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^{13}C NMR OF INDAZOLES

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The carbon-13 chemical shifts and some selected coupling constants of 183 indazoles are reported. The main conclusions of the original references are briefly summarized.

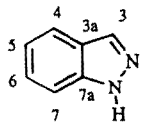
Key Words: ^{13}C NMR, *chemical shifts, coupling constants, indazoles*

INTRODUCTION

This review deals with the ^{13}C NMR spectroscopy of indazoles. All the available information comes from 50 references, reported in chronological order [1-50] and from spectra obtained for this review, quoted as "this work."

RESULTS AND DISCUSSION

The results are gathered in three tables: Table 1 contains the data of NH-indazoles, Table 2 those of 1-substituted indazoles while Table 3 reports the 2-substituted indazoles.



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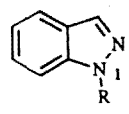

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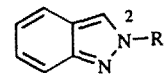

138-183

From this review quaternary indazolium salts as well as indazolinones and other non-aromatic derivatives (for instance, 4,5,6,7-tetrahydroindazoles which were considered pyrazole derivatives) have been excluded [51]. Concerning the ^{1}H-^{13}C coupling constants, only ^{1}J is reported in the tables for reasons which will be discussed later.

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CHEMICAL SHIFTS

The chemical shifts of all indazole carbons and those of simple substituents are reported in the tables.

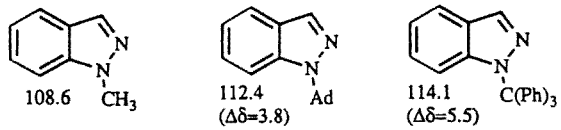
i) Relationships Between Chemical Shifts and Total Charge Densities. With moderate success indazole [1] and azole (including indazole) [6] chemical shifts have been correlated (slope −146.4 ppm/e and −216 ppm/e) [1, 6] with total charge densities (CNDO/S and CNDO/2 calculations) [1, 6]. STO-3G calculations have been used to explain the chemical shift of C-3 carbon in 1-methyl vs. 2-methylindazole [13].

ii) Substituents Chemical Shifts (SCS): Empirical Modeling. One of the more studied aspects is the effect of protonation (either by trifluoroacetic acid or by sulfuric acid) and the quaternization on the chemical shifts of indazole carbons [6, 18, 35, 39]. These induced shifts have been used to show that 3-aminoindazole **2** protonates on indazole N-2 atom and not on the amino group [18].

The SCS of "benzenic" carbons (C-4 to C-7) parallel those of naphthalene [2]. For seven substituents (NH_2, CH_3, Br, F, N_3, Cl, I) the SCS of the "heterocyclic" carbon C-3 are linearly related to SCS of benzene:

$$\delta(\text{C-3}) = -6.5 + 0.99\ \delta_{ipso}\ (r = 0.988)\ [2].$$

Carbon C-7 is very sensitive to bulky effects due to substituents on N-1 (δ-effect), for instance between 1-methylindazole **101** and either 1-adamantylindazole **53** [19] or 1-tritylindazole **134** [22]:



101 **53** **134**

Several publications of the same group deal with empirical modelling of the chemical shifts of sp^3 carbons (CH_3, CH_2-Az, CH_2-CH_2-Az, CH_2-CH_2-$CONH_2$, ...) directly linked to the nitrogen atom of azoles (Az) [12, 22, 30, 32]. These studies include indazol-1-yl and indazol-2-yl substituents. The chemical shifts of these carbons are linearly related, for instance

$$\delta(CH_2Az) = 2.5 + 0.78\ \delta(CH_3)\ [12],$$
$$\delta(CH_2CH_2CONH_2) = 11.3 + 0.95\ \delta(CH_3)\ [30],$$
$$\delta(CH_2CH_2Az) = 17.5 + 0.88\ \delta(CH_3)\ [32].$$

The chemical shifts of a large collection of azoles without *C*-substituents but with many different *N*-substituents have been statistically analyzed (unbalanced analysis of variance) [29].

COUPLING CONSTANTS

i) $^1J(^1H,^{13}C)$ Coupling Constants of Indazole Carbon Atoms. From the beginning of indazole studies it appears that C-3 being an "heterocyclic" carbon has a ^1J coupling constant much larger (188 Hz) than those of "benzene" carbons C-4 to C-7 (about 160 Hz) [1, 3, 8]. First order [1] as well as LAOCN analyzed spectra [3, 8] yield the following order for these last couplings: C-7 (164 Hz) > C-4 (162 Hz) > C-5 (160 Hz) > C-6 (159 Hz) for indazole **1** and 3-azidoindazole **7**. Empirical modeling of heterocyclic coupling constants of azoles (including those of C-3 of 1*H* and 2*H*-indazoles) has been reported [29].

ii) $^nJ(^1H,^{13}C)$ Coupling Constants of Indazole Carbon Atoms. We have not reported long-range couplings in the tables for the following reasons:

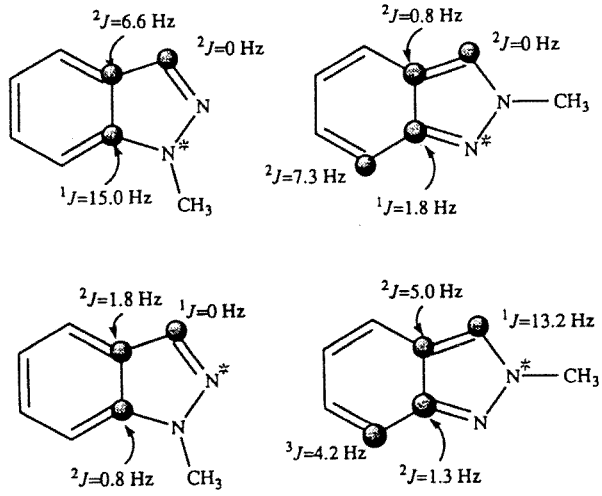
1) ^{1}H-coupled ^{13}C NMR spectra show sometimes complex multiplets (mainly with old 60-100 MHz spectrometers) which have to be analyzed as X-parts of second-order systems. Iterative analyses (LAOCN3, PANIC) are necessary and this has been done only twice: for indazole **1** and for 3-azidoindazole **7** [3, 8].

2) Unless the aromatic region is expanded using small spectral windows at acquisition time, the digital resolution of routine ^{13}C spectra is generally poor (0.5 to 1 Hz/pt).

The most interesting results concern carbon C-3. In the specific case of NH-indazoles, the width at half-height of the C-3 (also C-3a, C-7 and C-7a) signal is strongly dependent on solvent. When the NH exchange rate is slow, a coupling with H-1 is observed (7-10 Hz). When the rate is fast, narrow signals are obtained on which the coupling with H-4 can be measured (2.0 to 2.5 Hz) [2, 3, 8]. This last coupling is also observed in 1-substituted- but not in 2-substituted-indazoles (an additional proof that NH-indazoles are 1*H*-tautomers) [5].

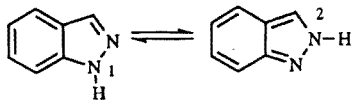
iii) Couplings with Nuclei Other than Hydrogen. For 3-fluoroindazole **33** (Table 1), ^{13}C-^{19}F coupling constants have been measured [2]. Some $^{1}J(^{13}C,^{13}C)$ coupling constants between ring carbons of 1-vinylindazole **135** (Table 2, footnote *e*) have been measured [31]. This $^{1}J(^{13}C,^{13}C)$ coupling has also been reported between the vinyl carbons in 1-vinylindazole **135** (Table 2) and 2-vinylindazole **176** (Table 3) (78.2 and 77.8 Hz respectively) and related to the energy of the LUMO and to the proximity of the "pyridinic" nitrogen lone pair [33].

A study of ^{13}C-^{15}N coupling constants of [$^{15}N_1$]-labeled indazoles including indazole itself **1**, 1-methylindazole **101** and 2-methylindazole **155** alternatively labeled on N-1 and on N-2 has been reported [11]. We have summarized below some of the most interesting couplings measured ($N^* = {}^{15}N$). The fact that $^{1}J(^{13}C,^{15}N)$ = 13-15 Hz when the nitrogen is N-1 and 0-2 Hz when the nitrogen is N-2 is coherent with the results obtained for pyrazoles [53].



APPLICATIONS

i) Annular Tautomerism of Indazoles. The annular tautomerism of indazoles concerns the position of the NH-proton:



Although there is no doubt that the 1*H*-tautomer is much more stable than the 2*H* one [52-55], carbon-13 NMR chemical shifts (comparison of compounds **1**, **101** and **155**) have been used to confirm this result [2].

ii) Functional Tautomerism. While 3-aminoindazoles, for instance **2**, are true indazoles (the proportion of the 2*H*-3-imino tautomer is so weak that it can be neglected), in the case of 3-hydroxyindazole **35** both tautomers are present in solution [in the solid state (x-ray crystallography and ^{13}C CPMAS NMR spectroscopy) only the indazolinone is present] [20].

TABLE 1. ^{13}C Chemical Shifts (pp/TMS) and ^{1}J (^{13}C-^{1}H) Coupling Constants (in parentheses, Hz) of NH-indazoles

No	Substituents	Solvent	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	Others	References
1	2	3	4	5	6	7	8	9	10	11	12
1	None[a]	DMSO-d_6	133,4 (188,0)	122,8	120,4 (162,7)	120,1 (162,0)	125,8 (159,9)	110,0 (163,9)	139,9		[1, 8, 9]
		TFA	136,1	122,1	124,2	127,6	131,9	113,1	141,4		[18]
		H_2SO_4	129,79 (200,6)	118,44	121,36 (170,6)	124,74 (168,3)	133,75 (165,2)	109,89 (172,3)	138,07		[35]
2	3-Amino	DMSO-d_6	149,0	113,9	120,1	117,2	125,9	109,2	141,4		[2]
		TFA	151,6	113,2	123,1	125,5	136,7	113,5	146,1		[18]
3	5-Amino	DMSO-d_6	131,37	123,90	100,53	142,08	118,07	110,20	134,87		[36]
4	5-Amino-3-chloro	DMSO-d_6	129,83	120,51	97,75	143,26	119,54	111,14	135,62		[36]
5	6-Amino	DMSO-d_6	133,10	115,58	120,45	112,30	147,55	90,55	142,12		[36]
6	6-Amino-3-chloro	DMSO-d_6	131,97	111,97	118,64	113,40	148,86	90,42	143,57		[36, 49]
7	3-Azido	DMSO-d_6	139,6	114,0	118,5 (163,6)	120,4 (162,7)	127,2 (160,7)	110,7 (165,4)	141,6		[2, 3, 8]
8	Benzo[*e*]	DMSO-d_6	132,5	121,2	122,9	128,8	126,9	111,5	(*b*)	C-8 122,9; C-9 127,1; C-10 124,1; C-11 128,5	[4]
9	Benzo[*f*]	DMSO-d_6	133,7	125,3	118,7	128,0	132,0	104,5	138,6	C-8 128,8; C-9 122,8; C-10 125,3; C-11 127,5	[4]
10	Benzo[*g*]	DMSO-d_6	134,51 (188,5)	120,0	119,3	121,9	131,8	119,1	137,07	C-8 121,6; C-9 126,3; C-10 126,3; C-11 128,5	[4, 41]
		Acetone-d_6	135,0	121,9	120,1	122,6*	133,4	120,8	139,2	C-8 129,5; C-9 127,1; C-10 127,1; C-11 122,8*	[4]
		HMPT	133,5	121,7*	119,5	121,5*	132,5	119,7	138,4	C-8 128,7; C-9 125,9**; C-10 126,0**; C-11 123,2	[4]

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
11	3-Bromo	DMSO-d_6	120,3	122,0	119,0	121,3	127,3	110,7	140,9		[2]
12	3-Bromo-4-nitro	DMSO-d_6	117,1	112,2	141,1	118,5	126,4	117,1	142,7		[10]
13	3-Bromo-5-nitro	DMSO-d_6	123,4	121,3	116,7	142,7	121,9	111,3	142,0		[10]
14	3-Bromo-6-nitro	DMSO-d_6	120,9	125,0	120,4	115,5	146,6	107,5	139,4		[10]
15	5-Bromo-benzo[*g*]	DMSO-d_6	133,3	119,1	123,2	(*b*)	128,8	114,1	(*b*)	C-8 127,5*; C-9 127,4*; C-10 127,4*; C-11 122,3	[4]
16	6-Bromo-benzo[*e*]	DMSO-d_6	132,9	120,8	117,8	126,5	(*b*)	115,8	(*b*)	C-8 123,7; C-9 128,1; C-10 125,5; C-11 127,4	[4]
17	5-*t*-Butyl	$CDCl_3$	134,40	123,22	115,86	143,87	125,71	109,54	138,70	C 34,65; CH_3 31,63	This work
		DMSO-d_6	133,30 (186,7)	122,70	115,20 (158,1)	142,36	124,58 (156,1)	109,55 (163,4)	138,23	C 34,21; CH_3 31,37	This work
18	7-*t*-Butyl	$CDCl_3$	134,7	124,1	118,7	121,1	122,7	133,3	138,3	C 34,6; CH_3 30,1	This work
19	3-Chloro	DMSO-d_6	132,1	118,5	119,4	121,3	127,3	110,9	141,1		[2]
20	3-Chloro-benzo[*f*]	DMSO-d_6	132,8	120,8	117,3	128,6	132,8	106,0	139,7	C-8 129,0; C-9 123,7; C-10 126,2; C-11 127,8	[4]
21	3-Chloro-4-nitro	DMSO-d_6	130,5	110,4	141,1	118,9*	126,7	117,7*	143,1		[16]
22	3-Chloro-5-nitro	DMSO-d_6	135,40	118,86	116,46	143,00	122,12	112,19	142,36		[16, 36]
23	3-Chloro-6-nitro	DMSO-d_6	132,99	122,47	120,13	115,70	146,93	107,83	139,70		[16, 36, 49]
24	3-Chloro-7-nitro	DMSO-d_6	134,8	123,5	127,6	124,8	121,1	132,4*	133,2*		[16]
25	3-Chloro-6-(N-phenylamino)	DMSO-d_6	132,02	113,66	119,25	114,85	143,91	92,59	142,80		[45]
26	3-Chloro-6-(N-*p*-tolylamino)	DMSO-d_6	132,01	113,34	119,25	114,57	144,68	91,49	142,94		[45, 49]
27	3,5-Dibromo-benzo[*g*]	DMSO-d_6	120,7*	120,5*	121,1	118,7	129,4	115,5	137,9	C-8 127,8; C-9 128,6**; C-10 128,2**; C-11 122,4	[4]
28	4,6-Dimethyl	$CDCl_3$	132,75	121,82	130,55	122,98	136,97	106,82	140,77	CH_3-4 18,58*; CH_3-6 21,79*	This work
		DMSO-d_6	132,10 (186,2)	121,54	129,74	122,17 (155,4)	135,52	106,22 (161,0)	140,30	CH_3-4 18,20*; CH_3-6 21,29*	This work

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
29	3,5-Dinitro	DMSO-d_6	149,76	114,44	117,17 (175,4)	144,71	122,57 (168,6)	113,54 (171,0)	143,00		This work
30	(*E*)-3-Ethoxy-methylenhydrazino-carbonyl-5-bromo	DMSO-d_6	136,5	123,2	123,5	115,2	129,7	113,3	140,0	C=O 157,2	[9]
31	(*Z*)-3-Ethoxy-methylenhydrazino-carbonyl-5-bromo	DMSO-d_6	137,2	123,2	123,7	114,8	129,6	113,1	139,8	C=O 158,0	[9]
32	5-Ethyl	$CDCl_3$	134,0	123,4	118,5	136,8	127,9	109,6	138,9	CH_2 28,6; CH_3 16,1	This work
33	3-Fluoro	DMSO-d_6	156,8	107,7	118,2	121,0	128,0	111,1	141,8	J_{C3-F} = 244; J_{C3a-F} = 25,5; J_{C4-F} = 4	[2]
34	3-Hydrazinocarbonyl-5-bromo	DMSO-d_6	137,1	123,7	123,7 (168)	114,6	129,4 (170)	113,1 (168)	139,2	C=O no value	[9]
35	3-Hydroxy	DMSO-d_6	156,8	113,0	120,5	118,9	127,6	110,5	143,0		[20, 21, 28]
		Methanol-d_4	162,7	116,2	123,1	121,5	131,7	112,2	147,2		[21, 28]
		2,2,2,-Trif-luoroethanol	167,0	117,6	124,6	124,2	134,8	114,1	149,8		[21, 28]
		None	160,8	114,0	123,8	120,3	131,3	111,4	144,3		[20]
36	3-Hydroxy-5-bromo	DMSO-d_6	154,5	113,7	122,0	110,2	129,3	112,0	140,5		[20]
37	3-Hydroxy-5,7-dibromo	DMSO-d_6	154,9	114,8	121,7	109,8	130,9	103,7	139,4		[20]
38	3-Iodo	DMSO-d_6	93,3	126,7	120,3	121,1	127,1	110,4	140,3		[2]
39	3-Methoxy	DMSO-d_6	156,6	111,2	119,2	119,0	127,1	110,2	142,1	OCH_3 55,8	[21, 28]
		Methanol-d_4	158,7	112,9	120,5	120,4	128,7	110,9	143,9	OCH_3 56,7	[21, 28]
		2,2,2,-Tri-fluoro-ethanol	160,0	114,0	121,9	121,3	130,3	111,7	144,7	OCH_3 57,4	[21, 28]
40	11-Methoxy-benzo[g]	DMSO-d_6	133,9	118,0	119,7	121,1	133,4	114,8	137,6	C-8 108,7; C-9 157,7; C-10 116,9; C-11 123,4	[4]

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
41	3-Methyl	DMSO-d_6	140,9*	122,1	119,8	119,3	125,8	109,9	140,8*	CH_3 no value	[2]
42	3-Methyl-benzo[*e*]	DMSO-d_6	139,2	(*b*)	122,1	128,9	126,9	111,7	(*b*)	CH_3 15,2; C-8 122,3; C-9 127,5*; C-10 123,5*; C-11 128,7	[4]
43	3-Methyl-benzo[*g*]	DMSO-d_6	141,1	120,1	118,5	121,1	131,9	117,6	138,0	C-8 128,4; C-9 126,5*; C-10 126,2*; C-11 122,0	[4, 41]
44	7-Methyl	DMSO-d_6	133,74 (186,8)	122,59	117,77 (161,3)	120,44 (158,0)	125,61 (156,9)	119,87	140,09	CH_3 16,79 (127,0)	This work
45	4-Nitro	DMSO-d_6	132,2	115,2	141,7	118,3	125,2	117,9	139,5		[10]
46	5-Nitro[c]	DMSO-d_6	136,62	122,10	118,69	141,95	120,77	110,01	141,68		[2, 10, 36]
47	6-Nitro	DMSO-d_6	134,11	126,00	121,80	114,70	145,91	106,94	138,64		[2, 10, 36]
48	7-Nitro	DMSO-d_6	135,6	127,1	129,8	123,4	120,1	132,0*	131,9*		[2]
49	3-(2'-Oxo-1',3',4'-oxadiazol-5'-yl)	DMSO-d_6	130,1	120,1	120,4 (166,4)	122,6 (162,2)	127,3 (161,2)	111,1 (166,0)	140,9		[14]
50	5-Phenyl	Acetone-d_6 (low solubility)	135,07	(*b*)	119,31	(*b*)	126,80	111,22	(*b*)	C-2' 129,65; C-3' 127,92; C-4' 127,54	This work
		DMSO-d_6	133,84 (188,4)	123,52	118,20 (160,4)	132,74	125,58 (159,0)	110,57 (164,8)	139,42	C-1' 140,82; C-2' 126,78; C-3' 128,83; C-4' 126,67	This work

*Assignments of these signals may be reversed.

**Assignments of these signals may be reversed.

[a][^{15}N-1] Indazole **1a** and [^{15}N-2]-indazole **1b** are described in Ref. 11 (solvent: DMSO-d_6): *J*C-4/N-1) 1.5; *J*(C-6/N-1) 2.0; *J*(C-7/N-1) 1.8; *J*(C-3a/N-1) 5.9; *J*(C-7a/N-1) 13.6; *J*(C-4/N-2) 1.1; *J*(C-6/N-2) 0.6; *J*(C-3a/N-2) 1.8; *J*(C-7a/N-2) 1.1.

[b]Signal not observed.

[c][^{15}N-2]-5-Nitroindazole **46a** is described in Ref. 11 (solvent: DMSO-d_6): *J*(C-4/N-2) 1.1; *J*(C-3a/N-2) 1.8; *J*(C-7a/N-2) 1.3.

TABLE 2. ^{13}C Chemical Shifts (pp/TMS) and ^{1}J (^{13}C-^{1}H) Coupling Constants (in parentheses, Hz) of N-substituted 1H-indazoles[a]

Compound	Substituents	Solvent	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	Others	References
1	2	3	4	5	6	7	8	9	10	11	12
51	1-Acetyl	$CDCl_3$	139,4 (190)	126,1	120,6 (163,5)	124,1 (161,5)	129,2 (157,5)	115,3 (174)	139,4	C=O 170,7; CH_3 22,7 (130,5)	[5]
52	1-Acetyl-3-methoxy	$CDCl_3$	159,8	117,6	124,0	119,6	130,2	115,9	117,6	C=O 170,3; CH_3 22,9; OCH_3 56,4	[20]
53	1-Adamantyl	$CDCl_3$	131,5 (187,6)	125,6	119,9 (162,9)	121,3 (159,7)	125,0 (161,3)	112,4 (161,2)	138,0	C-1' 60,5	[19]
54	1-Amino	DMSO-d_6	129,1 (187,3)	121,7	120,6 (162)	120,3 (162)	126,0 (160)	109,8 (166)	138,7		[29]
55	1-Bromocarbonyl-3-ethoxy	$CDCl_3$	138,2	119,8	120,5	125,6	130,7	115,1	140,5	C=O 160,6	[42]
56	1-Bromocarbonyl-3-methoxy	$CDCl_3$	138,2	119,5	120,3	125,6	130,9	115,1	140,7	C=O 161,2	[42]
57	1-Bromocarbonyl-3-methyl	$CDCl_3$	138,2	127,6	120,5	125,5	130,0	114,5	139,2	C=O 151,6	[42]
58	1-Bromocarbonyl-3-phenyl	$CDCl_3$	139,2	130,9	(b)	(b)	130,1	115,0	140,4	C=O 152,5	[42]
59	1-Bromocarbonyl-3-tribromomethyl	$CDCl_3$	139,3	121,6	122,8	125,8	130,9	114,9	141,6	C=O 160,9	[42]
60	(*E*)-1-Carboxyethyl-3-hydroxy	DMSO-d_6	(b)	111,7	129,0	118,9	129,0	111,7	148,8	CH_3 19,2	[20]
61	(*Z*)-1-Carboxyethyl-3-hydroxy	DMSO-d_6	169,0	112,2	128,6	118,4	128,6	112,2	149,4	CH_3 20,6	[20]
		None	(b)	109,8	131,0	120,3	131,0	115,4	150,9	CH_3 18,5	[20]
62	1-Carboxyethyl-3-methyl	$CDCl_3$	140,2	125,7	120.0	123,2	128,8	114,3	148,8	C=O 150,4	[42]
63	1-Carboxymethyl-3-methyl	Acetone-d_6	140,4	125,9	120,1	123,5	129,0	114,4	149,1	C=O 151,0	[42]
64	1-Carboxymethyl-3-methyl-amino	$CDCl_3$	141,1	128,2	118,8	123,0	129,6	115,0	151,7	C=O 153,8	[42]

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
65	1-(2'-Carboxamidoethyl)	DMSO-d_6	132,7 (189,3)	123,5	120,6	120,3	125,8	109,7	139,2	CH_2-1' 44,4 (145,3); CH_2-2' 35,2 (128,0); C=O 171,8	[30]
66	1-(2'-Carboxamidoethyl)-5-chloro	DMSO-d_6	132,3 (191,2)	124,3	119,7	125,0	126,3	111,6	137,9	CH_2-1' 44,7 (139,2); CH_2-2' 35,2 (125,6); C=O 171,8	[30]
67	1-(2'-Carboxamidoethyl)-6-nitro	DMSO-d_6	136,2 (193,8)	122,5	118,7	141,0	120,7	110,8	141,6	CH_2-1' 44,9 (144,4); CH_2-2' 35,0 (128,3); C=O 171,7	[30]
68	1-Chlorocarbonyl-3-methyl	$CDCl_3$	140,1	127,4	120,6	125,5	130,1	114,9	146,4	C=O 151,7; CH_3 no value	[42]
69	1-[2'-(Chloromethyl)benzyl]-3-hydroxy-5-nitro	DMSO-d_6	156,77	111,85	118,67	140,15	122,05	109,97	142,40	N-CH_2 48,74	[38]
70	1-[2'-(Chloromethyl)-phenethyl]-3-hydroxy-5-nitro	DMSO-d_6	156,64	111,27	118,51	139,69	121,41	109,56	142,06	N-CH_2 48,95	[38]
71	1-(5'-Chloropentyl)-3-hydroxy	$CDCl_3$	156,24	112,34	121,17	119,21	128,41	108,59	141,36	N-CH_2 47,82	[38]
72	1-(5'-Chloropentyl)-3-hydroxy 5-nitro	DMSO-d_6	156,39	111,23	118,63	139,75	121,55	109,84	141,96	N-CH_2 47,67	[38]
73	1-(4'-Chlorobenzoyl)	DMSO-d_6	141,08	125,91	121,62	124,94	129,56	115,01	139,22	C=O 166,49	This work
74	1-(2'-Cyanoethyl)	DMSO-d_6	133,61	123,51	120,85*	120,68*	126,23	109,58	139,33	N-CH_2 43,63	This work
75	1,5-Dinitro	DMSO-d_6	139,1	124,5	119,2	144,8	125,5	114,8	136,8		[10]
76	1,4-Dinitro-3-bromo	DMSO-d_6	123,2	115,1	141,8	121,9*	132,4	119,2*	137,0		[10]
77	1,5-Dinitro-3-bromo	DMSO-d_6	129,7	124,7	117,4	145,3	126,8	115,5	137,8		[10]
78	1,6-Dinitro-3-bromo	DMSO-d_6	128,5	127,9	122,8	121,1	149,5	109,9	134,9		[10]
79	1,4-Dinitro-3-chloro	DMSO-d_6	134,9	113,4	141,6	122,4*	132,7	119,7*	137,6		[16]
80	1,5-Dinitro-3-chloro	DMSO-d_6	139,8	122,3	117,0	145,5	127,0	115,8	138,3		[16]
81	1,6-Dinitro-3-chloro	DMSO-d_6	138,9	125,6	122,3	121,3	149,7	110,2	135,6		[16]

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
82	1-Diphenylmethyl	$CDCl_3$	132,7	123,3	119,7	120,0	125,2	108,6	138,9	N–CH 65,3	[22]
83	(*E*)-1-(N-Formamidyl)	DMSO-d_6	133,0 (192,1)	122,6	121,3*	122,0* (162,0)	127,9 (161,2)	109,0 (166,5)	139,6		[43]
84	(*Z*)-1-(N-Formamidyl)	DMSO-d_6	132,3 (191,5)	122,4	121,2 (163,0)	121,5 (160,6)	127,3 (161,2)	108,9 (166,4)	138,9		[43]
85	1-(Hex-5′-enyl)-3-hydroxy	$CDCl_3$	156,09	112,22	121,10	119,00	128,22	108,58	141,16	N–CH_2 47,90	[38]
86	1-(Hex-5′-enyl)-3-hydroxy-5-nitro	DMSO-d_6	156,38	111,20	118,60	139,69	121,49	109,72	141.91	N–CH_2 47,63	[38]
87	1-Hydroxymethyl	$CDCl_3$	133,1 (175,8)	124,1	120,7	120,7	126,0	110,0	138,8	N–CH_2 no value	[29]
88	1-Hydroxymethyl-3-methyl	$CDCl_3$	143,4	123,9	120,7 (160,1)	120,5 (159,9)	127,3 (160,7)	109,3 (163,7)	140,3	CH_3 11,5 (128,0); N–CH_2 70,5 (157,1)	[37]
89	1-Hydroxymethyl-5-nitro	DMSO-d_6	136,30	123,25	118,76	141,81*	120,88	110,84	140,70*	N–CH_2 71,24	This work
90	1-Hydroxymethyl-6-nitro	DMSO-d_6	133,86	127,28	121,97	115,17	145,64	107,00	137,49	N–CH_2 71,36	This work
91	1-[2′-(Hydroxymethyl)-benzyl]-3-hydroxy-5-nitro	DMSO-d_6	156,53	111,58	118,54	139,95	121,82	109,99	142,26	N–CH_2 48,83	[50]
92	1-[2′-(Indazol-1″-yl)ethyl]	$CDCl_3$	133,7 (188,4)	123,6	120,3* (161,0)	120,6* (161,2)	126,1 (161,5)	108,2 (164,1)	139,7	N–CH_2 48,2 (141,6)	[32]
93	1-[(Indazol-1′-yl)methyl]	$CDCl_3$	134,4	122,3	121,4*	121,0*	127,0	110,0	139,6	N–CH_2–N 60,1	[12]
94	1-[(Indazol-1′-yl)-(2′-fluoro-phenyl)-methyl]	$CDCl_3$	134,7	124,8	121,2	121,6	127,1	109,8	139,6	N–CH 70,0	[47]
95	1-[(Indazol-1′-yl)-(4′-fluoro-phenyl)-methyl]	$CDCl_3$	134,8	124,7	121,0	121,5	126,8	110,6	139,6	N–CH 74,0	[47]
96	1-[(Indazol-1′-yl)-(4′-nitro-phenyl)-methyl]	$CDCl_3$	135,2	124,8	121,2	121,8	127,2	110,3	139,5	N–CH 73,7	[47]
97	1-[(Indazol-1′-yl)-phenylmethyl]	$CDCl_3$	134,6	124,7	121,4	120,9	126,7	110,7	139,7	N–CH–N 74,6	[22]
		DMSO-d_6	134,6	124,2	121,3	121,0	126,6	110,7	139,6	N–CH–N 72,8	[44]
		Acetone-d_6	134,8	124,9	121,5	121,0	126,8	110,9	139,9	N–CH–N 74,8	[44]

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
98	1-[2'-(Indazol-2"-yl)ethyl]	DMSO-d_6	133,3 (189,3)	123,3	120,4* (161,3)	120,8* (160,5)	125,4 (159,0)	109,0 (165,6)	139,5	N(1-ind)–CH_2 48,4 (142,7); N(2-ind)–CH_2 52,2 (142,9) see Table 3 for the (indazol-2'-yl) group	[32]
99	1-[(Indazol-2'-yl)methyl]	DMSO-d_6	134,3	(b)	121,4	120,8	126,6	110,2	139,2	N–CH_2-N 63,4; see Table 3 for the (indazol-2'-yl) group	[12]
100	1-(5'-Iodopentyl)-3-hydroxy-5-nitro	DMSO-d_6	156,58	111,45	118,82	139,95	121,75	110,06	142,16	N–CH_2 47,85	[38]
101	1-Methyl[c]	DMSO-d_6	132,4 (188)	123,8	120,8 (164)	120,3 (161)	126,0 (159)	109,6 (165)	139,7	N–CH_3 35,3 (139)	[2, 6]
		$CDCl_3$	132,4 (188)	123,8	120,8 (161)	120,2 (161,5)	125,9 (159)	108,6 (161)	139,7	N–CH_3 35,2 (138)	[5]
		Acetone-d_6	132,9	124,9	121,4	120,8	126,5	109,8	140,7	N–CH_3 35,5	[7]
		SO_4H_2	128,14 (203,7)	118,90	121,89 (168,2)	124,77 (165,5)	133,60 (166,0)	108,78 (170,9)	138,69	N–CH_3 33,51	[35]
102	1-Methyl-5-amino	DMSO-d_6	129,92	124,59	100,57	142,31	117,92	109,55	134,45	N–CH_3 35,12	[36]
103	1-Methyl-6-amino	DMSO-d_6	131,91	125,97	120,77	112,19	147,73	89,51	141,64	N–CH_3 34,68	[36, 49]
104	1-Methyl-benzo[g]	DMSO-d_6	132,4	121,0*	119,2	122,1	132,5	120,7*	135,0	C-8 128,8; C-9 126,3**; C-10 126,0**; C-11 122,1	[4]
105	1-Methyl-3-carboxymethyl	DMSO-d_6	134,7	124,2	124,5*	122,4*	128,0	112,1	142,1	N–CH_3 37,7; C=O 163,7; OCH_3 53,0	[23]
106	1-Methyl-3-hydroxy	DMSO-d_6	154,7	112,8	120,3	118,7	127,3	109,4	142,2	CH_3 35,0	[20, 21, 28]
		Methanol-d_4	157,7	113,8	122,6	121,7	131,7	111,0	145,5	CH_3 35,5	[21, 28]
		2,2,2-Tri-fluoroethanol	162,3	115,3	124,3	123,8	134,8	112,1	148,5	CH_3 36,5	[21, 28]
		None	155,8	112,1	121,7	118,1	127,3	109,3	140,2	CH_3 34,1	[20]

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
107	1-Methyl-3-hydroxy-5-nitro	DMSO-d_6	156,25	111,25	118,51	139,63	121,43	109,77	142,11	CH_3 35,19	[38]
108	1-[(3'-Methyl-indazol-1'-yl)-(2'-fluorophenyl)-methyl]-3-methyl	$CDCl_3$	142,9	124,3	120,3	120,6	126,8	109,9	140,4	N–CH 69,9	[47]
109	1-[(3'-Methyl-indazol-1'-yl)-(4'-fluorophenyl)-methyl]-3-methyl	$CDCl_3$	143,0	124,3	120,1	120,5	126,5	110,8	140,5	N–CH 73,5	[47]
110	1-[(3'-Methyl-indazol-1'-yl)-(4'-nitrophenyl)-methyl]-3-methyl	$CDCl_3$	143,6	124,4	120,3	120,9	126,9	110,5	140,5	N–CH 73,3	[47]
111	1-Methyl-3-methoxy	DMSO-d_6	155,2	111,4	119,2	118,8	127,0	109,1	141,7	N–CH_3 34,8; OCH_3 55,8	[20, 21]
		Methanol-d_4	157,5	113,3	120,7	120,1	128,7	109,8	143,5	N–CH_3 35,0; OCH_3 56,7	[21]
		2,2,2-Tri-fluoroethanol	158,4	113,6	121,5	121,2	130,0	110,4	144,1	N–CH_3 35,0; OCH_3 58,0	[21]
112	1-Methyl-3-methoxy-5-nitro	$CDCl_3$	158,14	111,71	118,54	140,69	122,47	108,43	142,94	N–CH_3 35,46; OCH_3 56,50	[38]
113	1-Methyl-5-nitro[d]	DMSO-d_6	135,7	122,6	118,7	141,7*	120,6	110,3	141,3*	N–CH_3 35,8	[2]
114	1-Methyl-6-nitro	DMSO-d_6	132,7	126,2	121,6	114,3	145,4	106,4	137,9	N–CH_3 35,7	[2, 49]
115	1-Methyl-6-(N-phenylamino)	DMSO-d_6	132,18	118,12	121,44	114,28	143,10	92,97	140,97	N–CH_3 35,12	[45, 49]
116	1-Methyl-6-[N-(4'-methoxy)-phenylamino]	DMSO-d_6	132,05	117,29	121,30	113,22	144,24	90,13	141,11	N–CH_3 34,96	[45, 49]
117	1-Methyl-6-[N-(4'-methyl)-phenylamino]	DMSO-d_6	132,06	117,66	121,30	113,60	143,10	91,59	140,98	N–CH_3 34,99	[45, 49]
118	1-[N=CH-(5'-Nitrofur-2'-yl)]	DMSO-d_6	135,2 (193,1)	123,4	123,0 (162,2)	121,7 (164,5)	128,0 (160,9)	110,0 (169,5)	137,6		[25]
119	1-Nitro-3-bromo	DMSO-d_6	129,3	124,4	121,0	126,6	132,4	114,1	135,5		[10]
120	1-Nitro-3-chloro	DMSO-d_6	139,5	120,3	122,0	126,8	132,6	114,3	136,1		[16]

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
121	1-(4'-Nitrophenyl)	DMSO-d_6	137,9 (192)	125,9	121,9 (165)	122,7 (163)	128,3 (160)	111,0 (166)	137,9		[29]
122	1-Phenyl	$CDCl_3$	135,4	125,3	121,5	121,3	127,1	110,4	138,7		[15, 17]
		DMSO-d_6	135,6 (193)	125,0	121,5	121,5	127,3 (162)	110,3 (165)	138,0		[29]
123	1-Phenyl-3-bromo-5-nitro	$CDCl_3$	126,2	124,5	118,4	143,2	123,2	111,2	141,5		[17]
124	1-Phenyl-3-bromo-6-nitro	$CDCl_3$	123,5	121,8	117,2	147,8	107,8	138,1	127,2		[17]
125	1-Phenyl-3,5-dinitro	DMSO-d_6	150,1	116,2	117,8	145,4	123,8	113,9	142,0		[17]
126	1-Phenyl-3,6-dinitro	$CDCl_3$	148,5	119,8	122,5	120,5	147,7	109,0	137,2		[17]
127	1-Phenylmethyl	$CDCl_3$	133,3	124,4	120,6*	121,0*	126,2	109,2	139,6	N–CH_2 52,8	[22]
128	1-Phenyl-6-nitro	$CDCl_3$	136,1	128,0	122,8	116,1	146,6	106,9	136,8		[17]
129	1-[2'-(Pyrazol-1''-yl)-ethyl]	$CDCl_3$	133,9 (189,6)	123,6	120,6 (162,1)	120,6 (162,1)	126,3 (160,0)	108,5 (163,5)	140,0	N(ind)–CH_2 48,6 (140,8); N(pyr)–CH_2 51,4 (141,9)	[32]
130	1-Tosyl	DMSO-d_6	142,4	125,7	122,1	124,5	129,6	112,5	139,6		[29]
131	1-Tributylstannyl	$CDCl_3$	136,8 (184)	124,9	120,9 (161)	119,6 (159)	125,1 (158,5)	111,1 (159)	148,4		[29]
132	1-Triflyl	$CDCl_3$	145,0 (192,8)	126,7	122,5 (168)	126,2 (164)	130,8 (164)	113,2 (171)	141,2		[29]
133	1-[(7',8',8'-Trimethyl-4',5',6',7'-tetrahydro-4',7'-methanoindazol-2'-yl)methyl]	$CDCl_3$	134,3	124,6	121,1	120,8	126,7	110,0	139,3	N–CH_2–N 63,2	[48]
134	1-Triphenylmethyl	$CDCl_3$	133,2	125,5	120,6	120,8	125,4	114,1	141,0	N–C 78,4	[22]

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
135	1-Vinyl[c]	$CDCl_3$	135,59	124,77	121,13	121,63	127,10	109,18	138,46	N–CH– 129,85; $-CH_2$ 98,17	[34]
		DMSO-d_6	136,0 (192,0)	124,2	121,9 (162,4)	121,3 (163,5)	127,5 (161,7)	109,6 (164,8)	138,2	N–CH– 130,1 (178,7); $-CH_2$ 98,0 (161,4)	[32]
		Acetone-d_6[f]	136,13	125,18	121,47	122,01	127,47	109,61	138,86	N–CH– 130,33; $-CH_2$ 98,23	[24, 31]
136	1-Vinyl-3-vinyloxy	$CDCl_3$[g]	135,59	115,01	120,09	121,22	128,53	108,90	140,51	N–CH– 129,21; $-CH_2$ 95,74; O–CH– 146,24 $-CH_2$ 95,74	[34]

*Assignments of these signals may be reversed.

**Assignments of these signals may be reversed.

[a]This compound is described in Ref. 26 without any assignment of signals: **137** 1-phenyl-3-(4'-dimethylaminophenyl)indazole ($CDCl_3$): 16.66, 48.42, 114.46, 115.86, 124.21, 125.34, 125.97, 126.72, 127.32, 130.15, 130.85, 132.85, 133.35, 144.46, 150.70, 151.84.

[b]This carbon is not assigned.

[c][^{15}N-1]-1-Methylindazole **101**a and [^{15}N-2]-1-methylindazole **101**b are described in Ref. 11 (solvent: DMSO-d_6): *J*(C-4/N-1) 1.6; *J*(C-6/N-1) 1.8; *J*(C-7/N-1) 1.1; *J*(C-3a/N-1) 6.6; *J*(C-7a/N-1) 15.0; *J*(Me-1/N-1) 13.8; *J*(C-4/N-2) 0.9; *J*(C-6/N-2) 0.5; *J*(C-3a/N-2) 1.8; *J*(C-7a/N-2) 0.8; *J*(Me-1/N-2) 5.5.

[d][^{15}N-2]-1-Methyl-5-nitroindazole **113**a is described in Ref. 11 (solvent: DMSO0d_6): *J*(C-4/N-2) 1.3; *J*(C-3a/N-2) 1.8; *J*(C-7a/N-2) 1.3.

[e]$^1J(^{13}C/^{13}C)$ have been measured in Ref. 31: *J*(C-3/C-3a) 53.0; *J*(C-3a/C-4) 61.8; *J*(C-5/C-6) 56.2; *J*(C-6/C-7) 60.4; *J*(C-7/C-7a) 64.4; *J*(C-7a/C-3a) 57.4.

[f]Solvent: pure liquid in 10% acetone-d_6 + Cr(acac)3.

[g]Reference: HMDS.

TABLE 3. ^{13}C Chemical Shifts (pp/TMS) and ^{1}J (^{13}C-^{1}H) Coupling Constants (in parentheses, Hz) of N-substituted 2H-indazoles[a]

Compound	Substituents	Solvent	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	Others	References
1	2	3	4	5	6	7	8	9	10	11	12
138	2-Acetyl	$CDCl_3$	123,1 (191,5)	122,1	124,0 (160,5)	121,4 (165)	129,0 (161)	118,8 (167)	150,7	C=O 170,8; CH_3 21,8 (130,5)	[5]
139	2-Acetyl-benzo[g]	DMSO-d_6	126,2	119,8	119,1	122,4	133,2	124,8	148,3	C-8 128,8; C-9 128,4*; C-10 127,3*; C-11 122,8	[4]
140	2-Adamantyl	$CDCl_3$	121,1 (188,2)	121,1	118,4 (161,5)	120,3 (159,6)	125,4 (157,6)	117,6 (161,1)	148,1	C-1′ 60,1	[19]
141	2-Amino	DMSO-d_6	124,8	(b)	120,0	120,7	124,8	116,3	(b)		[29,40]
142	2-Benzyl	$CDCl_3$	122,8	122,2	120,1	121,8	125,9	117,6	149,0	N–CH_2 57,5	[22]
143	2,4-Dinitro	DMSO-d_6	124,9	113,0	140,7	119,7	129,4	127,5	145,7		[10]
144	2,5-Dinitro	DMSO-d_6	124,3	118,4	121,5	144,5	123,7	120,2	145,8		[10]
145	2,6-Dinitro	DMSO-d_6	124,6	121,9	120,9	118,3	148,9	116,5	143,4		[10]
146	2,7-Dinitro	DMSO-d_6	123,8	122,9	131,3	129,9	122,2	142,3	137,2		[10]
147	2-(2′,4′-Dinitrophenyl)	DMSO-d_6	125,4 (197)	122,4	123,0 (162,5)	121,1 (168,5)	128,0 (169)	117,4 (165)	150,0		[29]
148	2-Diphenylmethyl	$CDCl_3$	123,3	121,4	120,3	121,8	126,1	117,7	148,9	N–CH 71,0	[22]
149	(*E*)-2-(N-Formamidyl)	DMSO-d_6	124,6	120,7	120,7	122,3	126,9	117,2	146,3	N–CHO 164,8	[43]
150	(*Z*)-2-(N-Formamidyl)	DMSO-d_6	124,6	120,4	120,7	121,9	126,5	117,2	145,9	N–CHO 160,0	[43]
151	2-Hydroxy-3-methyl	DMSO-d_6	121,8	118,4	118,9	119,4	124,6	114,7	139,7	CH_3 7,9	[27, 28]
		Methanol-d_4	125,2	120,5	120,0	122,2	127,7	112,7	137,8	CH_3 8,1	[27, 28]
		2,2,2-Trifluoroethanol	128,7	121,2	120,9	124,1	130,4	110,6	134,6	CH_3 8,2	[27, 28]

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
152	2-(2'-Hydroxy-2'-phenylethyl)	DMSO-d_6	124,65	121,09	120,53*	120,68*	125,24	116,78	147,92	N–CH_2 60,10; CH 71,72; C-1' 142,43; C-2' 125,98; C-3' 128,14; C-4' 127,40	This work
98	2-[2'-(Indazol-1''-yl)-ethyl]	DMSO-d_6	124,3 (192,3)	121,2	120,4* (161,3)	120,6* (161,7)	125,9 (160,7)	116,8 161,3	148,2	N–CH_2 52,2(142,9); see Table 2 for the (indazol-1''-yl) group	[32]
99	2-[(Indazol-1'-yl)-methyl]	DMSO-d_6	124,0	120,8	121,4	124,0	126,2	117,2	148,4	N–CH_2–N 63,4; see Table 2 for the (indazol-1'-yl) group	[12]
153	2-[(Indazol-2'-yl)-methyl]	DMSO-d_6	125,0	121,0	121,3	123,5	126,5	117,2	148,7	N–CH_2–N 66,9	[12]
154	2-Methoxy-3-methyl	DMSO-d_6	123,9	118,9	120,0	120,7	126,5	116,4	141,7	CH_3 8,0	[27]
		Methanol-d_4	125,1	119,4	120,5	121,7	127,4	116,9	143,2	CH_3 8,0	[27]
		2,2,2-Trifluoro-ethanol	127,3	(*b*)	121,3	122,7	128,9	117,1	143,9	CH_3 8,4	[27]
155	2-Methyl[c]	$CDCl_3$	123,1 (186,5)	121,8	119,6 (162,5)	121,2 (159)	125,4 (157,5)	116,8 (162,5)	148,7	CH_3 39,7(140)	[5]
		DMSO-d_6	124,3 (194)	121,8	120,4 (164)	120,9 (160)	125,2 (160)	116,8 (165)	148,3	CH_3 39,7(139)	[2, 6]
		Acetone-d_6	125,9	123,0	121,7	120,9	124,4	117,9	149,6	CH_3 40,3	[7]
		H_2SO_4	132,19 (201,5)	119,09	121,06 (*b*)	124,77 (164,5)	133,27 (164,7)	109,53 (171,5)	138,79	N–CH_3 38,09	[35]
156	2-Methyl-5-amino	DMSO-d_6	120,75*	122,78	97,23	142,11	120,06*	117,12	144,11	N–CH_3 39,54	[36]
157	2-Methyl-6-amino	DMSO-d_6	123,81	115,78	120,31	115,78	146,25	94,09	150,17	N–CH_3 39,23	[36, 49]

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
158	2-Methyl-benzo[g]	DMSO-d_6	126,3	118,3	119,0	122,5	131,8	125,0	145,2	C-8 128,3; C-9 126,2*; C-10 125,6*; C-11 121,7	[4]
159	2-Methyl-3-carboxy-methyl	DMSO-d_6	125,0	124,2	122,3*	126,2*	127,6*	119,2	147,9	N–CH_3 42,6; C=O 161,4	[23]
160	2-Methyl-3-hydroxy	DMSO-d_6	160,7	117,5	122,8	120,8	131,1	112,0	145,9	N–CH_3 30,3	[20, 21]
		Methanol-d_4	163,0	118,1	123,8	122,6	132,9	112,9	147,1	N–CH_3 31,0	[21]
		2,2,2-Tri-fluoroethanol	163,8	118,2	124,1	124,1	134,0	113,4	147,2	N–CH_3 31,7	[21]
		None	158,5	116,5	124,1	121,6	131,4	110,1	144,8	N–CH_3 30,4	[20]
161	2-Methyl-5-nitro[d]	DMSO-d_6	128,7	120,0	119,3[e]	141,8	120,1[e]	117,6	149,1	CH_3 40,6	[2]
162	2-Methyl-6-nitro	DMSO-d_6	126,1	124,0	122,2	114,5	146,0	114,5	147,8	CH_3 40,8	[2, 49]
163	2-Methyl-7-nitro	DMSO-d_6	127,7	125,3	129,8	124,5	119,5	136,3	139,6	CH_3 40,6	[2]
164	2-Methyl-5-(N-phenylamino)	DMSO-d_6	122,84	117,63	103,87	136,55	118,64	117,63	145,10	N–CH_3 39,76	[45]
165	2-Methyl-6-(N-phenylamino)	DMSO-d_6	124,25	117,19	119,50	117,06	140,66	98,27	149,26	N–CH_3 39,58	[45, 49]
166	2-[N=CH-(5'-nitrofur-2'-yl)]	DMSO-d_6	124,5 (197,5)	121,5	121,2 (167,0)	122,4 (156,3)	128,3 (162,0)	117,0 (168,3)	146,1		[25]
167	2-(4'-Nitrophenyl)	DMSO-d_6	122,9 (199)	122,4	122,8 (167)	120,9 (167)	127,8 (167)	117,4 (167)	150,0		[29]
168	2-Phenyl	$CDCl_3$	126,9	122,9	120,5	120,5	122,6	118,1	149,9		[15, 17]
		DMSO-d_6	121,4 (189)	122,5	122,1 (161)	120,9 (165)	126,8 (159)	117,5 (163)	149,0		[29]
169	2-Phenyl-3-bromo	$CDCl_3$	106,2	123,1	119,8	123,1	127,7	118,3	149,3		[15]
170	2-Phenyl-3,5-dibromo	$CDCl_3$	105,4	124,1	121,8	116,5	131,3	120,0	147,6		[15]
171	2-Phenyl-3,7-dibromo	$CDCl_3$	107,6	123,5	119,3	123,5	130,3	111,5	147,6		[15]

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
172	2-Phenyl-3,5,7-tribromo	$CDCl_3$	106,9	124,2	121,4	115,7	133,3	112,9	146,5		[15]
173	2-[2'-(Pyrazol-1''-yl)-ethyl]	$CDCl_3$	124,0 (189,8)	121,7	120,3 (162,6)	121,7 (160,7)	126,2 (159,4)	117,3 (163,2)	149,4	N–CH_2 53,3	[32]
174	2-Triphenylmethyl	$CDCl_3$	125,9	121,7	121,7	120,3	121,1	118,2	148,5	N– C 79,5	[22]
175	2-Triflyl	DMSO-d_6	128,0 (198,6)	123,2	126,2 (162,5)	121,3 (167,2)	131,3 (161,2)	119,2 (168,1)	153,8		[29]
176	2-Vinyl	$CDCl_3$	127,00	121,91	121,12	120,23	122,36	117,54	149,31	=CH 138,48; $=CH_2$ 104,24	[34]
		DMSO-d_6	123,1 (193,3)	121,8	121,1 (163,4)	122,1 (161,2)	127,1 (160,0)	117,3 (162,2)	148,8	CH= 134,1 (182,1); $=CH_2$ 104,56(160,6)	[32]
		Acetone-d_6[f]	127,50	122,83	121,34*	122,75*	122,75*	118,24	149,94	CH= 134,58; $=CH_2$ 104,6	[24]
177	2-Vinyl-3-vinyloxy	$CDCl_3$[g]	141,37	108,79	121,24	118,91	127,61	117,87	148,61	N–CH= 128,08; $=CH_2$ 104,71; O–CH= 148,13; $=CH_2$ 95,89	[34]

*Assignments of these signals may be reversed.

[a]These compounds are described in Ref. 46 without any assignment of signals:

178 2-acetylamino-3-methylindazole(DMSO-d_6): 10.3, 21.7, 117.9, 120.0, 121.5, 121.6, 127.5, 133.1, 146.0, 169.6.

179 2-benzoylamino-3-methylindazole ($CDCl_3$): 9.3, 116.0, 119.5, 120.4, 121.0, 127.5, 127.9, 128.0, 128.6, 130.8, 132.7, 134.1, 145.6, 166.0.

180 2-benzoylamino-3-phenylindazole ($CDCl_3$): 116.8, 119.4, 120.8, 122.5, 127.5, 127.9, 128.0, 128.5, 128.8, 129.0, 129.2, 130.9, 132.5, 145.9, 166.1.

181 2-benyloxycarbonylamino-3-methylindazole (DMSO-d_6): 9.3, 67.4, 117.2, 119.2, 120.9, 126.95, 128.3, 128.5, 128.6, 128.7, 128.85, 129.0, 132.55, 136.2, 145.2, 155.3.

182 2-ethoxycarbonylamino-3-methylindazole (DMSO-d_6): 9.3, 14.7, 62.1, 117.1, 119.2, 120.8, 120.9, 126.8, 132.5, 145.1, 155.4.

183 2-(2'-hydroxybenzoyl)amino-3-methylindazole ($CDCl_3$): 8.7, 112.6, 116.5, 117.2, 118.6, 118.7, 119.6, 120.3, 126.3, 127.9, 132.3, 134.4, 145.3, 159.9, 168.1.

[b]This value is absent.

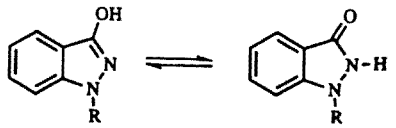
[c][^{15}N-1]-2-Methylindazole **155**a and [^{15}N-2]-2-methylindazole **155**b are described in Ref. 11 (solvent: DMSO-d_6): J(C-3a/N-1) 0.7; J(C-6/N-1) 3.1; J(C-7/N-1) 7.3; J(C-7a/N-1) 1.8; J(Me-2/N-1) 6.4; J(C-3/N-2) 13.2; J(C-3a/N-2) 5.0; J(C-4/N-2) 3.3; J(C-6/N-2) 0.6; J(C-7/N-2) 4.2; J(C-7a/N-2) 1.3; J(Me-2/N-2) 12.8.

[d][^{15}N-2]-2-Methyl-5-nitroindazole **161**a is described in Ref. 11 (solvent: DMSO-d_6): J(C-3/N-2) 13.4; J(C-3a/N-2) 4.8; J(C-4/N-2) 3.5; J(C-7/N-2) 4.0; J(C-7a/N-2) 0.7; J(Me-2/N-2).

[e]According to Ref. 11, assignment of these two signals have to be reversed.

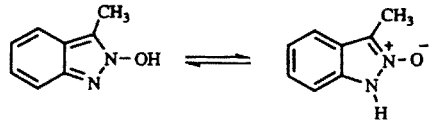
[f]Solvent: pure liquid to 10% acetone-d_6 + Cr(acac)3.

[g]Reference: HMDS.



The most sensitive carbons are C-6 and mainly C-4, the heterocyclic carbons (including C-3) being almost useless for studying tautomerism [20]. The percentage of the OH-tautomer decreases from DMSO (85%) [20, 21], to methanol (33%) and 2,2,2-trifluoroethanol (2%) [21, 28]. The case of 1-methyl-3-hydroxyindazole **106** was also studied by the same group [21, 28].

Another case of function tautomerism concerns 2-hydroxy-3-methylindazole **151**. This compound exists in two tautomeric forms:



Using the chemical shifts of carbons C-7 and C-7a, Schilf, Stefaniak and Webb established that the percentage of 2-hydroxy tautomer decreases from 82% in DMSO, 46% in methanol to 7% in 2,2,2-trifluoroethanol [27].

iii) Rotational Isomerism. The E/Z rotational isomer of azolide (*N*-acetylazole) **138** was determined by interpolation (very low activation barrier) using ^{13}C chemical shifts but the result (75% of Z) was considered unreliable [5]. The case of formamido derivatives **83**-E/**84**-Z and **149**-E/**150**-Z, where the barrier is high enough to observe both isomers, has also been studied by ^{13}C NMR spectroscopy [43].

iv) Positional Isomerism. Several publications report that 1- and 2-substituted indazoles can be easily identified by using ^{13}C NMR spectroscopy [2, 7, 23]. When C-3 is unsubstituted, its signal is readily identified by the large ^{1}J coupling constant. In this case only, ^{13}C NMR spectroscopy is probably the best method to differentiate 1*H*- and 2*H*-indazoles as the C-3 signal of 2-substituted isomers is generally 10 ppm upfield from the C-3 signals of 1-substituted ones. In all other cases, this problem may be solved more easily using ^{1}H NMR spectroscopy [53, 56-58], and we will not develop this aspect more.

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