitro[c]	DMSO	−208	—	NO_2: −17	16
	1-Methyl-4-nitro	DMSO	−208.5	−127.7	NO_2: −18.0	15
			^2J(N1H2) = 7.8, ^2J(N1H5) = 3.3, ^2J(N3H2) = 12.4 ^2J(N1Me) = 1.7			
52	1-Methyl-5-nitro	$CDCl_3$	−222.3	—	NO_2: −26	15
	1-Methyl-5-nitro	DMSO	−219.4	—	NO_2: −25	15
53	1,2-Dimethyl-4-nitro	DMSO	−210.3	−130.2	—	15
54	1,2-Dimethyl-5-nitro	DMSO	−224.1	−121.0	—	15
			^2J(N1Me1) = 1.8, ^3J(N1H4) = 1.8, ^3J(N1Me2) = 2.0 ^2J(N3H4) = 9.5, ^3J(N3Me2) = 2.5			
55	1-Methyl-2-methylthio	DMSO	−222.8	−121.3	—	47

Table 2. *Continued*

No.	Compound	Solvent	N-1	N-3	Substituents	Ref.
56	1-$CH_2CHOHMe$-2-methyl-4-nitro	DMSO	−203.3	−132.0	—	15
57	1-$CH_2CHOHMe$-2-methyl-5-nitro	DMSO	−216.4	−120.5	—	15
58	1-$CH_2CHOHCH_2Cl$-2-methyl-4-nitro	DMSO	−205.7	−131.7	—	15
59	1-$CH_2CHOHCH_2Cl$-2-methyl-5-nitro	DMSO	−218.7	−120.4	—	15
60	1-*β*-*D*-ribofuranosyl-tri-O-Ac-5-amino[b]	$CDCl_3$	−212.8 ^2J(N1H2) = 7.8 ^3J(N1H4) = 3.6 ^2J(N1C4) = 8.4	−128.3 ^2J(N3H2) = 10.8 ^2J(N3H4) = 9.0 ^1J(N1C5) = 11.2	NH_2: −354.5 ^1J(NH2) = 85.5	48
61	1-CH_2COCH_3-4-nitro	DMSO	−208.0 ^2J(N1H2) = 8.2 ^2J(N1H5) = 3.0 ^2J(N1CH_2) = 2.3	−126.7 ^2J(N3H2) = 12.1	NO_2: −18.3	49
62	1-CH_2COCH_3-4,5-dinitro	DMSO	−213.5 ^2J(N1H2) = 7.8 ^2J(N1CH_2) = 1.3	−130.7 ^2J(N3H2) = 12.4	4-NO_2: −18.3; 5-NO_2: −32.6	49
63	1-CH_2COCH_3-2,4-dinitro	DMSO	−213.1 ^2J(N1CH_2) = 1.9	−129.7	2-NO_2: −31.1, 4-NO_2: −22.7	49
64	1-*β*-*D*-ribofuranosyl-3,5-di-*O*-acetyl-5-acetylamino[b]	$CDCl_3$	−207.2 ^2J(N1H2) = 7.4 ^3J(N1H4) = 2.7 ^1J(N1C2) = 11.4, ^1J(N1C5) = 17.7	−133.0 ^2J(N3H2) = 10.5 ^2J(N3H4) = 9.1 ^2J(N1C4) = 8.0,	NHAc: −269.9 ^1J(NH) = 93.3 ^1J(NHC5) = 20.4	48
65	1-*β*-*D*-ribofuranosyl-2,5-di-*O*-acetyl-5-acetylamino[b]	$CDCl_3$	−207.1 ^2J(N1H2) = 7.2 ^3J(N1H4) = 2.7 ^1J(N1C2) = 10.8, ^1J(N1C5) = 17.7	−133.3 ^2J(N3H2) = 10.7 ^2J(N3H4) = 9.3 ^2J(N1C4) = 7.9	NHAc: −269.0 ^1J(NH) = 93.0 ^1J(NHC5) = 21.8	48
66	1-*β*-*D*-ribofuranosyl-2,3-*O*-isopropylidene-4-ethoxycarbonyl-5-amino[b]	$CDCl_3$	−214.9 ^1J(N1C2) = 9.5, ^2J(N1C4) = 7.6, ^1J(N1C5) = 18.1	−136.6 ^2J(N3H2) = 11.1	NH_2: −332.5 ^1J(NH_2) = 85.3	48
67	1-*α*-*D*-ribofuranosyl-2,3-*O*-isopropylidene-4-ethoxycarbonyl-5-amino[b]	$CDCl_3$	−216.1 ^1J(N1C2) = 9.6, ^2J(N1C4) = 7.5, ^1J(N1C5) = 18.8	−136.8 ^2J(N3H2) = 11.8	NH_2: −334.8 ^1J(NH) = 83.7	48
68	1-*β*-*D*-ribofuranosyl-tri-*O*-acetyl-5-amino-4-carboxylic acid	$CDCl_3$	−217.4	−135.4	NH_2: −333.8 ^1J(NH_2) = 85.6	48
69	1-Benzyl	DMSO	−206.1 ^2J(N1H2) = 6.8 ^2J(N1H5) = 7.2	−119.1 ^2J(N3H2) = 10.9 ^2J(N3H4) = 10.9	—	This work
70	1-Vinyl	$CDCl_3$	−196.3	−119.5	—	50
71	1-Vinyl-2-methyl	$CDCl_3$	−200.9	−122.6	—	50
72	1-Phenyl	DMSO	−194.4	−114.4	—	33

Table 2. *Continued*

No.	Compound	Solvent	N-1	N-3	Substituents	Ref.
73	1-Acetyl	$CDCl_3$	−171.9	−113.9	—	15
	1-Acetyl	DMSO	−170.0	−110.3	—	15
			^2J(N1H2) = 8.2, ^2J(N1H5) = 4.1, ^2J(N3H2) = 11.5 ^2J(N3H4) = 10.0, ^3J(N1H4) = 4.1, ^3J(N3H5) = 1.6			
74	1-Amino	DMSO	−198.3	−126.4	NH_2: −311.0	29
			^2J(N1H2) = 11.0, ^2J(N1H5) = 3.2			
	1-Amino	TFA	−193.4	−217.0	NH_2: −309.0	51
				^1J(N3H3) = 102.8		
				^2J(N3H2) = ^2J(N3H4) = 4.5, ^3J(N3H5) = 3.9		
	1-Amino	H_2SO_4	−214.1	−209.8	NH_2: −308.4	51
			^2J(N1H2) = 12.9	^1J(N3H3) = 104.5		
			^2J(N1H5) = 2.0	^2J(N3H2) = ^2J(N3H4) = 4.0, ^3J(N3H5) = 3.8		
75	1-N = CH-C_6H_5	DMSO	−164.4	−73.0	N=CH: −121.9	This work
			^2J(N1H2) = 14.6, ^2J(N3H2) = 3.4, ^2J(N = CH) = 21.9 ^2J(N1H5) = ^3J(N1H4) = 3.5			

[a] Coupling constants from ^{1}H NMR spectroscopy.
[b] Coupling constants from ^{13}C NMR spectroscopy.
[c] From ^{14}N NMR spectroscopy

Table 3. Nitrogen-15 chemical shifts and some coupling constants of pyrazole derivatives III

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
76	Pyrazole[a]	$CHCl_3$	−133.3	−133.3	—	52
	Pyrazole	$CHCl_3$	−134.7	−134.7	—	14
	Pyrazole	$CDCl_3$	−132.2	−132.2	—	18
	Pyrazole	$CDCl_3$	−134.0	−134.0	—	15
	Pyrazole[d,e]	$CDCl_3$	−132.2	−132.2	—	53
			^2J(N1H5) = ^2J(N2H3) = 8.8, ^3J(N1H4) = ^3J(N2H4) = 3.5 ^3J(N1H3) = ^3J(N2H5) = 4.5 ^2J(N1C4) = ^2J(N2C4) = 1.5, ^2J(N1C3) + ^1J(N2C3) = 5.7			
	Pyrazole	CCl_4	^2J(N1H5) = ^2J(N2H3) = 8.9 ^3J(N1H4) = ^3J(N2H4) = 3.4, ^3J(N1H3) = ^3J(N2H5) = 4.3		—	23
	Pyrazole[b]	THF	−168.2	−81.9	—	54
			^1J(N1H1) = 105			
	Pyrazole	DMSO	−173.1	−79.8	—	14
	Pyrazole	Solid	−167.8	−90.5	—	55
	Pyrazole	Solid	−167.8	−90.5	—	54
	Pyrazole	CF_3CH_2OH	−143.4	−143.4	—	14
	Pyrazole	CH_3CO_2H	−144.4	−144.4	—	14
	Pyrazole	H_2O	−139.0	−139.0	—	14
	Pyrazole	TFA	−188.2	−188.2	—	15
77	3-Methyl[a]	$CHCl_3$	−133.8	−133.8	—	52
	3-Methyl	$CHCl_3$	−134.3	−139.8	—	14
	3-Methyl	$CDCl_3$	−133.4	−138.3	—	15
	3-Methyl	DMSO	−133.4	−141.9	—	15
	3-Methyl (inclusion compound)	Solid	−173	−93	—	56
	3-Methyl	CF_3CH_2OH	−145.7	−148.3	—	14
	3-Methyl	CH_3CO_2H	−151.1	−155.9	—	14
	3-Methyl	TFA	−195.6	−192.5	—	15
78	4-Undecyl	Solid	−169.2	−96.4/−113.5	—	57
79	3,5-Dimethyl	$CHCl_3$	−139.8	−139.8	—	14
	3,5-Dimethyl[d,e]	$CDCl_3$	^3J(N1H4) = ^3J(N2H4) = 3.1, ^3J(NMe) = 2.6			This work
			^2J(N1C4) = ^2J(N2C4) = 1.8			
	3,5-Dimethyl[b]	THF	−172.3	−94.3	—	54
			^1J(N1H1) = 102			
	3,5-Dimethyl	Solid (260 K)	−171.3	−96.8	—	54
	3,5-Dimethyl	CF_3CH_2OH	−150.2	−150.2	—	14
	3,5-Dimethyl	CH_3CO_2H	−165.7	−165.7	—	14
80	3,4,5-Trimethyl	Solid	−175.1	−99.3	—	54
81	3-Methyl-4,5-trimethylene[d]	$CDCl_3$	^1J(N2C3) = 3.8		—	58
	3-Methyl-4,5-trimethylene	DMSO	−103.2	−168.5	—	58
			^1J(N1N2) = 11.5			
	3-Methyl-4,5-trimethylene	THF (180 K)	−103.4	−170.6	—	58
			^1J(N1N2) = 11.5, ^1J(N1H1) = 107.0			
82	3-Methyl-4,5-tetramethylene	DMSO	−158.3	−164.0	—	58

Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
83	3-Methyl-4,5-pentamethylene	DMSO	−125.9	−160.3	—	58
84	3,5-Di-*tert*-butyl[b]	THF	−179(br)	−89(br)	—	54
	3,5-Di-*tert*-butyl	Solid	−178.1	−96.8	—	54
85	3-Phenyl-5-methyl[b]	THF	−152.9	−65.3	—	59
			^1J(N1H1) = 104, ^2J(N2H1) = 7.3, ^1J(N1N2) = 11.6			
	3-Phenyl-5-methyl[c]	toluene	−147.5	−78.9	—	59
			^1J(N1N2) = 11.6			
	3-Phenyl-5-methyl	Solid	−170.9	−102.6	—	54
86	3-Methyl-5-phenyl[b]	THF	−163.3	−59.7	—	59
			^1J(N1H1) = 104			
	3-Methyl-5-phenyl[c]	toluene	−153.3	−69.2	—	59
	3-Methyl-5-phenyl	Solid	−172.1	−101.0	—	54
87	3,5-Dimethyl-4-bromo	Solid	−174.6	−99.6	—	54
88	3,5-Diphenyl[b]	THF	−180.3	−83.2	—	54
			^1J(N1H1) = 106			
	3,5-Diphenyl	Solid	−175.0	−102.0	—	54
89	3,5-Diphenyl-4-methyl	Solid (220 K)	−174.6	−90.6	—	54
90	3,5-Diphenyl-4-bromo[b]	THF	−175.0	−80.3	—	54
			^1J(N1N2) = 16, ^1J(N1H1) = 106			
	3,5-Diphenyl-4-bromo	Solid (220 K)	−174.7	−90.5	—	54
91	3-Ethoxycarbonyl[a]	$CHCl_3$	−104	−104	—	52
92	3-Amino	DMSO	−175.7	−138.4	NH_2: −339.2	This work
	3-Amino	TFA	−218.2	−220.6	NH_2: −334.4	This work
93	4-Amino	DMSO	—	—	NH_2: −354.4	This work
		CD_3OD	—	—	NH_2: −360.5	This work
		DMSO + TFA	−127.5	−127.5	NH_2: −349.2	This work
94	3-Anilino-4-ethoxycarbonyl-5-amino	DMSO	−218.7	−145.6	—	60
95	4-Nitro	solid	−166.5/-179.3	−134.8	—	54
96	3,5-Dimethyl-4-nitro	solid	−173.6	−105.8	—	54
97	3,5-Di-*tert*-butyl-4-nitro	Solid	−182.8	−97.0	—	54
98	1-Methyl[a]	$CHCl_3$	−180.8	−72.6	—	52
	1-Methyl	$CHCl_3$	−180.8	−76.5	—	14
	1-Methyl	$CDCl_3$	−179.3	−73.7	—	18
	1-Methyl	$CDCl_3$	−180.8	−76.5	—	15
	1-Methyl	DMSO	−180.8	−73.7	—	29
	1-Methyl	DMSO	−178.4	−71.6	—	61
			^2J(N1H5) = 4.0	^2J(N2H3) = 12.7		
			^3J(N1H3) = 8.2	^3J(N2H4) = 6.0		
			^2J(N1Me) = 1.8	^3J(N2Me) = 2.0		
	1-Methyl	CF_3CH_2OH	−182.2	−94.4	—	14
	1-Methyl[a]	CH_3OH	−180	−80	—	14
	1-Methyl	CH_3CO_2H	−181.4	−93.6	—	14
	1-Methyl	TFA	−190.8	−185.3	—	46

Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
99	1,3-Dimethyl[a]	$CHCl_3$	−182.8	−70.8	—	52
	1,3-Dimethyl	DMSO	−184.1	−74.4	—	61
			^2J(N1H5) = 4.4	^3J(N2H4) = 6.0		
			^2J(N1Me1) = 1.7	^3J(N2Me1) = 1.9		
				^3J(N2Me3) = 2.7		
100	1,5-Dimethyl[a]	$CHCl_3$	−178.6	−71.7	—	52
	1,5-Dimethyl	DMSO	−180.4	−73.0	—	61
			^3J(N1H3) = 8.1	^2J(N2H3) = 12.6		
			^2J(N1Me1) = 1.6	^3J(N2H4) = 5.4		
			^3J(N1Me5) = 2.2	^3J(N2Me1) = 2.3		
	1,5-Dimethyl	DMSO	−180.4	−73.5	—	This work
101	1,3,5-Trimethyl	Acetone	−186.7	−76.4	—	This work
102	1-Methyl-3,5-di-*tert*-butyl	DMSO	−190.8	−74.8	—	This work
103	1-Methyl-3,5-diphenyl	DMSO	−184.2	−77.1	—	This work
104	1,3-Dimethyl-4,5-trimethylene	DMSO	−198.5	−65.8	—	58
105	1,3-Dimethyl-4,5-tetramethylene	DMSO	−193.1	−81.2	—	58
106	1,3-Dimethyl-4,5-pentamethylene	DMSO	−192.5	−83.1	—	58
107	1,5-Dimethyl-3,4-trimethylene	DMSO	−179.7	−89.8	—	58
108	1,5-Dimethyl-3,4-tetramethylene	DMSO	−187.9	−84.0	—	58
109	1,5-Dimethyl-3,4-pentamethylene	DMSO	−190.7	−83.8	—	58
110	1,5-Dimethyl-3-ethoxycarbonyl	DMSO	−172.6	−64.7	—	This work
111	1-Methyl-3-benzoyl	DMSO	−171.1	−60.6	—	61
			^2J(N1H5) = 4.5	^3J(N2H4) = 5.5		
			^2J(N1Me) = 1.9	^3J(N2Me) = 2.1		
112	1-Methyl-4-benzoyl	DMSO	−171.7	−69.2	—	61
			^2J(N1H5) = 4.1	^2J(N2H3) = 12.5		
			^3J(N1H3) = 9.0	^3J(N2Me) = 2.0		
			^2J(N1Me) = 1.8			
113	1-Methyl-5-benzoyl	DMSO	−173.8	−55.0	—	61
			^3J(N1H3) = 7.3	^2J(N2H3) = 12.7		
			^2J(N1Me) = 1.9	^3J(N2H4) = 5.2		
				^3J(N2Me) = 2.2		
114	1-Methyl-3-cyano	DMSO	−166.5	−60.6	CN: −123.3	61
			^2J(N1H5) = 4.3	^3J(N2H4) = 5.9		
			^2J(N1Me) = 2.0	^3J(N2Me) = 2.3		
115	1-Methyl-5-cyano	DMSO	−171.1	−55.0	—	61
			^3J(N1H3) = 8.2	^2J(N2H3) = 12.4		
			^2J(N1Me) = 2.0	^3J(N2H4) = 5.0		
				^3J(N2Me) = 2.0		
116	1-Methyl-3-amino	DMSO	−199.9	−107.3	NH_2: −336.1	62
	1-Methyl-3-amino	DMSO	−201.7	−109.1	NH_2: −338.3	61
			^2J(N1H5) = 4.0	^3J(N2H4) = 6.0		
			^2J(N1Me) = 1.8	^3J(N2Me) = 2.0		
	1-Methyl-3-amino	TFA	−197.7	−187.0	NH_2: −332.3	62
117	1-Methyl-4-amino	DMSO	−189.7	−78.2	NH_2: −354.1	62

Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
118	1-Methyl-5-amino	DMSO	−203.6	−97.5	NH_2: −340.9	62
	1-Methyl-5-amino	TFA	−208.9	−221.0	NH_2: −330.9	62
	1-Methyl-5-amino	DMSO	−201.4	−94.2	NH_2: −338.7	61
			^3J(N1H3) = 7.0	^2J(N2H3) = 12.3	^1J(NH2) = 80.0	
			^2J(N1Me) = 1.9	^3J(N2H4) = 4.1		
				^3J(N2Me) = 2.1		
119	1-Methyl-3-nitro	DMSO	−173.7	−75.9	NO_2: − 20.0	61
			^2J(N1H5) = 4.0	^3J(N2H4) = 6.6		
			^2J(N1Me) = 1.9	^3J(N2Me) = 2.3		
	1-Methyl-3-nitro	DMSO	−173.3	−76.0	NO_2: −20.0	This work
120	1-Methyl-4-nitro	DMSO	−172.0	−69.8	NO_2: −18.3	61
			^2J(N1H5) = 3.0	^2J(N2H3) = 12.1		
			^3J(N1H3) = 9.1	^3J(N2Me) = 2.3		
			^2J(N1Me) = 2.0	^3J(N2H5) = 1.0		
	1-Methyl-4-nitro	DMSO	−172.0	−69.6	NO_2: −18.3	This work
121	1-Methyl-5-nitro	DMSO	−182.1	−56.6	NO_2: −26.3	61
			^3J(N1H3) = 7.4	^2J(N2H3) = 12.5		
			^2J(N1Me) = 2.1	^3J(N2H4) = 4.0		
				^3J(N2Me) = 2.3		
	1-Methyl-5-nitro	DMSO	−181.5	−56.9	NO_2: −26.1	This work
122	1-Methyl-3,4-dinitro	DMSO	−180.3	−78.3	3-NO_2: −26.3	61
			^2J(N1H5) = 2.0	^3J(N2Me) = 2.4	4-NO_2: −26.1	
			^2J(N1Me) = 2.1			
123	1-Methyl-3,5-dinitro	DMSO	−179.9	−69.5	3-NO_2: − 24.1	61
			^2J(N1Me) = 2.3	^3J(N2H4) = 5.0	5-NO_2: −29.3	
				^3J(N2Me) = 2.5		
124	1-Methyl-3-cyano-4-nitro	DMSO	−166.4	−58.4	CN: −113.6	61
			^2J(N1H5) = 3.2	^3J(N2Me) = 2.2	NO_2: −24.1	
			^2J(N1Me) = 2.1			
125	1-Methyl-4-nitro-5-cyano	DMSO	−163.9	−58.6	NO_2: −23.8	61
			^3J(N1H3) = 9.0	^2J(N2H3) = 11.8		
			^2J(N1Me) = 2.2	^3J(N2Me) = 2.2		
126	1-Methyl-3-carboxy-4-nitro	DMSO	−175.5	−68.7	NO_2: −21.0	61
			^2J(N1H5) = 3.0	^3J(N2Me) = 2.1		
			^2J(N1Me) = 2.1			
127	1-Methyl-4-nitro-5-carboxy	DMSO	−174.2	−70.5	NO_2: −20.8	61
			^3J(N1H3) = 9.3	^2J(N2H3) = 12.1		
			^2J(N1Me) = 2.0	^3J(N2Me) = 2.3		
128	1-Methyl-3-benzoyl-4-nitro	DMSO	−174.0	−69.4	NO_2: −21.1	61
			^2J(N1H5) = 3.3	^3J(N2Me) = 2.1		
			^2J(N1Me) = 2.0			
129	1-Methyl-4-nitro-5-benzoyl	DMSO	−173.8	−58.6	NO_2: −20.8	61
			^3J(N1H3) = 9.3	^2J(N2H3) = 12.2		
			^2J(N1Me) = 2.0	^3J(N2Me) = 2.2		

Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
130	1-Methyl-3-carboxamido-4-amino	DMSO	−185.6 ^2J(N1H5) = 4.5 ^2J(N1Me) = 2.0	−80.2 ^3J(N2Me) = 2.1	$CONH_2$: −282.7	61
131	1-Methyl-4-amino-5-carboxamido	DMSO	−188.1 ^3J(N1H3) = 7.9 ^2J(N1Me) = 2.0	−67.0 ^2J(N2H3) = 11.8 ^3J(N2Me) = 2.3	$CONH_2$: −275.4	61
132	1-Methyl-3-carboxamido-4-nitro	DMSO	−177.3 ^2J(N1H5) = 3.5 ^2J(N1Me) = 2.2	−71.7 ^3J(N2Me) = 2.1	NO_2: −20.3 $CONH_2$: −268.8	61
133	1-Methyl-4-nitro-5-carboxamido	DMSO	−175.6 ^3J(N1H3) = 9.3 ^2J(N1Me) = 2.0	−73.4 ^2J(N2H3) = 12.1 ^3J(N2Me) = 2.2	NO_2: −19.5 $CONH_2$: −263.9	61
134	1-Methyl-4-nitro-5-amino	DMSO	−207.4 ^3J(N1H3) = 7.0 ^2J(N1Me) = 2.0	−92.4 ^2J(N2H3) = 12.0 ^3J(N2Me) = 2.4	NO_2: −18.9 NH_2: −318.3	61
135	1-Methyl-4-amino-5-nitro	DMSO	−201.6 ^3J(N1H3) = 9.1 ^2J(N1Me) = 1.8	−55.3 ^2J(N2H3) = 12.7 ^3J(N2Me) = 2.1	NO_2: −26.1	61
136	1,3-Dimethyl-5-methoxy	DMSO	−208.5	−98.1	—	This work
137	1,5-Dimethyl-3-methoxy	DMSO	−204.7	−112.8	—	This work
138	1-Methyl-3,5-diphenyl-4-hydroxy	$CDCl_3$	−197.2	−92.5	—	63
139	1,3-Dimethyl-4,5-dichloro	DMSO	−188.8 ^2J(N1Me1) = 1.9	−76.9 ^3J(N2Me1) = 2.0	—	61
140	1-Methyl-3,5-dinitro-4-chloro	DMSO	−182.2 ^2J(N1Me) = 2.2	−74.7 ^3J(N2Me) = 2.5	3-NO_2: −28.2 5-NO_2: −32.4	61
141	1-Methyl-3-nitro-4-chloro-5-carboxy	DMSO	−174.8 ^2J(N1Me) = 2.2	−69.2 ^3J(N2Me) = 2.5	NO_2: −26.0	61
142	1-Methyl-3-carboxy-4-chloro-5-nitro	DMSO	−178.7 ^2J(N1Me) = 2.3	−59.2 ^3J(N2Me) = 2.4	NO_2: −30.5	61
143	1-Methyl-4-bromo	DMSO	−176.1 ^2J(N1H5) = 4.1 ^3J(N1H3) = 8.2 ^2J(N1Me) = 2.0	−68.8 ^2J(N2H3) = 12.2 ^3J(N2Me) = 2.0	—	61
144	1,5-Dimethyl-4-bromo	DMSO	−179.2	−74.0	—	This work
145	1,3-Dimethyl-4,5-dibromo	DMSO	−183.4 ^2J(N1Me1) = 1.8	−70.2 ^3J(N2Me1) = 2.0 ^3J(N2Me3) = 2.8	—	61
146	1,5-Dimethyl-3,4-dibromo	DMSO	−177.7 ^2J(N1Me1) = 1.7 ^3J(N1Me5) = 2.3	−78.2 ^3J(N2Me1) = 2.2	—	61
147	1-Methyl-3-nitro-4-bromo	DMSO	−173.8 ^2J(N1H5) = 3.6 ^2J(N1Me) = 2.1	−73.4 ^3J(N2Me) = 2.1	NO_2: −23.6	61
148	1-Methyl-4-nitro-5-bromo	DMSO	−171.1 ^3J(N1H3) = 8.7 ^2J(N1Me) = 2.0	−68.9 ^2J(N2H3) = 12.4 ^3J(N2Me) = 2.1	NO_2: −22.3	61

Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
149	1-Methyl-3,5-dinitro-4-bromo	DMSO	−179.8	−72.0	3-NO_2: −26.8	61
			^2J(N1Me) = 2.3	^3J(N2Me) = 2.5	5-NO_2: −31.6	
150	1-Ethyl	$CDCl_3$	−166.5	−80.1		64
			^3J(N1H4) = ^3J(N1H3) = 7.2, ^2J(N2H3) = 13.9			
151	1-CH_2COCH_3	DMSO	−169.7	−68.9	—	49
	1-CH_2COCH_3	DMSO	−177.5	−72.0	—	This work
			^3J(N1H3) = 9.2	^2J(N2H3) = 12.5		
			^3J(N1H4) = 5.2	^3J(N2H4) = ^3J(N2CH_2) = 2.5		
			^2J(N1H5) = 2.7			
			^2J(N1CH_2) = 2.6			
152	1-CH_2COCH_3-3-nitro	DMSO	−174.0	−76.2	NO_2: −20.4	61
153	1-CH_2COCH_3-4-nitro	DMSO	−174.0	−69.7	NO_2: −18.8	61
			^3J(N1H3) = 10.2	^2J(N2H3) = 13.6		
			^2J(N1CH_2) = 1.7	^3J(N2CH_2) = 2.3		
154	1-CH_2COCH_3-3,4-dinitro	DMSO	−181.0	−78.1	3-NO_2: −26.8	61
			^2J(N1CH_2) = 2.5	^3J(N2CH_2) = 2.7	4-NO_2: −26.7	
155	1-(1-Adamantyl)	$CDCl_3$	−145.7	−82.8	—	65
156	1-Benzyl	CH_3CN	−167.7	−73.5	—	66
	1-Benzyl[d,e]	$CDCl_3$	−169.9	−76.9	—	This work
			^1J(N1C5) = 12.8, ^2J(N1C4) = 5.5, ^2J(N2C4) = 1.9, ^1J(N1N2) = 12.7 ^3J(N1H3) = 8.3, ^3J(N1H4) = 5.8, ^2J(N1H5) = 4.7, ^2J(N1CH_2) = ^3J(N2CH_2) = 1.7, ^2J(N2H3) = 12.6, ^3J(N2H4) = 1.1			
	1-Benzyl	C_6D_6	−169.7	−70.7	—	This work
			^1J(N1N2) = 12.8			
	1-Benzyl	Acetone	−167.8	−71.1	—	This work
			^1J(N1N2) = 13.0			
	1-Benzyl	DMSO	−167.3	−72.9	—	This work
			^1J(N1N2) = 12.9			
157	1-Benzyl-3-methyl-4-acetyl	$CDCl_3$	−173.1	−75.7	—	15
	1-Benzyl-3-methyl-4-acetyl	DMSO	−168.9	−72.9	—	15
			^2J(N1H5) = 3.6			
158	1-Benzyl-4-acetyl-5-methyl	$CDCl_3$	−167.0	−91.4	—	15
	1-Benzyl-4-acetyl-5-methyl	DMSO	−163.2	−75.5	—	15
			^3J(N1H3) = 10.5,	^2J(N2H3) = 12.0		
159	1,3-CH_2pz-5-methyl[f]	$CDCl_3$	−173.8	−79.1	—	This work
	1,3-CH_2pz-5-methyl[f]	CD_3OD	−173.6	−85.5	—	This work
160	1-$C(CD_3)_2OH$[d,e]	Acetone at −50 °C	−140.3	−80.6	—	53
			^1J(N1C5) = 13.4, ^3J(N1H3) = 7.5, ^3J(N1H4) = 5.2, ^2J(N1H5) = 4.0, ^2J(N2H3) = 12.9, ^1J(N1N2) = 13.4			
161	1-Trityl	$CDCl_3$	−155.9	−71.1	—	65
162	1-[(Pyrazol-1-yl)CH_2]	$CDCl_3$	−170.7	−77.4	—	This work
163	1-[(Pyrazol-1-yl)$_2$CH]	$CDCl_3$	−170.0	−79.0	—	This work

Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
164	1-[(Pyrazol-1-yl)$_3$C]	$CDCl_3$	−167.2	−77.1	—	This work
165	1-[(3,5-Dimethylpyrazol-1-yl)$_2$CH] 3,5-dimethyl	$CDCl_3$	−178.9	−83.7	—	This work
166	1-Vinyl	$CDCl_3$	−160.2	−78.6	—	50
167	1-Vinyl-3-methyl	$CDCl_3$	−164.9	−83.1	—	50
168	1-Vinyl-5-methyl	$CDCl_3$	−163.8	−91.1	—	50
169	1-Vinyl-3,5-dimethyl	$CDCl_3$	−168.7	−89.6	—	50
170	1-Vinyl-4-nitro	$CDCl_3$	−160.3	−78.9	NO_2: −21.3	50
171	1-Vinyl-3,5-dimethyl-4-nitro	$CDCl_3$	−168.4	−92.2	NO_2: −16.7	50
172	1-Vinyl-4-bromo	$CDCl_3$	−154.6	−70.2	—	50
173	1-Phenyl[d]	$CDCl_3$	−160.6	−78.6	—	67
			^2J(N1C3) = 1.2, ^2J(N1C4) = 6.2, ^2J(N2C4) = 2.1, ^1J(N1C5) = 12.1, ^1J(N1N2) = 12.8			
	1-Phenyl	C_6D_6	−160.1	−75.3		68
	1-Phenyl	DMSO	−159.9	−77.3	—	33
174	1-Phenyl-3,5-dimethyl[d]	$CDCl_3$	^2J(N2-3Me) = 8.7, ^2J(N2C4) = 1.9, ^2J(N1Me5) = 0.7			69
			^2J(N1C4) = 6.4			
175	1-Phenyl-3-methyl-5-ethyl[d]	$CDCl_3$	^2J(N2Me3) = 8.8, ^2J(N2C4) = 1.5		—	69
	1-Phenyl-3-methyl-5-ethyl[e]	$CDCl_3$	^3J(N2Me3) = 2.8		—	70
176	1-Phenyl-3-methyl-5-isobutyl[d]	$CDCl_3$	^2J(N2Me3) = 8.5, ^2J(N2C4) = 1.8		—	69
	1-Phenyl-3-methyl-5-isobutyl[e]	$CDCl_3$	^3J(N2Me3) = 2.9			70
177	1-Phenyl-3-methyl-5-benzyl[e]	$CDCl_3$	^3J(N2Me3) = 2.9		—	70
178	1-Phenyl-3-methyl-4,5-tri(CH_2)[e]	$CDCl_3$	^3J(N2Me3) = 3.0			70
179	1,5-Diphenyl	DMSO	−166.5	−68.4	—	This work
180	1-Phenyl-3-methyl-5-phenyl[e]	$CDCl_3$	^2J(N2Me3) = 2.8			70
181	1-Phenyl-3-ethyl-5-methyl[d]	$CDCl_3$	^2J(N2-3CH_2) = 8.8, ^2J(N2C4) = 1.5, ^3J(N2-CH_3/Et) = 1.5			69
	1-Phenyl-3-ethyl-5-methyl[e]	$CDCl_3$	^3J(N2-3CH_2) = 2.4			70
182	1-Phenyl-3-ethyl-5-benzyl[d]	$CDCl_3$	^2J(N2-3CH_2) = 8.2, ^2J(N2C4) = 1.8			69
	1-Phenyl-3-ethyl-5-benzyl[e]	$CDCl_3$	^3J(N2-3CH_2) = 2.4			70
183	1-Phenyl-3-benzyl-5-methyl[d]	$CDCl_3$	^2J(N2-3CH_2) = 8.6, ^2J(N2C4) = 1.8			69
	1-Phenyl-3-benzyl-5-methyl[e]	$CDCl_3$	^3J(N2-3CH_2) = 2.7			70
184	1-Phenyl-3-benzyl-5-ethyl[d]	$CDCl_3$	^2J(N2-3CH_2) = 8.2, ^2J(N2C4) = 1.8			69
	1-Phenyl-3-benzyl-5-ethyl[e]	$CDCl_3$	^3J(N2-3CH_2) = 2.6			70
185	1,5-Diphenyl-3-benzyl[e]	$CDCl_3$	^3J(N2-3CH_2) = 2.2			70
186	1,3-Diphenyl-5-methyl[d]	$CDCl_3$	^2J(N2-3C_{ipso}) = 8.5, ^2J(N2C4) = 1.8			69
187	1,3-Diphenyl-5-benzyl[d]	$CDCl_3$	^2J(N2-3C_{ipso}) = 8.2, ^2J(N2C4) = 1.8			69
188	1-Phenyl-3-amino	$CDCl_3$	−182.7	−118.9	NH_2: −339.9	This work
	1-Phenyl-3-amino	DMSO	−185.4	−122.5	NH_2: −335.8	62
	1-Phenyl-3-amino	TFA	−182.1	−177.2	NH_2: −330.3	62
189	1-Phenyl-4-amino	DMSO	−170.8	−82.0	NH_2: −349.6	62
	1-Phenyl-4-amino	TFA	−135.2	−127.0	NH_2: −348.4	62
190	1-Phenyl-5-amino	DMSO	−181.9	−93.5	NH_2: −334.0	62
	1-Phenyl-5-amino	TFA	−206.7	−210.4	NH_2: −329.0	62

Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
191	1-Phenyl-4-chloro	DMSO	−163.1	−77.8	—	This work
192	1-Acetyl	$CDCl_3$	−139.9	−77.0	—	64
			^3J(N1H4) = ^3J(N1H3) = 8.9, ^2J(N2H3) = 13.5			
193	1-Ethoxycarbonyl-3-methyl-4-acetyl	$CDCl_3$	−167.9	−83.2	—	15
	1-Ethoxycarbonyl-3-methyl-4-acetyl	DMSO	−166.7	−78.9	—	15
				^2J(N1H5) = 3.4, ^3J(N2H5) = 1.9		
194	1-Ethoxycarbonyl-4-acetyl-5-methyl	$CDCl_3$	−159.9	−80.6	—	15
	1-Ethoxycarbonyl-4-acetyl-5-methyl	DMSO	−159.2	−76.0	—	15
				^3J(N1H3) = 9.0, ^2J(N2H3) = 13.7		
195	1-Carboxamido	DMSO	−153.4	−81.4	NH_2: −295.7	64
				^3J(N1H4) = ^3J(N1H3) = 7.6, ^2J(N2H3) = 13.5, $^1J(NH_2)$ = 91.0		
196	1-Carboxamido-3-methyl	DMSO	−158.8	−87.4	NH_2: —	66
197	1-Amino	DMSO	−162.1	−72.4	NH_2: −297.1	29
	1-Amino[d,e]	$CDCl_3$	−168.0	−78.0	NH_2: −300.8	29
				^1J(N1C5) = 16.5, ^1J(N2C3) = 1.9, ^2J(N1C4) = 6.4, ^1J(N1N2) = 14.0, ^3J(N1H4) = 7.2		
	1-Amino	TFA	−177.4	−178.4	NH_2: −305.1	51
			^3J(N1H3) = 10.1	^2J(N2H3) = 10.5		
			^3J(N1H4) = 3.5	^3J(N2H4) = 5.6		
	1-Amino	H_2SO_4	−186.0	−195.2	NH_2: −301.8	51
			^3J(N1H3) = 10.4	^1J(N2H2) = 110.8		
			^3J(N1H4) = 3.3	^2J(N2H3) = 10.5, ^3J(N2H4) = 5.6		
198	1-Methylamino	$CDCl_3$	−151.8	−82.4	NH: −299.1	65
199	1-NHCHO (*Z* isomer)	DMSO	−176.4	−71.9	NH: −230.5	71
				^1J(NH) = 101.2, ^2J(CH) = 22.8		
200	1-NHCHO (*E* isomer)	DMSO	−173.4	−70.1	NH: −226.6	71
				^1J(NH) = 98.7, ^2J(CH) = 12.7		
201	1-$NHCOCH_3$ (*Z* isomer)	DMSO	−172.6	−71.9	NH: −232.9	64
				^2J(N1H5) = 3.5, ^3J(N1H3) = ^3J(N1H4) = 8.8 ^2J(N2H3) = 13.1		
202	1-$NHCOCH_3$ (*E* isomer)	DMSO	−170.8	−70.4	NH: −230.3	64
203	1-N=CH-C_6H_5	DMSO	−136.5	−69.3	N=C: −95.0	64
204	1-N=P(C_6H_5)$_3$	$CDCl_3$	−167.2	−78.1	N=P: −147.4	64
205	1,1-Bis(3-R,4-R′-1-pyrazolyl)[g]	DMSO	−211.5	−137.1	—	60
206	1-Azopyrazole[h]	$CDCl_3$	−144.0	−154.5	—	60
207	1-Nitro	$CDCl_3$	−109.1	−86.1	1-NO_2: −59.0	15
	1-Nitro	DMSO	−108.5	−84.6	1-NO_2: −56.9	15
				^2J(N1H5) = 3.1, ^3J(N1H3) = 10.3, ^3J(N1H4) = 7.4 ^2J(N2H3) = 13.5		
	1-Nitro[d,e]	Acetone	−107.8	−82.5	—	53
				^1J(N1C5) = 11.6, ^2J(N1C4) = 7.9, ^2J(N2C4) = 2.0, ^1J(N1N2) = 14.7 ^3J(N1H4) = 7.6, ^3J(N1H3) = 10.6, ^2J(N1H5) = 3.1, ^2J(N2H3) = 14.4		
	1-Nitro	Acetone	−108.2	−83.8	1-NO_2: −56.6	72

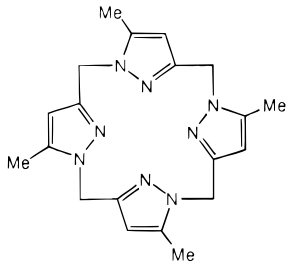
Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
208	1,3-Dinitro	Acetone	−113.1 ^2J(N1H5) = 2.5 ^3J(N1H4) = 8.2	−93.6	1-NO_2: −63.2 ^4J(H4) = 1.1 3-NO_2: −25.1	72
209	1,4-Dinitro	Acetone	−109.9 ^2J(N1H5) = 2.0 ^3J(N1H3) = 8.8	−84.2 ^2J(N2H3) = 12.6	1-NO_2: −63.0 4-NO_2: −23.2	72
210	1,3,4-Trinitro	Acetone	−117.0 ^2J(N1H5) = 3.0	−95.6	1-NO_2: −68.6 3-NO_2: −31.0 4-NO_2: −30.8	72
211	1-Nitro-3-methyl	Acetone	−112.5 ^2J(N1H5) = 3.0 ^3J(N1H4) = 8.0	−88.1 ^3J(N2Me) = 3.2	1-NO_2: −55.7	72
212	1,3-Dinitro-5-methyl	Acetone	−114.0 ^3J(N1Me) = 2.1 ^3J(N1H4) = 8.1	−92.4	1-NO_2: −59.8 ^4J(H4) = 1.5 3-NO_2: −24.2	72
213	1,4-Dinitro-3-methyl	Acetone	−116.6 ^2J(N1H5) = 1.3,	−88.6 ^3J(N2Me) = 3.5	1-NO_2: −62.3 4-NO_2: −21.2 ^4J(Me) = 0.4	72
214	1,4-Dinitro-3,5-dimethyl	Acetone	−114.8 ^3J(N1Me) = 2.3,	−91.7 ^3J(N2Me) = 3.4	1-NO_2: −58.9 4-NO_2: −18.9 ^4J(Me) = 0.8	72
215	1,3,4-Trinitro-5-methyl	Acetone	−118.8 ^3J(N1Me) = 2.2	−98.6	1-NO_2: −65.7 3-NO_2: −29.8 4-NO_2: −28.8	72
216	1,3-Dinitro-4-cyano	Acetone	−113.4 ^2J(N1H5) = 1.9	−91.6	1-NO_2: −68.1 3-NO_2: −30.2 4-CN: −109.4	72
217	1-Nitro-4-(1,4-dinitropyrazolyl)	Acetone	−107.2 ^3J(N1H3) = 10.5,^2J(N1H5) = 4.7, ^2J(N2H3) = 13.5	−83.4	1-NO_2: −60.2	73
218	1,4-Dinitro-3-(1-nitropyrazolyl)	Acetone	−113.6 ^2J(N1H5) = 1.6	—	1-NO_2: −64.5 4-NO_2: −23.7	73
219	1-Hydroxy	$CDCl_3$	−144.0 ^3J(N1H3) = ^3J(N1H4) = 8.5, ^2J(N2H3) = 13.3	−107.6	—	64
220	1-[(Pyrazol-1-yl)BH_2]$^-$	DMSO	−137.3 ^3J(N1H3) = 6.7, ^3J(N1H4) = 6.7, ^2J(N2H3) = 12.8	−70.4	—	74
221	1-[(Pyrazol-1-yl)$_2$BH]$^-$	DMSO	−141.9 ^3J(N1H3) = 7.7, ^3J(N1H4) = 7.7, ^2J(N2H3) = 13.0	−68.8	—	74
222	1-[(Pyrazol-1-yl)$_3$B]$^-$	DMSO	−147.5 ^3J(N1H3) = 6.0, ^3J(N1H4) = 5.5, ^2J(N2H3) = 13.4 ^2J(N1H5) = 5.5, ^1J(N1-^{11}B) = 30	−67.3	—	74

Table 3. *Continued*

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
223	1-[(3,5-Dimethylpyrazol-1-yl)$_2$BH]-3,5-dimethyl[d,e]	DMSO	−151.7 ^2J(N1C4) = 3.2, ^1J(N1C5) = 9.2, ^2J(N2Me3) = 9.0 ^3J(N1Me3) = 2.6, ^2J(N1Me5) = 1.6, ^1J(N1N2) = 13.3 ^3J(N1H4) = 3.8, ^3J(N1Me5) = 1.7, ^3J(N2Me3) = 2.6	−75.3	—	75
224	1-Trifluoromethanosulfonyl	$CDCl_3$	−162.0	−72.3	—	64
225	1-Trimethylsilyl	$CDCl_3$	−162.9	−72.5	—	64

[a] From ^{14}N NMR spectroscopy.
[b] THF at 170-175 K, blocked prototropic tautomerism.
[c] toluene at 190 K, blocked prototropic tautomerism.
[d] Coupling constants from ^{13}C NMR spectroscopy.
[e] Coupling constants from ^{1}H NMR spectroscopy.
[f] Tetrazaporphyrinogens.



[g] 3-Anilino-4-ethoxycarbonyl-5-amino.
[h] 1-N=NC(NHPh)=C(CN)CO_2Et-3-anilino-4-ethoxycarbonyl-5-amino.

Reference Data Review

Table 4. Nitrogen-15 chemical shifts and some coupling constants of 1,3,4-triazole derivatives IV

No.	Compound	Solvent	N-1	N-3	N-4	Substituents	Ref.
226	1-Methyl[a]	CH_3OH	−222	−82	−82	—	2
	1-Methyl	DMSO	−217.1	−60.3	−60.3	—	18
	1-Methyl	DMSO	−217.8	−59.8	−59.8	—	28,29
	1-Methyl	TFA	−206.8	−130.5	−130.5	—	46
				^2J(N1H2) = ^2J(N1H5) = 6.7			
227	1-Methyl-2-methoxy	DMSO	−243.0	−112.0	−75.0	—	76
228	1-Methyl-2-methylthio	DMSO	−218.9	−60.9	−65.3	—	77
229	1-Methyl-2-amino	DMSO	−241.6	−112.0	−75.4	NH_2: −339.6	78
	1-Methyl-2-amino	H_2O	−238.8	−128.7	−95.5	NH_2: −340.9	78
			^2J(N1H5) = 8.2, ^3J(N3H5) = 2.1, ^2J(N4H5) = 11.0, ^2J(N1Me) = 1.4				
230	1-Benzyl-2-amino-5-methylthio	DMSO	−227.1	−109.4	−74.4	NH_2: −333.9	79
231	1-Benzyl-2-amino-5-SCH_2R	DMSO	−226.0	−107.3	−62.9	NH_2: −333.5	79
232	1-Phenyl	DMSO	−193.7	−58.2	−58.2	—	33
233	1-Amino	DMSO	−198.2	−66.1	−66.1	NH_2: −315.5	29
	1-Amino	TFA	−190.4	−133.4	−133.4	NH_2: −313.2	51
	1-Amino	H_2SO_4	−209.6	−131.9	−131.9	NH_2: −308.8	51
				^2J(N1H2) = ^2J(N1H5) = 5.4, ^2J(N3H2) = ^2J(N4H5) = 12.0			

[a] From ^{14}N NMR spectroscopy

methane were positive whereas in recent papers they are negative (we have followed the latter convention).

RESULTS AND DISCUSSION

Additive models

The early attempts by Webb and co-workers to use additive models succesfully in the case of azoles have been described in their reviews.[1–4]

N-Substituents. The chemical shifts of the *N*-methyl nitrogen atoms (N-1) are known for all parent azoles in DMSO with the exception of isoindole (solvent: diethyl ether) and pentazole (unknown compound). A multiple regression taking into account the number and position of 'pyridine-like' nitrogen atoms (Nα and Nβ), the benzo- and isobenzo-annelations led to Eqn (12):

$$\delta^{15}\text{N-Me} = -235.8 + 55.7\ \text{N}\alpha + 16.5\ \text{N}\beta - 16.3\ \text{Benzo} + 14.5\ \text{Isobenzo}, n = 17, r^2 = 0.96 \quad (12)$$

Equation (12) predicts for 1-methylpentazole δ^{15}N-Me = −91.5 ppm.

1-Methylpentazole is not stable but we have reported in Table 10 the value of *N*-R for 1-*p*-dimethylaminophenylpentazole (**321**) (−80.0 ppm). For the nine azoles **I**–**IX**, the values of *N*-R are known for R = methyl and R = phenyl (both in DMSO):

$$^{15}N\text{-Me} = -3.24 + 1.105\ \delta^{15}N\text{-Ph}, \quad n = 9, r^2 = 0.999 \quad (13)$$

Equation (13) predicts (assuming that the effect of the *p*-dimethylamino group is not important) for 1-methylpentazole $\delta^{15}N$-Me = −91.6 ppm.

Including azoles and benzazoles and using for 1-phenylbenzimidazole a value of −212.1 ppm for the *N*-Ph (see below), Eqn (14) is found:

$$\delta^{15}N\text{-Me} = -5.15 + 1.086\ \delta^{15}N\text{-Ph}, \quad n = 12, r^2 = 0.998 \quad (14)$$

Other correlations concerning *N*-1 (that is, *N*-R) are as follows:

$$\delta^{15}N\text{-vinyl} = 13.78 + 0.991\ \delta^{15}N\text{-Me}, \quad n = 11, r^2 = 0.96 \quad (15)$$

Worse point 1*H*-indole **360** (exp. −258.2, model −227.7 ppm). Without 1*H*-indole:

$$\delta^{15}N\text{-vinyl} = -4.35 + 0.881\ \delta^{15}N\text{-Me}, \quad n = 10, r^2 = 0.991 \quad (16)$$

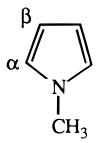
$$\delta^{15}N\text{-vinyl} = 3.17 + 1.026\ \delta^{15}N\text{-Ph}, \quad n = 7, r^2 = 0.990 \quad (17)$$

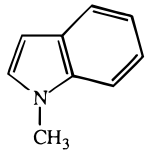
$$\delta^{15}N\text{-amino} = 9.49 + 0.953\ \delta^{15}N\text{-Me}, \quad n = 11, r^2 = 0.998 \quad (18)$$

(1-aminoindole **362**, exp. −201.8, model −232.2 ppm)

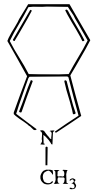
$$\delta^{15}N\text{-acetyl} = 15.82 + 0.860\ \delta^{15}N\text{-Me}, \quad n = 4, r^2 = 0.997 \quad (19)$$

C-substituents. In this case instead of dealing with small subsets we treated a large collection of data simultaneously. We used a matrix of presence–absence containing only 1s and 0s to describe the azoles, an approach





C_6H_4-benzo annelation



C_6H_4-isobenzo annelation

Table 5. Nitrogen-15 chemical shifts and some coupling constants of 1,2,4-triazole derivatives V

No.	Compound	Solvent	N-1	N-2	N-4	Substituents	Ref.
234	1,2,4-Triazole	DMSO	−127.4	−127.4	−134.7	—	18
	1,2,4-Triazole	DMSO	−136.5	−136.5	−136.5	—	76
	1,2,4-Triazole	DMSO	−123.3	−123.3	−135.7	—	80
	1,2,4-Triazole	TFA	−129.9	−129.9	−207.2	—	This work
235	3-Methoxy	DMSO	−167.6	−149.8	−155.9	—	76
236	3-Amino	H_2O	−138.7	−183.9	−175.6	NH_2: −336.1	78
			^2J(N1H5) = 12.4	^3J(N2H5) = 3.4	^2J(N4H5) = 11.9		
237	3-Methythio-5-amino	DMSO	−200.4	−118.2	−166.3	NH_2: −328.5	79
238	3-Morpholino-5-amino	DMSO	−216.0	−151.3	−187.2	NH_2: −329.7	79
239	3-Anilino-5-amino	DMSO	−216.4	−149.8	−184.1	NH_2: −329.7	79
240	1-Methyl[a]	Neat	−174	−85	−131	—	2
	1-Methyl	Acetone	−173.4	−83.7	−130.1	—	2
	1-Methyl	DMSO	−171.3	−82.2	−129.1	—	18
	1-Methyl	DMSO	−171.3	−81.9	−127.4	—	18
			^2J(N1H5) = 10.6,	^2J(N2H3) = 13.8			
	1-Methyl	DMSO	−171.3	−81.9	−127.4	—	76
	1-Methyl	DMSO	−171.3	−81.9	−127.4	—	29
	1-Methyl	DO^-	−171.2	−82.0	−127.5	—	28
			^2J(N1H5) = 10.6,	^2J(N2H3) = 13.8			
	1-Methyl	TFA	−164.3	−81.2	−208.5	—	46
			^2J(N1H5) = 13.0	^2J(N2H3) = 15.2	^2J(N4H5) = 13.3		
241	1-Methyl-3-amino	DMSO	−187.4	−130.4	−156.6	NH_2: −334.4	78
	1-Methyl-3-amino	DMSO	−187.5	−130.4	−156.5	NH_2: −334.3	This work
	1-methyl-3-amino	H_2O	−186.1	−137.7	−166.1	NH_2: −337.0	78
			^2J(N1H5) = 7.7		^2J(N4H5) = 11.3		
242	1-Methyl-5-amino	DMSO	−210.6	−98.0	−166.3	NH_2: −331.6	78
				^2J(N2H3) = 15.0	^2J(N4H3) = 13.0	$^1J(NH_2)$ = 85.1	
				^3J(N2Me) = 1.8	$^3J(N4NH_2)$ = 2.0		
	1-Methyl-5-amino	DMSO	−210.7	−98.2	−166.4	NH_2: −331.5	This work
	1-Methyl-5-amino	H_2O	−210.7	−108.6	−174.6	NH_2: −334.5	78
			^3J(N1H3) = 5.8	^2J(N2H3) = 14.6	^2J(N4H3) = 12.4		
243	1-Methyl-3-nitro	DMSO	−165.3	−84.7	−135.7	NO_2: −26.1	This work
244	1-Methyl-5-nitro	DMSO	−170.5	−68.4	−131.9	NO_2: −31.4	This work
245	1-Methyl-3-methoxy	DMSO	−184.4	−128.2	−157.8	—	76
246	1-Methyl-5-methoxy	DMSO	−207.7	−91.7	−166.8	—	76
247	1-Methyl-3-methylthio	DMSO	−160.8	−96.9	−125.0	—	77
248	1-Methyl-5-methylthio	DMSO	−174.0	−72.6	−124.4	—	77
249	1-Benzyl-3-amino-5-methylthio	DMSO	−181.6	−125.7	−153.9	NH_2: −330.6	79
250	1-Benzyl-3-amino-5-morpholino	DMSO	−201.0	−136.9	−171.0	NH_2: −331.5	79
251	1-Benzyl-3-morpholino-5-amino	DMSO	−212.6	−142.8	−187.2	NH_2: −327.9	79
252	1-Benzyl-3-methylthio-5-amino	DMSO	−198.0	−108.8	−166.0	NH_2: −327.0	79
253	1-CH_2COCH_3-3-nitro	DMSO	−166.3	−84.2	−135.9	NO_2: −26.6	49
			^2J(N1H5) = 10.8,	$^3J(N2CH_2)$ = 2.4			
			$^2J(N1CH_2)$ = 1.4,	^2J(N4H5) = 12.4			
254	1-CH_2COCH_3-3,5-dinitro	DMSO	−179.2	−75.4	−141.4	3-NO_2: −31.2	49
			$^2J(N1CH_2)$ = 2.1,	$^3J(N2CH_2)$ = 2.5		5-NO_2: −35.9	

Table 5. *Continued*

No.	Compound	Solvent	N-1	N-2	N-4	Substituents	Ref.
255	1-CH_2COCH_3-3-nitro-5-amino	DMSO	−204.3 ^2J(N1CH_2) = 1.3,	−99.5 ^3J(N2CH_2) = 2.5	−177.8	3-NO_2: −23.9 5-NH_2: −324.2 ^1J(NH_2) = 87.0	49
256	1-Vinyl	$CDCl_3$	−149.8	−89.5	−122.7	—	50
257	1-Vinyl-5-methyl	$CDCl_3$	−155.7	−89.8	−122.6	—	50
258	1-Vinyl-3-vinylthio	$CDCl_3$	−154.3	−103.0	−130.7	—	50
259	1-Vinyl-3-vinylthio-5-methyl	$CDCl_3$	−159.7	−104.4	−130.5	—	50
260	1-Phenyl	DMSO	−154.0	−89.5	−124.4	—	33
261	1-Amino	DMSO	−155.7	−79.8	−131.6	NH_2: −303.0	29
	1-Amino	TFA	−152.1 ^2J(N1H5) = 12.1	−78.8 ^2J(N2H3) = 13.3	−211.2 ^2J(N4H5) = 6.5	NH_2: −301.1	51
	1-Amino	H_2SO_4	−174.4 ^2J(N1H5) = 13.0	−90.1 ^2J(N2H3) = 14.1	−205.3	NH_2: −299.8	51
262	1-[(1,2,4-Triazol-1-yl)BH_2]$^-$	DMSO	−138.0 ^2J(N1H5) = 14.5	−77.2 ^2J(N2H3) = 14.8	−133.1 ^2J(N4H3) = ^2J(N4H5) = 12.6	—	81
263	1-[(1,2,4-Triazol-1-yl)$_2$BH]$^-$	DMSO	−144.1	−80.4	−132.0	—	81
	1-[(1,2,4-Triazol-1-yl)$_2$BH]$^-$	D_2O	−147.4 ^2J(N1H5) = 18	−92.5 ^2J(N2H3) = 15	−141.2 ^2J(N4H3) = ^2J(N4H5) = 13	—	81

[a] From ^{14}N NMR spectroscopy.

Table 6. Nitrogen-15 chemical shifts and some coupling constants of 1,2,5-triazole derivatives VI

No.	Compound	Solvent	N-1	N-2	N-5	Substituents	Ref.
264	1-Methyl	$CDCl_3$	−132.8	−51.1	−51.1	—	18
	1-Methyl	DMSO	−131.4	−50.1	−50.1	—	18
	1-Methyl	DMSO	−135.0	−54.0	−54.0	—	28
	1-Methyl	Acetone	−135.0	−54.0	−54.0	—	80
	1-Methyl[b]	CH_3OH	−134	−55	−55	—	2
	1-Methyl	CH_3OH	−132.8	−51.1	−51.1	—	80
	1-Methyl[b]	Neat	−132	−53	−53	—	2
265	1-$C(CD_3)_2OH$[a]	Acetone	^3J(N1H3) = ^3J(N1H4) = 8.35 ^2J(N2H3) = ^2J(N5H4) = 12.86 ^3J(N2H4) = ^3J(N5H3) = 0.91 ^1J(N1N2) = ^1J(N1N5) = 15.41			—	82
266	1-CH_2COCH_3-3-Nitro	DMSO	−131.0 ^3J(N1H4) = 9.9 ^2J(N1CH_2) = 1.8	−53.3 ^3J(N2CH_2) = 2.4	−39.2 ^2J(N5H4) = 12.3 ^3J(N5CH_2) = 2.3	3-NO_2: −25.7	49
267	1-CH_2COCH_3-3,4-dinitro	DMSO	−140.7 ^2J(N1CH_2) = 1.9	−46.2 ^3J(N2CH_2) = ^3J(N5CH_2) = 2.1	−46.2	3-NO_2: −32.5 4-NO_2: −32.5	49
268	1-Vinyl-3-nitro	$CDCl_3$	−121.3	−62.8	−48.6	3-NO_2: −28.5	50
269	1-Phenyl	DMSO	−119.1	−57.6	−57.6	—	33

[a] Coupling constants from ^{1}H NMR spectroscopy.
[b] From ^{14}N NMR spectroscopy.

Table 7. Nitrogen-15 chemical shifts and some coupling constants of 1,2,3-triazole derivatives VII

No.	Compound	Solvent	N-1	N-2	N-3	Substituents	Ref.
270	1,2,3-Triazole	$CDCl_3$	−61.9	−79.0	−61.9	—	18
	1,2,3-Triazole	DMSO	−69.0	−75.9	−69.0	—	18
	1,2,3-Triazole	DMSO	−68.8	−77.8	−68.8	—	15
	1,2,3-Triazole	Acetone	−64.8	−80.9	−64.8	—	80
	1,2,3-Triazole	CH_3OH	−70.5	−89.7	−70.5	—	80
	1,2,3-Triazole	H_2O	−56.6	−86.0	−56.6	—	80
	1,2,3-Triazole	CF_3CH_2OH	−53.0	−85.5	−53.0	—	80
	1,2,3-Triazole	Neat	−57.2	−85.5	−57.2	—	80
	1,2,3-Triazole[a]	Acetone	^2J(N1H5) = 10.12, ^3J(N1H4) = 1.91, ^1J(N1N2) = ^1J(N2N3) = 12.03			—	82
271	1-Methyl	$CDCl_3$	−145.0	−16.3	−30.7	—	18
	1-Methyl	DMSO	−143.0	−16.2	−29.2	—	18
	1-Methyl	DMSO	−143.3	−16.2	−28.4	—	28
	1-Methyl	Acetone	−144.5	−14.7	−27.9	—	2
	1-Methyl	Acetone	−144.9	−14.1	−27.1	—	80
	1-Methyl	CH_3OH	−144.3	−19.1	−41.7	—	80
	1-Methyl	NaOD	−143.3	−16.2	−28.7	—	28
	1-Methyl[b]	Neat	−144	−12	−30	—	2
272	1-$C(CD_3)_2OH$[a]	Acetone	^2J(N1H5) = 4.44, ^3J(N1H4) = 3.68 ^2J(N3H4) = 9.93, ^3J(N3H5) = 2.05 ^3J(N2H4) = 2.26, ^3J(N2H5) = 0.83 ^1J(N1N2) = 17.48, ^1J(N2N3) = 17.15			—	82
273	1-CH_2COCH_3-4-Nitro	DMSO	−135.8 ^2J(N1CH_2) = 1.7, ^3J(N2CH_2) = 2.2	−16.3	−36.8	NO_2: −24.7	49
274	1-Phenyl	DMSO	−125.5	−20.5	−25.0	—	33

[a] Coupling constants from ^{1}H NMR spectroscopy.
[b] From ^{14}N NMR spectroscopy.

Table 8. Nitrogen-15 chemical shifts and some coupling constants of 1,2,3,5-tetrazole derivatives VIII

No.	Compound	Solvent	N-1	N-2	N-3	N-5	Substituents	Ref.
275	1-Methyl	$CDCl_3$	−98.8	+4.4	−42.9	−68.7	—	2
	1-Methyl	DMSO	−102.2	−0.9	−47.1	−73.2	—	18
	1-Methyl	DMSO	−101.8	−0.8	−46.8 ^2J(N3H4) = 10.1	−72.8	—	28
	1-Methyl	DO^-	−101.8	−0.9	−46.9 ^2J(N3H4) = 10.1	−73.0	—	28
	1-Methyl	Neat	−103.4	−1.9	−48.6	−74.7	—	83
	1-Methyl	H_2SO_4	−96.4	−19.9	−144.2	−65.4	—	83
276	1,4-Dimethyl	Acetone	−104.9	−0.4	−50.7	−78.4	—	84
277	1-Methyl-4-CH_2CO_2Et	Acetone	−102.9	+1.6	−46.8	−75.0	—	84
278	1-Methyl-4-CH_2CH_2OMe	Acetone	−104.5	+0.8	−48.4	−77.4	—	84
279	1-Methyl-4-cyano	acetone	−96.7	+5.8	−61.5	−37.3	CN: −110.7	84
280	1-Methyl-4-vinyl	Neat + PhOH	−104.6	−1.6	−59.3	−79.3	—	83
281	1-Methyl-4-phenyl	DMSO	−102.8	+0.8	−53.9	−81.8	—	83
282	1-Methyl-4-amino	DMSO	−114.7[a]	−5.1	−81.5	−114.5[a]	NH_2: −338.2 $^1J(NH_2)$ = 84.7	85
	1-Methyl-4-amino	TFA	−30.3	−105.7	−108.4	−178.9	NH_2: −333.5	85
283	1-Methyl-4-acetylamino	DMSO	−107.6	+3.4	−66.8	−93.6	NH: −261.9 ^1J(NH) = 92.6	85
284	1-Methyl-4-methylthio	DMSO	−101.9	+1.8	−54.0	−82.2	—	86
	1-Methyl-4-methylthio	DMSO	−101.4	+2.3	−53.4	−81.6	—	87
	1-Methyl-4-methylthio	DMSO	−101.2	+2.3	−53.3	−81.5	—	85
	1-Methyl-4-methylthio	TFA	−11.6	−101.1	−79.5	−111[b]	—	85
285	1-Ethyl	Neat	−89.3	−0.8	−46.4	−75.0	—	83
286	1-Butyl	Neat	−93.1	−1.3	−47.6	−75.9	—	83
	1-Butyl	Neat + PhOH	−92.7	−3.4	−55.5	−75.7	—	83
287	1-*tert*-Butyl	Neat	−79.0	−3.9	−48.4	−73.9	—	83
	1-*tert*-Butyl	Neat + PhOH	−78.5	−6.0	−57.5	−73.0	—	83
288	1,4-Di-*tert*-butyl	$CDCl_3$	−85.0	−2.6	−52.4	−77.0	—	83
	1,4-Di-*tert*-butyl	$CDCl_3$ + AcOH	−84.7	−3.0	−56.5	−76.5	—	83
289	1-*tert*-Butyl-4-trifluoromethyl	Neat	−75.7	+3.2	−48.0	−68.8	—	83
290	1-CH_2COCH_3	DMSO	−103.6 ^3J(N1H4) = 6.7 ^2J(N1CH_2) = 1.6	+0.8 ^3J(N2CH_2) = 1.9	−46.6 ^2J(N3H4) = 12.6	−72.8 ^2J(N5H4) = 14.5 ^3J(N5CH_2) = 2.0	—	49
291	1-CH_2COCH_3-4-Nitro	DMSO	−99.2 ^2J(N1CH_2) = 1.5	+8.7 ^3J(N2CH_2) = 1.9	−53.7 ^3J(N5CH_2) = 2.1	−75.1	NO_2: −33.8	49
292	1-CH_2COCH_3-4-$C(NO_2)_3$	DMSO	−94.8 ^2J(N1CH_2) = 1.6	+9.9 ^3J(N2CH_2) = 1.9	−39.3 ^3J(N5CH_2) = 2.3	−61.2	$C(NO_2)_3$: −35.2	49
293	1-$CH_2COC_6H_5$-4-Nitro	DMSO	−99.0 ^2J(N1CH_2) = 1.8	+10.3 ^3J(N2CH_2) = 1.9	−52.4 ^3J(N5CH_2) = 2.1	−73.8	NO_2: −33.5	49
294	1-Phenyl	DMSO	−89.8	−6.2	−44.2	−80.6	—	83
295	1,4-Diphenyl	DMSO	−89.9	−4.7	−51.3	−90.4	—	83

[a] These assignments may be reversed.
[b] From ^{14}N NMR spectroscopy.

Table 9. Nitrogen-15 chemical shifts and some coupling constants of 1,2,3,4-tetrazole derivatives IX

No.	Compound	Solvent	N-1	N-2	N-3	N-4	Substituents	Ref.
296	Tetrazole	DMSO	−98.7	−5.8	−5.8	−98.7	—	18
	Tetrazole	DMSO	−98.3	−5.8	−5.8	−98.3	—	60
	Tetrazole	DMSO	−100.5	−4.5	−4.5	−100.5	—	87
297	5-Phenyl	DMSO	−88.4	−29.6	−29.6	−88.4	—	88
298	5-Amino[a]	DMSO	−145	−28	−28	−145	NH_2: −338.1 $^1J(NH_2)$ = 86.6	85
	5-Amino	TFA	−184.4	−29.2	−29.2	−184.4	NH_2: −329.2	85
	5-Amino	solid	−117.9	−37.2	−13.0	−115.0	NH_2:−334.9	89
299	5-Methylthio	DMSO	−100.5	−4.5	−4.5	−100.5	—	60
	5-Methylthio	DMSO	−101.2	−5.7	−5.7	−101.2	—	86
	5-Methylthio	DMSO	−102[a]	−6.0	−6.0	−102[a]	—	85
	5-Methylthio	TFA	−139.5	−16.4	−16.4	−139.5	—	85
	5-Methylthio	solid	−157.1 −159.1	−16.7	+5.9	−80.5 −84.4	—	90
300	1-Methyl	$CDCl_3$	−158.7	−14.5	+8.8	−54.4	—	2
	1-Methyl	DMSO	−151.4	−10.8	+12.3	−50.2	—	18
	1-Methyl	DMSO	−151.1 ^2J(N1H5) = 9.9	−10.8	+12.7	−49.9 ^2J(N4H5) = 12.2	—	28
	1-Methyl	C_6D_6	−150.6	−9.6	+12.5	−49.9	—	83
	1-Methyl	DO^-	−151.1 ^2J(N1H5) = 9.9	−10.9	+12.6	−49.9 ^2J(N4H5) = 12.2	—	28
301	1,5-Dimethyl	DMSO	−153.6	−9.5	+9.2	−52.6	—	15
	1,5-Dimethyl	DMSO	−153.6	−9.5	+8.0	−51.4	—	28
	1,5-Dimethyl	Acetone	−155.2	−10.2	+7.3	−55.2	—	84
302	1-Methyl-5-CH_2CO_2Et	Acetone	−153.1	−7.3	+9.4	−53.9	—	84
303	1-Methyl-5-CH_2CH_2OMe	Acetone	−154.1	−9.1	+9.2	−53.1	—	84
304	1,5-Pentamethylene	DMSO	−139.9	−8.5	+8.0	−51.4	—	28
305	1-Methyl-5-vinyl	DMSO	−157.2	−9.9	+8.8	−56.2	—	83
306	1-Methyl-5-amino	DMSO	−183.7	−21.7	+4.7	−90.8	NH_2: −337.1 $^1J(NH_2)$ = 86.8	85
	1-Methyl-5-amino	TFA	−183.9	−21.9	−31.9	−182.6	NH_2: −329.4	85
307	1-Methyl-5-acetylamino	DMSO	−160.5	−10.1	+8.7	−65.6	NH: −268.8	85
308	1-Methyl-5-methylthio	DMSO	−158.0	−7.4	+10.7	−55.7	—	86
	1-Methyl-5-methylthio	DMSO	−157.7	−7.0	+11.2	−55.3	—	85
	1-Methyl-5-methylthio	DMSO	−158.1	−7.1	+11.1	−55.6	—	87
	1-Methyl-5-methylthio	TFA	−157.1	−10.9	−17.2	−119.4	—	85
309	1-Ethyl	Neat	−138.1	−13.2	+10.8	−52.0	—	83
310	1-Butyl	$CDCl_3$	−142.0	−12.2	+11.5	−51.4	—	83
	1-Butyl	$CDCl_3$ + PhOH	−141.1	−11.7	+9.3	−55.4	—	83
	1-Butyl	Neat	−140.7	−11.5	+14.0	−49.6	—	83
	1-Butyl	Neat + PhOH	−140.2	−12.5	+6.2	−57.9	—	83
	1-Butyl	Neat + AcOH	−140.2	−12.5	+8.5	−56.4	—	83
	1-Butyl	H_2SO_4	−130.1	−11.1	−16.6	−147.1	—	83

Table 9. *Continued*

No.	Compound	Solvent	N-1	N-2	N-3	N-4	Substituents	Ref.
311	1-*tert*-Butyl	$CDCl_3$	−119.3	−14.6	+11.1	−52.4	—	83
	1-*tert*-Butyl	$CDCl_3$ + PhOH	−118.6	−14.5	+6.4	−58.5	—	83
312	1-CH_2COCH_3	DMSO	−152.2 ^2J(N1H5) = 8.4 ^2J(N1CH_2) = 1.7	−12.1 ^3J(N2CH_2) = 2.1	+10.1	−52.0 ^2J(N4H5) = 11.9	—	49
313	1-CH_2COCH_3-5-Amino	DMSO	−182.8 ^2J(N1CH_2) = 1.5	−22.7 ^3J(N2CH_2) = 2.0	+1.5	−100.4	—	49
314	1-Vinyl	Neat	−134.9	−18.7	+10.5	−52.0	—	83
315	1-Phenyl	DMSO	−133.7	−17.4	+13.2	−49.0	—	33
	1-Phenyl	DMSO	−133.8	−17.3	+13.1	−49.2	—	83
316	1,5-Diphenyl	DMSO	−140.6	−7.6	+9.7	−52.5	—	33
317	1-*p*-Methoxyphenyl	DMSO	−134.9	−17.6	+11.9	−50.0	—	83
318	1-*p*-Aminophenyl	DMSO	−133.2	−17.2	+10.4	−50.8	—	83
319	1-*p*-Bromophenyl	DMSO	−136.0	−18.5	+13.0	−49.4	—	83
320	1-[B(1,2,3,4-tetrazol-1-yl)H_2]$^-$	DMSO	−124.0	−4.1	−11.2	−54.7	—	81
	1-[B(1,2,3,4-tetrazol-1-yl)H_2]$^-$	D_2O	−124.1 ^2J(N1H5) = 10	+1.4 ^3J(N2H5) = 5	—	−64.3 ^2J(N4H5) = 14	—	81

[a] From ^{14}N NMR spectroscopy.

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we have used succesfully for ^{13}C NMR data.[9,10]

The reference compound is 1-methylpyrrole **12** since NH-polyazoles present the problem of annular tautomerism, yielding average signals which are dependent on the equilibrium constant. The selection of the descriptors reflects those groups that appear several times in the tables:

	Substituent	Column	
Position 1	CH_3	—	0 (ref.)
	CH_2COCH_3	1	1
	$CH{=}CH_2$	2	1
	C_6H_5	3	1
	$COCH_3$	4	1
	NH_2	5	1
Position 2	H	—	0 (ref.)
	N (aza)	6	1
	C_6H_4 (benzo)	7	1
	CH_3	8	1
	NH_2	9	1
	OCH_3	10	1
	SCH_3	11	1
	NO_2	12	1
Position 3	H	—	0 (ref.)
	N (aza)	13	1
	C_6H_4 (isobenzo)	14	1
	CH_3	15	1
	NH_2	16	1
	OCH_3	17	1
	C_6H_5	18	1
	NO_2	19	1
Position 4	H	—	0 (ref.)
	N (aza)	20	1
	CH_3	21	1
	NH_2	22	1
	SCH_3	23	1
	C_6H_5	24	1
	NO_2	25	1
	Cl	26	1
Position 5	H	—	0 (ref.)
	N (aza)	27	1
	CH_3	28	1
	NH_2	29	1
	OCH_3	30	1
	SCH_3	31	1
	C_6H_5	32	1
	NO_2	33	1
Solvents	Acetone, DMSO	—	0 (ref.)
	$CHCl_3$ ($CDCl_3$)	34	1

ref. = reference compound.

We have added column 34 to differentiate chloroform from other common solvents since we observed that the ^{15}N chemical shifts in this solvent are systematically different from those in acetone or DMSO (it is better to avoid chloroform if possible since sometimes it contains small amounts of HCl, which affect the ^{15}N chemical shifts).

The results of the multiple regressions are collected in Table 19. Some points which clearly deviate have been removed from the regressions (**247**, **313**, **314**), as follows.

N-1, no point has been removed, the largest deviations correspond to 1-methyl-1,2,3-triazole **271** (exp. −135.8, calc. −151.1 ppm) and to 1-methyl-3-methoxyindazole **394** (exp. −232.7, calc. −219.7 ppm). For 1-phenylbenzimidazole (unknown) the model predicts N-1 = −212.1 ppm (see above).

N-2, no point has been removed, the largest deviations correspond to 1-methyl-3-amino-1,2,4-triazole **241** (exp. −130.4, calc. −119.5 ppm) and to 1-methyl-5-amino-1,2,3,4-tetrazole **306** (exp. −21.7, calc. −32.7 ppm).

N-3, only 1-vinyl-1,2,3,4-tetrazole **314** has been removed (exp. 10.5, predicted 26.0 ppm). For 1-phenylbenzimidazole (unknown) the model predicts N-3 = −131.7 ppm.

N-4, only 1-acetonyl-5-amino-1,2,3,4-tetrazole **313** has been removed (exp. −100.4, predicted −96.3 ppm).

N-5, no point has been removed, the largest deviation corresponds to 1-methyl-1,2,3,5-tetrazole **275** in chloroform (exp. −68.7, calc. −70.8 ppm).

We do not pretend that the values corresponding to the points which have been removed are wrong or that the predicted values are the correct ones, the model being too rough for this, only that these values deserve further examination. Another compound whose chemical shifts are inconsistent with this additive approach is 1-methyl-3-thiomethyl-1,2,4-triazole **247**: its N-1 signal appears at −160.8 ppm, that is +10.5 ppm with respect to 1-methyl-1,2,4-triazole **240** (δN-1 = −171.3), while in other compounds the effect of the *S*-Me group is small and *negative*.

The coefficients of Table 19 deserve some comments:

(i) Intercepts. N-1 = −231.0 ppm compares well with 1-methylpyrrole **12** (DMSO: −230.1 ppm); N-2 = −73.1 ppm compares well with 1-methylpyrazole **98** (DMSO: −73.7 ppm); N-3 = −118.0 compares well with 1-methylimidazole **47** (DMSO: −118.1 ppm). N-4 and N-5 correspond to compounds containing at least another nitrogen atom at positions 2 or 3.

(ii) Substituents at position 1. The effects on N-1 show that the acetonyl group can be assimilated to the methyl group; vinyl and phenyl groups produce comparable effects much weaker than the acetyl group. These effects are similar to those observed for amines RNH_2; taking as reference CH_3NH_2, the effects of replacement of a CH_3 by a C_6H_5 (51 ppm), by a $COCH_3$ (115 ppm) and by an NH_2 (45 ppm),[3] there is a linear equation relating both effects:

$$\delta^{15}\text{N-1} = 0.376\ \delta^{15}\text{N}(RNH_2),$$
$$n = 4,\ r^2 = 0.996 \quad (20)$$

The slope, 0.37, reflects the dispersion of the electronic effect of R in the aromatic azole ring.

(iii) Substituents at positions 2 and 3.

(a) Pyrrole-like nitrogen atom (N-1). The effect of these substituents on N-1 are related [Eqn (21)] if the benzo (2,3-positions) and isobenzo (3,4-positions) are excluded. The lack of a good correlation is a consequence of the methoxy effect at position 3 (−27.4 ppm), which is abnormally large (without the methoxy, $n = 4$, $r^2 = 0.986$).

$$\delta^{15}\text{N-1(R3)} = -6.9 + 0.52\ \delta^{15}\text{N-1(R2)},$$
$$n = 5,\ r^2 = 0.938 \quad (21)$$

We have used in the ^{13}C NMR spectroscopy of aromatic and heteroaromatic compounds Smith and Proulx's approach to discuss the substituent chemical shifts (SCS). This approach uses a triparametric equation with terms describing the field and resonance effects, *F* and *R*, and an empirical steric effect *Q**.[117–119] Instead of using the four substituents at position 2 of Table 19 which are parametrized (CH_3, NH_2, OCH_3 and NO_2), we preferred to use the effects of substituents at positions 3, 4 and 5 on pyrazole N-1 (R1 = CH_3 if possible):

$$\delta^{15}\text{N-1(R3)} = -177.9 + 26.8R + 5.0Q^*,$$
$$n = 6,\ r^2 = 0.984 \quad (22)$$

$$\delta^{15}\text{N-1(R4)} = -178.4 + 4.6F + 13.3R + 1.5Q^*,$$
$$n = 4 \quad (23)$$

$$\delta^{15}\text{N-1(R5)} = -176.4 - 7.4F + 29.7R + 4.6Q^*,$$
$$n = 5,\ r^2 = 0.984 \quad (24)$$

We examined whether the effects on N-1 (Table 19) have some relationship with the well known effects of α- and β-substituents on the pyridine nitrogen atom. These effects, including the aza, benzo and isobenzo effects, 2-N 43.6, 2-C_6H_4 − 18.2, 2-CH_3 − 0.6, 2-NH_2 − 51.9, 2-OCH_3 − 48.2, 3-N 20.1, 3-C_6H_4 − 5.5, 3-CH_3 − 0.4 and 3-NH_2 − 0.6 ppm, are reported in Refs 3 and 4.

$$\delta^{15}\text{N-1 (R2 and R3)} = 0.7\ \delta^{15}\text{N}(\alpha + \beta\text{-pyridines}),$$
$$n = 9,\ r^2 = 0.64 \quad (25)$$

The regression equation (25) is not good owing to some large discrepancies, e.g. a 3-NH_2 substituent produces a large effect, −23.6 ppm, on N-1 in azoles whereas a β-NH_2 has no effect on the pyridine nitrogen

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Table 10. Nitrogen-15 chemical shifts of pentazole derivatives X

No.	Compound	Solvent	N-1	N-2	N-3	N-4	N-5	Ref.
321	1-*p*-Dimethylaminophenyl[a]	CH_2Cl_2 + MeOH	−73 ± 1	—	—	—	—	1
	1-*p*-Dimethylaminophenyl	$CDCl_3$ (−35 °C)	−80.0	−27.1	+4.9	+4.9	−27.1	91

[a] From ^{14}N NMR spectroscopy

Table 11. Nitrogen-15 chemical shifts of isoindole derivatives XI

No.	Compound	Solvent	N-1	Ref.
322	1-Methyl[a]	$(C_2H_5)_2O$	−218	92
	1-Methyl[a]	$(C_2H_5)_2O$	−218	28

[a] From ^{14}N NMR spectroscopy.

Table 12. Nitrogen-15 chemical shifts and some coupling constants of indole derivatives XII

No.	Compound	Solvent	N-1	Substituents	Ref.
323	Indole	$CDCl_3$	−255.4	—	93
	Indole	$CDCl_3$	−255.4	—	94
	Indole	$CDCl_3$	−259.1	—	95
	Indole	$CDCl_3$ + pyridine	−253.6	—	95
	Indole	DMSO	−247.3	—	93
	Indole	DMSO	−249.0	—	94
	Indole	DMSO	−245.5	—	96
	Indole	DMSO	−244.5	—	97
			^1J(N1H1) = 97.5		
324	2-Methyl	$CDCl_3$	−250.6	—	93
	2-Methyl	DMSO	−243.3	—	93
	2-Methyl	$CDCl_3$	−253.1	—	95
325	3-Methyl	$CDCl_3$	−260.4	—	93
	3-Methyl	DMSO	−261.6	—	93
326	5-Methyl	$CDCl_3$	−256.6	—	93
	5-Methyl	DMSO	−248.1	—	93
327	7-Methyl	$CDCl_3$	−257.6	—	93
	7-Methyl	DMSO	−247.9	—	93
328	2,3-Dimethyl	DMSO	−247.1	—	93
329	2,5-Dimethyl	DMSO	−244.5	—	93
330	3-Formyl	DMSO	−234.1	—	93
331	3-Acetyl	DMSO	−237.9	—	93
332	2-Carboxylic acid	DMSO	−246.6	—	93
333	3-Acetoxy	DMSO	−259.3	—	93
334	3-Acetic acid	DMSO	−250.5	—	93
335	3-Propionic acid	DMSO	−253.0	—	93
336	5-Cyano	$CDCl_3$	−249.3	—	93
	5-Cyano	DMSO	−242.5	—	93
337	5-Carboxylic acid	DMSO	−243.7	—	93
338	5-Nitro	DMSO	−237.7	—	97
			^1J(N1H1) = 96.5		
339	5-Cyano	DMSO	−238.9	—	97
			^1J(N1H1) = 98.1		
340	5-Methoxycarbonyl	DMSO	−240.7	—	97
			^1J(N1H1) = 95.7		
341	5-Bromo	DMSO	−242.9	—	97
			^1J(N1H1) = 95.3		
342	5-Chloro	DMSO	−243.0	—	97
			^1J(N1H1) = 98.0		
343	5-Fluoro	DMSO	−244.3	—	97
			^1J(N1H1) = 97.5, ^5J(N1F5) = 0.7		
344	5-Acetoxy	DMSO	−237.7	—	97
			^1J(N1H1) = 96.5		
345	5-Methyl	DMSO	−245.5	—	97
			^1J(N1H1) = 96.5		
346	5-Methoxy	DMSO	−246.0	—	97
			^1J(N1H1) = 95.1		
347	5-Dimethylamino	DMSO	−247.6	—	97
			^1J(N1H1) = 95.7		
348	5-Amino	DMSO	−250.4	—	93
349	5-Nitro	DMSO	−240.4	—	93
350	2-Methyl-5-nitro	DMSO	−238.7	—	96
351	5-Hydroxy	DMSO	−251.3	—	93
352	5-Methoxy	$CDCl_3$	−256.7	—	93
	5-Methoxy	DMSO	−248.6	—	93
353	6-Methoxy	$CDCl_3$	−255.7	—	93
354	7-Methoxy	$CDCl_3$	−259.6	—	93
355	5-Fluoro	$CDCl_3$	−257.0	—	93
356	5-Chloro	$CDCl_3$	−256.0	—	93
	5-Chloro	DMSO	−245.8	—	93
357	5-Bromo	DMSO	−245.6	—	93
358	1-Methyl[a]	Neat	−250	—	92
	1-Methyl	DMSO	−253.6	—	28
359	1-Methyl-2-methoxy	$CDCl_3$	−266.3	—	98
	1-Methyl-2-methoxy	DMSO	−267.3	—	99
360	1-Vinyl	$CDCl_3$	−258.2[b]	—	50
361	1-Acetyl	DMSO	−201.9	—	This work
362	1-Amino	DMSO	−201.8[c]	NH_2: −314.7	51
			^2J(N1H2) = ^3J(N1H3) = 4.2	$^1J(NH_2)$ = 71.3	

[a] From ^{14}N NMR spectroscopy
[b] Probably erroneous (see text), δ^{15}N-1 = −227.7 ppm.
[c] Probably erroneous (see text), δ^{15}N-1 = −232.2 ppm.

Table 13. Nitrogen-15 chemical shifts and some coupling constants of benzimidazole derivatives XIII

No.	Compound	Solvent	N-1	N-3	Substituents	Ref.
363	Benzimidazole[a]	Acetone	−185	−185	—	1
	Benzimidazole[a]	DMSO	−237	—	—	1
364	5,6-Dimethyl[b]	$CDCl_3$	^2J(N1H2) = ^2J(N3H2) = 10.3	—	—	100
365	2-Thiomethyl	DMSO	−186.4	−186.4	—	101
366	1-Methyl[a]	Acetone	−231	−134	—	1
	1-Methyl[a]	CCl_4	−237	−127	—	1
	1-Methyl	DMSO	−236.4	−136.3	—	102
	1-Methyl	DMSO	−236.4	−136.3	—	103
	1-Methyl	DMSO	−236.4	−136.3	—	28
	1-Methyl	TFA	−225.8	−230.4	—	46
			^2J(N1H2) = 6.1	^2J(N3H2) = 5.0, ^1J(N3H3) = 103.1		
367	1-Methyl-2-amino	DMSO	−265.6	−188.3	NH_2: −325.0	This work
368	1-Methyl-2-methoxy	DMSO	−264.5	−186.8	—	104
	1-Methyl-2-methoxy	CH_3OH	−261.8	−195.5	—	104
	1-Methyl-2-methoxy	CF_3CH_2OH	−263.2	−200.8	—	104
369	1-Methyl-2-methylthio	DMSO	−243.9	−145.9	—	101
	1-Methyl-2-methylthio	DMSO	−241.0	−143.0	—	105
370	1-[(Benzimidazol-1-yl)$_2$CH]	$CDCl_3$	−227.9	−131.4	—	This work
371	1-[(2-Me-benzimidazol-1-yl)$_2$CH] 2-methyl	$CDCl_3$	−231.0	−133.3	—	This work
372	1-Vinyl	$CDCl_3$	−216.2	−135.1	—	50
373	1-Vinyl-2-methyl	$CDCl_3$	−219.9	−139.1	—	50
374	1-Phenyl-2-methyl	DMSO	−217.1	−137.8	—	This work
			^3J(N1Me) = 1.8	^3J(N3Me) = 2.0		
375	1-Methoxy	DMSO	−174.0	−145.0	—	106
	1-Methoxy	Acetone	−174.3	−145.6	—	106
	1-Methoxy	CH_3OH	−174.0	−145.0	—	106
	1-Methoxy	CF_3CH_2OH	−167.6	−145.1	—	106
376	1-Methoxy-2-phenyl	DMSO	−179.4	−149.8	—	106
	1-Methoxy-2-phenyl	Acetone	−179.4	−147.6	—	106
	1-Methoxy-2-phenyl	CH_3OH	−179.4	−161.3	—	106
	1-Methoxy-2-phenyl	CF_3CH_2OH	−176.6	−163.0	—	106
377	1-Amino	DMSO	−215.4	−143.2	NH_2: −317.4	29
			^2J(N1H2) = 9.5	^2J(N3H2) = 11.9	^1J(NH_2) = 71.9	
	1-Amino	TFA	−209.2	−234.0	NH_2: −317.3	51
				^1J(N3H3) = 104.3		
	1-Amino	H_2SO_4	−229.1	−224.7	NH_2: −312.0	51
			^2J(N1H2) = 8.2	^1J(N3H3) = 104.6		
378	1-N = CH-C_6H_5	DMSO	−182.7	−76.0	N=CH: −136.8	107
			^2J(N1H2) = 14.5	^2J(N3H2) = 3.2	^2J(N=CH) = 11.5	

[a] From ^{14}N NMR spectroscopy.
[b] Coupling constants from ^1H NMR spectroscopy.

Table 14. Nitrogen-15 chemical shifts and some coupling constants of 2*H*-indazole derivatives XIV

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
379	1-Methyl[a]	Acetone	−161	−86	—	92
	1-Methyl[b,c]	DMSO	−161.0	−91.2	—	108
			^1J(N1C5) = 13.2, ^2J(N1C4) = 5.0, ^2J(N1C3) = 1.3, ^1J(N1Me) = 12.8, ^1J(N2C3) = 1.8, ^2J(N2C4) = 0.7, ^2J(N2Me) = 6.4, ^2J(N1H5) = 4.3, ^2J(N1Me) = 2.1, ^3J(N2Me) = 2.1			
	1-Methyl	DMSO	−162.1	−92.3	—	28
	1-Methyl	DMSO	−162.1	−92.3	—	29
	1-Methyl	$CDCl_3$	−160.9	−92.6	—	50
	1-Methyl	TFA	−185.7	−210.4	—	46
380	1-Methyl-5-nitro[b,c]	DMSO	−151.0	—	—	108
			^1J(N1C5) = 13.4, ^2J(N1C4) = 4.8, ^2J(N1C3) = 0.7, ^1J(N1Me) = 12.8, ^2J(N1H5) = 4.1, ^2J(N1Me) = 2.1			
381	1-Vinyl	$CDCl_3$	−151.0	−103.2	—	50
382	1-Phenyl	$CDCl_3$	−151.1	−101.2	—	This work
	1-Phenyl	DMSO	−146.3	−100.0	—	This work
383	1-*m*-Fluorophenyl	$CDCl_3$	−172.1	−119.1	—	This work
384	1-Methoxy-5-methyl	DMSO	−115.4	−115.8	—	109
	1-Methoxy-5-methyl	CH_3OH	−117.8	−124.9	—	109
	1-Methoxy-5-methyl	TFA	−120.0	−133.7	—	109
385	1-Amino	DMSO	−145.5	−94.8	NH_2: −289.1	29
	1-Amino	TFA	−172.9	−204.6	NH_2: −301.3	51
	1-Amino	H_2SO_4	−196.4	−212.6	NH_2: −300.1	51

[a] From ^{14}N NMR spectroscopy.
[b] Coupling constants from ^{13}C NMR spectroscopy.
[c] Coupling constants from ^1H NMR spectroscopy.

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Table 15. Nitrogen-15 chemical shifts and some coupling constants of 1*H*-indazole derivatives XV

No.	Compound	Solvent	N-1	N-2	Substituents	Ref.
386	Indazole[b,c]	DMSO	−194.4	−65.6	—	108
			^1J(N1C5) = 13.6, ^2J(N1C4) = 5.9, ^2J(N2C4) = 1.8, ^2J(N2C5) = 1.1 ^1J(N1H1) = 104.8, ^2J(N2H3) = 12.8, ^3J(N1H3) = 7.4			
	Indazole	DMSO	−196.3	−66.1	—	103
	Indazole	Acetone	−200.6	−65.1	—	14
	Indazole	CF_3CH_2OH	−207.2	−90.8	—	14
	Indazole	CH_3CO_2H	−204.4	−93.1	—	14
	Indazole	CH_3CO_2H + TFA	−207.9	−124.3	—	14
387	5-Nitro[b,c]	DMSO	—	−56.1	—	108
			^2J(N2C4) = 1.8, ^2J(N2C5) = 1.3 ^2J(N2H3) = 12.9			
388	3-Methoxy	DMSO	−226.1	−115.4	—	110
	3-Methoxy	DMSO	−223.9	−113.0	—	111
			^1J(N1H1) = 107.1			
	3-Methoxy	CH_3OH	−226.8	−121.4	—	110
	3-methoxy	CF_3CH_2OH	−232.1	−129.4	—	110
	3-Methoxy	DMSO-CF_3CH_2OH (2:1)	−225.6	−115.5	—	110
			^1J(N1H1) = 105.7			
389	3-Amino	DMSO	−223.9	−119.3	NH_2: −336.7	This work
	3-Amino	TFA	−253.2	−228.3	NH_2: −324.6	This work
390	3-Fluoro	DMSO	−221.9	−108.0	—	This work
				^2J(N2^{19}F) = 39.5		
391	1-Methyl[a]	Acetone	−201	−62	—	92
	1-Methyl[b,c]	DMSO	−202.8	−56.6	—	108
			^1J(N1C5) = 15.0, ^2J(N1C4) = 6.6, ^2J(N2C4) = 1.8 ^2J(N2C5) = 0.8 ^1J(N1Me) = 13.8, ^2J(N2Me) = 5.5 ^2J(N2H3) = 12.8, ^3J(N2Me) = 2.0, ^3J(N1H3) = 7.6, ^2J(N1Me) = 1.7			
	1-Methyl	DMSO	−203.8	−57.6	—	28
	1-Methyl	DMSO	−203.8	−57.6	—	29
	1-Methyl	$CDCl_3$	−202.8	−56.5	—	50
	1-Methyl	TFA	−218.3	−180.8	—	46
392	1-Methyl-5-nitro[b,c]	DMSO	—	−47.9	—	108
			^2J(N2C4) = 1.8, ^2J(N2C5) = 1.3, ^2J(N2Me) = 5.9 ^2J(N2H3) = 13.2, ^3J(N2Me) = 2.0			
393	1-Methyl-3-hydroxy	DMSO	−236.7	−110.4	—	111
394	1-Methyl-3-methoxy	DMSO	−232.7	−104.8	—	110
	1-Methyl-3-methoxy	DMSO	−231.8	−104.0	—	111
	1-Methyl-3-methoxy	CH_3OH	−232.4	−108.9	—	110
	1-Methyl-3-methoxy	CF_3CH_2OH	−235.5	−116.6	—	110
395	1-Methyl-3,5-dibromo	$CDCl_3$	−204.9	−64.7	—	This work
396	1-Vinyl	$CDCl_3$	−185.5	*−71.3*	—	50
397	1,3-Diphenyl	$CDCl_3$	−189.2	−70.6	—	This work
398	1-*m*-Fluorophenyl	$CDCl_3$	−206.8	−83.9	—	This work
399	1-Ethoxycarbonyl-3-hydroxy	DMSO	−210.3	−125.7	—	111
400	1-Amino	DMSO	−184.6	−56.3	NH_2: −305.9	29
			^3J(N1H3) = 10.6, ^2J(N2H3) = 12.7, ^1J(NH_2) = 72.7			

[a] From ^{14}N NMR spectroscopy.
[b] Coupling constants from ^{13}C NMR spectroscopy.
[c] Coupling constants from ^{1}H NMR spectroscopy.

Table 16. Nitrogen-15 chemical shifts of 2*H*-benzotriazole derivatives XVI

No.	Compound	Solvent	N-1	N-2	N-5	Substituents	Ref.
401	1-Methyl[a]	Neat	−119	−62	−62	—	28
	1-Methyl	$CDCl_3$	−119.2	−63.1	−63.1	—	18
	1-Methyl	Acetone	−121.9	−66.1	−66.1	—	103
	1-Methyl	DMSO	−117.0	−62.5	−62.5	—	18
	1-Methyl	DMSO	−116.8	−62.6	−62.6	—	28
	1-Methyl	DMSO	−117.0	−62.6	−62.6	—	29
	1-Methyl	CH_3OH	−123.6	−69.5	−69.5	—	103
	1-Methyl	TFA	−131.4	−91.2	−91.2	—	46
			^2J(N1Me) = 6.1	^3J(N2Me) = ^3J(N5Me) = 5.8			
	1-Methyl	H_2SO_4	−141.2	−115.0	−115.0	—	46
402	1-Vinyl	$CDCl_3$	−110.3	−71.0	−71.0	—	50
403	1-Amino[b]	DMSO	−99.5	−83.2	−83.2	NH_2: −274.9	29
	1-Amino[c]	DMSO	−98.3	−83.5	−83.5	NH_2: −274.1	This work
	1-Amino	TFA	−95.5	−120.7	−120.7	NH_2: −284.8	51
	1-Amino	H_2SO_4	−112.1	−132.7	−132.7	NH_2: −285.8	51

[a] From ^{14}N NMR spectroscopy.
[b] With $Cr(acac)_3$.
[c] Without $Cr(acac)_3$.

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Table 17. Nitrogen-15 chemical shifts and some coupling constants of 1*H*-benzotriazole derivatives XVII

No.	Compound	Solvent	N-1	N-2	N-3	Substituents	Ref.
404	Benzotriazole	DMSO	−96.7	−7.5	−96.7	—	18
	Benzotriazole	DMSO	−96.7	−7.9	−96.7	—	103
	Benzotriazole	$CDCl_3$	−103.4	−11.6	−103.4	—	18
	Benzotriazole	CH_3OH	−108.7	−14.5	−108.7	—	103
	Benzotriazole	Acetone	−102.0	−10.3	−102.0	—	103
	Benzotriazole	Not reported	−103.8	−12.0	−103.8	—	112
	Benzotriazole	Acetone	−102.0	−10.3	−102.0	—	113
	Benzotriazole	TFA	−158.0	−29.4	−158.0	—	113
	Benzotriazole	TFA	−158.0	−29.8	−158.0	—	This work
	Benzotriazole	Solid	−157.6	−11.8	−56.4	—	113
405	5-Nitro	DMSO	—	—	—	NO_2: −10.4	113
	5-Nitro	TFA	−152.5[a]	−17.6	−142.0[a]	NO_2: −14.4	113
	5-Nitro	Solid	−158.6	−11.2	−38.6	NO_2: +0.8	113
406	6-Nitro	Solid	−155.6	−9.3	−45.3	NO_2: +0.8	113
407	7-Nitro	DMF	−154.7	+2.6	-37.8	NO_2: −14.4	113
			^1J(NH) = 106.5				
	7-Nitro	TFA	−157.3[b]	−20.7	−136.7[b]	NO_2: −18.1	113
	7-Nitro	Solid	−155.6	−14.5	−52.1	NO_2: +3.8	113
408	5-Bromo	Acetone (−85 °C)	−156.9	—	—	—	113
			^1J(NH) = 106.6				
	5-Bromo	TFA	−158.2	−29.3	−158.2	—	113
	5-Bromo	Solid	−153.4	−8.8	−57.8[c]	—	113
409	6-Bromo	Acetone	−158.2	—	—	—	113
			^1J(NH) = 121.8[d]				
	6-Bromo	Solid	−153.4	−8.8	−60.7[c]	—	113
410	1-Methyl[e]	Acetone	−162	−4	−40	—	2
	1-Methyl	Acetone	−164.7	−1.5	−41.1	—	103
	1-Methyl	$CDCl_3$	−164.1	−2.2	−42.2	—	18
	1-Methyl	DMSO	−161.8	−0.9	−40.8	—	18
	1-Methyl	DMSO	−161.5	−1.1	−41.0	—	28
	1-Methyl	DMSO	−161.5	−1.1	−41.0	—	29
	1-Methyl	CH_3OH	−167.0	−7.8	−55.0	—	103
	1-Methyl	TFA	−155.5	−27.7	−161.6	—	46
			^2J(N1Me) = 5.5	^3J(N2Me) = 6.4			
411	1-Vinyl	$CDCl_3$	−147.5	−7.8	−37.9	—	50
412	1-Amino	DMSO	−147.8	−1.9	−50.4	NH_2: −307.3	29
	1-Amino	TFA	−143.1	−32.0	−168.3	NH_2: −303.1	51
	1-Amino	H_2SO_4	−163.9	−39.1	−160.6	NH_2: −300.5	51
413	1-Methoxy	Acetone	−116.1	−16.8	−52.9	—	114
	1-Methoxy	DMSO	−112.3	−14.7	−50.9	—	114
	1-Methoxy	CH_3OH	−116.7	−20.2	−63.2	—	114
414	1-Benzyloxy	DMSO	−115.6	−13.2	−50.1	—	115
415	1-Methoxy-4-nitro	DMSO	−108.2	−7.4	−53.1	NO_2: −13.1	114
416	1-Methoxy-6-nitro	DMSO	−108.6	−11.8	−50.1	NO_2: −1.9	114

[a,b,c] These assignments may be reversed
[d] Probably wrong.
[e] From ^{14}N NMR spectroscopy.

Table 18. Nitrogen-15 chemical shifts of carbazole derivatives XVIII

No.	Compound	Solvent	N-1	Substituents	Ref.
417	Carbazole[a]	Acetone	−268	—	2
	Carbazole	DMSO	−262.6	—	116
	Carbazole	DMSO	−263.7	—	46
			^1J(N1H1) = 97.4		
	Carbazole	H_2SO_4	−309.6	—	46
418	1-Methyl[a]	Acetone	−278	—	2
	1-Methyl	Acetone	−275.4	—	2
	1-Methyl	DMSO	−272.7	—	28
	1-Methyl	DMSO	−272.7	—	29
	1-Methyl	H_2SO_4	−308.2	—	46
419	1-Phenyl	$CDCl_3$	−249.9	—	This work
420	1-Amino	DMSO	−249.2	NH_2: −322.9	29

[a] From ^{14}N NMR spectroscopy.

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Table 19. Coefficients of the multiple regressions[a]

	N-1	N-2	N-3	N-4	N-5
Values	170	108	58	30	20
r^2	0.983	0.983	0.995	0.999	0.997
Intercept	−231.0 ± 1.6	−73.1 ± 1.6	−118.0 ± 2.4	−133.2 ± 1.9	−50.5 ± 1.2
1-CH_2COCH_3	1.2 ± 1.9	1.8 ± 1.9	−4.5 ± 3.1	−0.1 ± 1.5	0.1 ± 1.7
1-$CH{=}CH_2$	18.5 ± 1.8	−9.0 ± 2.0	4.8 ± 3.5	1.9 ± 1.5	−8.8 ± 1.7
1-C_6H_5	16.7 ± 1.6	−5.8 ± 1.6	1.8 ± 2.6	2.0 ± 1.4	−8.2 ± 1.3
1-$COCH_3$	43.4 ± 3.0	−4.0 ± 5.7	7.4 ± 4.4	—	—
1-NH_2	14.7 ± 2.0	−3.9 ± 2.4	−4.9 ± 3.4	−6.1 ± 1.7	−20.3 ± 2.1
2-N	57.8 ± 1.4	—	87.8 ± 2.3	7.7 ± 1.4	—
2-C_6H_4 (benzo)	−19.1 ± 1.3	15.4 ± 2.2	−16.8 ± 2.4	—	—
2-CH_3	−5.7 ± 2.5	—	−5.1 ± 2.7	—	—
2-NH_2	−35.3 ± 4.5	—	−49.4 ± 4.5	−15.4 ± 2.3	—
2-OCH_3	−25.2 ± 3.3	—	−48.7 ± 4.5	−15.0 ± 2.3	—
2-SCH_3	−13.1 ± 3.8	—	−2.9 ± 3.8	−5.3 ± 2.3	—
2-NO_2	−0.9 ± 3.1	—	−1.0 ± 6.1	—	—
3-N	21.2 ± 1.3	59.8 ± 1.6	—	73.2 ± 1.0	−21.1 ± 1.3
3-C_6H_4 (isobenzo)	11.2 ± 2.1	−17.9 ± 2.1	—	—	−12.7 ± 1.5
3-CH_3	−7.2 ± 2.7	−3.6 ± 2.5	—	—	—
3-NH_2	−23.6 ± 3.2	−42.9 ± 3.0	—	−31.1 ± 2.2	—
3-OCH_3	−27.4 ± 3.7	−45.8 ± 3.5	—	−32.3 ± 2.2	—
3-C_6H_5	−6.9 ± 4.8	−11.0 ± 4.4	—	—	—
3-NO_2	−2.4 ± 2.0	−5.9 ± 2.0	—	−10.6 ± 1.7	10.0 ± 1.8
4-N	1.9 ± 1.5	−3.6 ± 1.6	51.4 ± 2.5	—	—
4-CH_3	2.6 ± 6.3	−7.7 ± 5.7	−7.1 ± 6.1	—	−6.8 ± 2.0
4-NH_2	−15.2 ± 3.2	−3.6 ± 3.0	−37.9 ± 6.1	—	-42.9 ± 2.0
4-SCH_3	6.1 ± 6.3	−5.0 ± 5.7	−9.8 ± 6.1	—	−10.0 ± 1.5
4-C_6H_5	2.8 ± 4.7	−6.3 ± 4.3	−9.9 ± 4.7	—	−10.4 ± 1.5
4-NO_2	−0.4 ± 1.8	0.4 ± 2.1	−6.1 ± 3.3	—	−4.7 ± 1.7
4-Cl	−3.7 ± 4.6	−3.0 ± 4.2	—	—	—
5-N	44.4 ± 1.7	20.5 ± 1.7	−13.4 ± 3.2	—	—
5-CH_3	−2.8 ± 2.3	−1.1 ± 2.2	−13.2 ± 5.9	1.2 ± 1.5	—
5-NH_2	−32.8 ± 2.4	−15.9 ± 2.3	−15.9 ± 4.6	−40.3 ± 1.3	—
5-OCH_3	−33.3 ± 3.8	−18.2 ± 4.2	—	−41.3 ± 2.2	—
5-SCH_3	−7.4 ± 3.8	6.9 ± 4.1	−10.1 ± 5.9	−1.1 ± 1.6	—
5-C_6H_5	−7.2 ± 4.0	10.8 ± 3.7	−13.4 ± 6.1	−2.2 ± 2.3	—
5-NO_2	−5.9 ± 2.0	11.3 ± 2.6	0.0 ± 4.3	−5.8 ± 1.6	—
$CHCl_3$	−3.7 ± 1.4	0.1 ± 1.6	−3.0 ± 2.6	−0.5 ± 1.5	0.8 ± 1.3

[a] Examples of the use of this table: (i) a known compound, e.g. 1-vinyl-5-methyl-1,2,4-triazole (**257**) (δN-1 = −155.7, δN-2 = −89.8. δN-4 = −122.6 ppm in $CHCl_3$): δN-1 = −231.0 (intercept) + 18.5 (1-vinyl) + 57.8 (2-N) + 1.9 (4-N) − 2.8 (5-Me) − 3.7 ($CHCl_3$) = −159.3 ppm; δN-2 = −73.1 (intercept) − 9.0 (1-vinyl) − 3.6 (4-N) − 1.1 (5-Me) + 0.1 ($CHCl_3$) = −86.7 ppm; δN-4 = −133.2 (intercept) + 1.9 (1-vinyl) + 7.7 (2-N) + 1.2 (5-Me) − 0.5 ($CHCl_3$) = −122.9 ppm; (ii) an unknown compound, e.g. 1,2-dimethyl-benzimidazole, in DMSO: δN-1 = −231.0 (intercept) − 5.7 (2-Me) − 19.1 (2-C_6H_4) + 21.2 (3-N) = −234.6 ppm; δN-3 = −118.0 (intercept) − 5.1 (2-Me) − 16.8 (2-C_6H_4, benzo) = −139.9 ppm.

Table 20. Papers dealing with the use of ^{15}N NMR spectroscopy for determining the protonation site and for the study of tautomerism

Protonation site

Imidazoles (histidine and histamine);[39,41,42,44] *N*-methylazoles and *N*-methylbenzazoles;[46] *N*-aminoazoles;[51] *C*-aminopyrazoles;[62] *C*-amino-1,2,4-triazoles;[78] 1,2,3-triazole;[82] benzotriazole[111]

Tautomerism: annular

4(5)-Nitroimidazole;[15] all azoles;[18] pyrazoles;[54] polymethylenepyrazoles (Mills-Nixon effect);[58] 3(5)-phenylpyrazoles;[59] 1,2,4-triazoles;[76] indazoles and benzotriazoles[101]

Tautomerism: functional

3-Hydroxyindazole;[108,109] mercaptoimidazoles and −tetrazoles;[47] pyrazolinones;[67] mercapto-1,2,4-triazoles;[77] mercaptotetrazoles;[86] oxo and mercaptotetrazoles;[87] 1-hydroxybenzotriazole[113]

Table 21. N-1 Coupling constants (^1H,^{15}N): comparison between pyrrole and other *N*-substituted azoles

No.	Azole	R	2	3	4	5	^2J(N1H2)	^3J(N1H3)	^3J(N1H4)	^2J(N1H5)	Solvent
12	Pyrrole	H	CH	CH	CH	CH	4.5	5.4	5.4	4.5	$CDCl_3$[a]
156	Pyrazole	$CH_2C_6H_5$	N	CH	CH	CH	—	8.3 (+2.9)	5.8 (+0.4)	4.7 (+0.2)	$CDCl_3$[a]
47	Imidazole	CH_3	CH	N	CH	CH	7.6 (+3.1)	—	3.5 (−1.9)	5.5 (+1.0)	$CDCl_3$[a]
272	1,2,3-Triazole	$C(OH)(CH_3)_2$	N	N	CH	CH	—	—	3.7 (−1.7)	4.4 (−0.1)	Acetone[a]
240	1,2,4-Triazole	CH_3	N	CH	N	CH	—	Missing	—	10.6 (+6.1)	DMSO
265	1,2,5-triazole	$C(OH)(CH_3)_2$	N	CH	CH	N	—	8.3 (+2.9)	8.3 (+2.9)	—	Acetone[a]
229	1,3,4-Triazole	CH_3	CNH_2	N	N	CH	—	—	—	8.2 (+3.7)	H_2O
300	1,2,3,4-Tetrazole	CH_3	N	N	N	CH	—	—	—	9.9 (+5.4)	DMSO
290	1,2,3,5-Tetrazole	CH_2COCH_3	N	N	CH	N	—	—	6.7 (+1.3)	—	DMSO
362	Indole	NH_2	CH	CH	Benzo	Benzo	4.2 (-0.3)	4.2 (-0.3)	—	—	DMSO
377	Benzimidazole	NH_2	CH	N	Benzo	Benzo	9.5 (+5.0)	—	—	—	DMSO
379	2*H*-Indazole	CH_3	N	Isobenzo	Isobenzo	CH	—	—	—	4.3 (−0.2)	DMSO[a]
391	1*H*-Indazole	CH_3	N	CH	Benzo	Benzo	—	7.6 (+2.2)	—	—	DMSO[a]

[a] Coupling constants from ^1H NMR spectroscopy.

Table 22. N-2 Coupling constants (^{1}H, ^{15}N): comparison between pyrazole and other *N*-substituted azoles

No.	Azole	R	3	4	5	^{2}J(N2H3)	^{3}J(N2H4)	^{3}J(N2H5)	Solvent
156	Pyrazole	$CH_2C_6H_5$	CH	CH	CH	12.6	1.1	Missing	$CDCl_3$[a]
272	1,2,3-Triazole	$C(OH)(CH_3)_2$	N	CH	CH	—	2.3 (+1.2)	0.8	Acetone[a]
240	1,2,4-Triazole	CH_3	CH	N	CH	13.8 (+1.2)	—	Missing	DMSO
265	1,2,5-Triazole	$C(OH)(CH_3)_2$	CH	CH	N	12.9 (+0.3)	0.9 (-0.2)	—	Acetone[a]
290	1,2,3,5-Tetrazole	CH_2COCH_3	CH	N	N	14.5 (+1.9)	Missing	—	DMSO
391	1*H*-indazole	CH_3	CH	Benzo	Benzo	12.8 (+0.2)	—	—	DMSO[a]

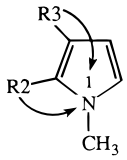
[a] Coupling constants from ^{1}H NMR spectroscopy.

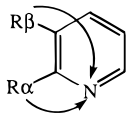
Table 23. N-3 Coupling constants (^{1}H, ^{15}N): comparison between imidazole and other *N*-substituted azoles

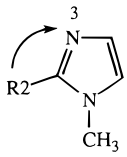
No.	Azole	R	2	4	5	^{2}J(N3H2)	^{2}J(N3H4)	^{3}J(N3H5)	Solvent
47	Imidazole	CH_3	CH	CH	CH	10.8	9.0	1.7	$CHCl_3$[a]
272	1,2,3-Triazole	$C(OH)(CH_3)_2$	N	CH	CH	—	9.9 (+0.9)	2.0 (+0.3)	Acetone[a]
242	1,2,4-Triazole	1-Methyl-5-amino	CNH_2	CH	N	—	13.0 (+4.0)	—	DMSO
253		1-CH_2COCH_3-3-nitro	CH	CNO_2	N	12.4 (+1.6)	—	—	DMSO
300	1,2,3,4-Tetrazole	CH_3	N	N	CH	—	—	Missing	DMSO
		CH_3	CH	N	N	12.2 (+1.4)	—	—	DMSO
	1,2,3,5-Tetrazole	CH_2COCH_3	N	CH	N	—	12.6 (+3.6)	—	DMSO
377	Benzimidazole	NH_2	CH	Benzo	Benzo	11.9 (+1.1)	—	—	DMSO

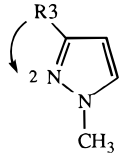
[a] Coupling constants from ^{1}H NMR spectroscopy.

Reference Data Review









atom. Nevertheless, considering the different nature of the pyrrole-like N-1 atom in azoles with the pyridine-type nitrogen, the regression shows at least that the effects are somewhat related, being weaker (slope = 0.7) in azoles.

(b) Pyridine-like nitrogen atoms (N-2 and N-3). The effect of substituents at position 2 on N-3 and those at position 3 on N-2 are not identical although they are linearly related (those observed on N-3 being larger):

$$\delta^{15}\text{N-3 (R2)} = 6.73 + 1.31\ \delta^{15}\text{N-2 (R3)},$$
$$n = 6,\ r^2 = 0.994 \quad (26)$$

Both are related to α-pyridine effects:

$$\delta^{15}\text{N-2 (R3)} = 2.60 + 1.05\ \delta^{15}\text{N(α-pyridines)},$$
$$n = 5,\ r^2 = 0.927 \quad (27)$$

$$\delta^{15}\text{N-3 (R2)} = 10.0 + 1.36\ \delta^{15}\text{N(α-pyridines)},$$
$$n = 5,\ r^2 = 0.904 \quad (28)$$

(iv) It has been reported that substituents at position 5 on the benzene ring in indoles (Table 12) modify the chemical shift of N-1 and that the SCS follow a Hammett relationship [Eqn (29)]:[97]

$$\delta^{15}\text{N-1} = 0.003 + 8.02\ \sigma_p,\ n = 10,\ r^2 = 0.974 \quad (29)$$

(v) The use of chloroform compared with other solvents produces a statiscally significant effect only on N-1 (*ca* −4 ppm).

Solvent effects and protonation.

Since ^{15}N chemical shifts are so sensitive to solvent effects (mainly HB donor solvents for the pyridine-like nitrogen atoms), a discussion of the effect of the structure on the chemical shifts must be carried out in the same solvent, e.g. DMSO (acetone and $CDCl_3$ can be used when the value in DMSO is not known, but alcohols and water should not).

In a series of remarkable papers, Webb and co-workers[120–122] reported a careful study of solvents effects on the ^{15}N chemical shifts of compounds **1**,[120] **12**,[120] **47**,[121] **98**,[121] **226**,[122] **240**,[122] **264**[122] and **271**.[122] The main conclusions were that (i) δN-1 depends on the solvent polarity (ii) other nitrogen chemical shifts depend on the solvent acidity and (iii) in the case of triazoles, the most basic nitrogen is the most sensitive to solvent acidity.[122] The difference in chemical shifts of the *N*-methyl atom between DMSO and chloroform amounts to −2.5 ppm.[120–122]

Although we have reported data in TFA, the problem of the use of ^{15}N chemical shifts for determining the protonation site is not discussed in this review, the interested reader can consult the papers reported in Table 20.

Tautomerism

We have reported in Table 20 some references concerning the use of ^{15}N NMR spectroscopy for studying the tautomerism (annular or functional)[123] of azoles. In the case of *N*-H-azoles the numbering of the different nitrogen atoms is somewhat arbitrary. For instance, in Table 3, 3-methylpyrazole **77**, N-1 = −133.4, N-2 = −141.9 ppm (in DMSO); this means that if we represent this compound as the 3-methyl tautomer, N-1 is the nitrogen far from the methyl group and N-2 is the nitrogen adjacent to it.

^{15}N chemical shifts vs theoretical calculations

Regarding the relationships between δ^{15}N and total charge densities, they are in general not entirely satisfactory. Many workers[28,83,84] have attempted to do this and even if they may be useful for assigning N atoms with very different chemical shifts, they cannot be used for fine analyses; however, see e.g. Refs 83, 84 and 87 for good linear relationships but for restricted families of compounds (in this case tetrazoles). In more recent papers, the program IGLOO has increasingly been used to calculate chemical shifts.

Coupling constants

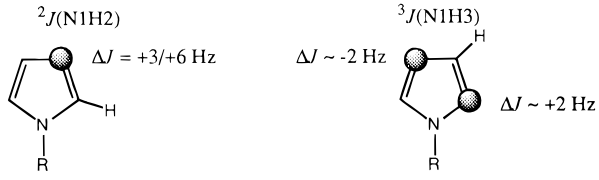
Concerning the coupling constants, we prepared [$^{15}N_2$]-1-benzylpyrazole **156** and determined carefully all the coupling constants involving ^{1}H, ^{13}C and ^{15}N nuclei. In some spectra carried out in this work using the INEPT sequence (**150**, **192**, **195**, **219**), the ^{1}H, ^{15}N coupling constants are approximate, because in some cases the resolution cannot permit differentiation of coupling constants with similar values. In these cases we have reported the average value ^3J(N1H3) = ^3J(N1H4).

(a) ^{1}H, ^{15}N coupling constants. The ^1J(NH) coupling constant is present in pyrroles, indoles and carbazoles but annular tautomerism generally prevents its observation in NH-polyazoles. A value of about 97 Hz is observed for pyrroles, indoles, carbazoles and imidazoles; the value increases about 7 Hz (105 Hz) for pyrazoles, 1*H*-indazoles and 1*H*-benzotriazoles owing to the 2-aza substitution. This shows that neither the benzo annelation nor the 3-aza substitution modifies the value of the ^1J(NH) coupling constant.

In Table 21 we have gathered the coupling constants (*J* in Hz) of N-1 with the CH ring protons of pyrrole and some substituted azoles (azapyrroles). We have tried to restrict this search to *N*-alkyl substituents except for indole and benzimidazole for which the corresponding data were not available. The value of ^2J is only modified if there is a nitrogen atom in α position respect to the CH (+3.1 to +6.1 Hz).The same effect is observed in ^3J, but in this case the change is smaller; if the nitrogen atom is adjacent to N-1 an increase (+1.3 to +2.9 Hz) is observed; however, a decrease (−1.7 to −1.9 Hz) is observed if the nitrogen atom is in β position respect to N-1.

We compiled similar tables for N-2 (Table 22) and N-3 (Table 23), the number of coupling constants being considerably reduced. The ^2J(N2H3) and ^2J(N3H2) coupling constants are large and relatively insensitive to the substitution pattern (Tables 22 and 23) whereas ^{3}J(N2H4), ^3J(N2H5) and ^3J(N3H5) are always small; ^2J(N3H4) is large and depends on the presence of a nitrogen atom at position 5 (Table 23).

(b) ^{13}C, ^{15}N coupling constants. Only N-1



shows large ^1J couplings with the carbon atoms: 11–14 Hz with C-2, C-5 and N-C (for instance *N*-methyl and *N*-benzyl), ^2J(N1C3 or C4) amounts to 5–6 Hz if between N-1 and C-3 (C-4) there is a carbon atom but only to 1 Hz if there is another nitrogen atom. The ^{13}C, ^{15}N coupling constants of N-2 and N-3, either ^1J or ^2J, are always between 0 and 2 Hz.

(c) ^{15}N, ^{15}N coupling constants. The ^1J coupling is large, 12–18 Hz, and depends on the substituent on N-1 and on the aza effect (it shows the largest values on triazoles **265** and **272**) whereas ^2J is always small, about 1 Hz (**32** and **67**).

EXPERIMENTAL

The spectra quoted in Tables 1–18 as 'This work' were recorded with different instruments using standard conditions: UNED, Madrid (Bruker AC200); IQM, Madrid (Varian 500 Unity); Montpellier (Bruker AC250 and Bruker DRX400).

The spectra reported as 'This work' in Tables 1–18 correspond to 45 compounds which are (i) commercial products, (ii) described in our previous papers and (iii) described in the literature. Only in the few cases where the literature procedure was not followed are the syntheses reported below.

Commercial products: **4**, **69**, **79**, **92**, **361**, **367**, **404**.

Described previously by us: **75**,[124] **93**,[10] **100**,[10] **101**,[10] **102**,[10] **103**,[10] **110**,[10] **119**,[10] **120**,[10] **121**,[10] **144**,[10] **156**,[10] **159**,[10] **162**,[10] **163**,[10] **164**,[10] **165**,[10] **179**,[10] **188**,[10] **191**,[10] **242**,[125] **370**,[126] **371**,[127] **382**,[11] **383**,[127] **389**,[11] **390**,[11] **398**,[128] **403**,[129] **419**.[9]

Described in the literature: **243**,[130] **244**,[130] **374**,[131] **395**,[132] **397**.[133]

New synthetic procedures: **136**, **137** (new compound), **151**.

1,3-Dimethyl-5-methoxypyrazole (136)

In a round-bottomed flask provided with a refrigerant and mechanical stirrer were placed 4.03 g of methyl acetylacetate (0.035 mol), 5.0 g of methylhydrazine hydrogensulfate (0.035 mol) and 100 ml of methanol. After 2 h of reflux, the cooled solution was basified with aqueous sodium hydroxide (2.8 g in 10 ml of water). A solid (sodium sulfate) precipitated, which was filtered off. The methanol was removed under reduced pressure. The remaing aqueous solution was extracted three times with diethyl ether (3 × 25 ml). The ethereal solution was dried over sodium sulfate and the ether removed under reduced pressure. The residue was purified by column chromatography [silical gel; eluent, dichloromethane–diethyl ether (1:1)]. Compound **136**, 1.32 g (30% yield), b.p. 70 °C/14 mmHg.[134]

1,5-Dimethyl-3-methoxypyrazole (137)

In a round-bottomed flask provided with a refrigerant and mechanical stirrer were placed 0.56 g of 3(5)-methyl-5(3)-methoxypyrazole (0.005 mol),[135] 1.38 g of potassium carbonate (0.01 mol), 1.25 ml of iodomethane (0.02 mol), two pellets of sodium hydroxide and 25 ml of acetonitrile. After 3 h of reflux, the solid residue was eliminated by filtration and the hot solution was evaporated under reduced pressure. The residue was purified by column chromatography [silica gel; eluent, dichloromethane–diethyl ether (9:1). Compound **137**, 0.20 g (32% yield) is an oil (b.p. 74–75 °C/14 mmHg). Found: C, 56.86, H, 7.63, N, 22.09. $C_6H_{10}N_2O$ requires C, 57.13, H, 7.99, N, 22.20%.

1-Acetonylpyrazole (151)

In a round-bottomed flask provided with a refrigerant and mechanical stirrer were placed 1.0 g of pyrazole (14.7 mmol) and 0.58 ml of chloroacetone (7.34 mmol). The mixture is stirred under reflux for 1 h. The residue was directly purified by column chromatography [silica gel; eluent, chloroform–ethanol (99:1)]. Compound **151** was obtained in 95% yield (0.86 g). The procedure described by Semenov *et al.*[49] uses non-commercial bromoacetone.

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Note added in Proof

Recently [G. Otting, B. A. Messerle and L. P. Soler, *J. Am. Chem. Soc.* **118**, 5096 (1996)] reported the measurement and determination of the absolute sign of the ^1H,^{15}N, ^{13}C,^{15}N and ^{15}N,^{15}N coupling constants of compound **163** [δN1 = −169.5 and δN2 = −76.8 (solvent: $CDCl_3$)].

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