The Structure of Indazolinone and Derivatives in the Solid State and in Solution: an *X*-Ray and Nuclear Magnetic Resonance Study

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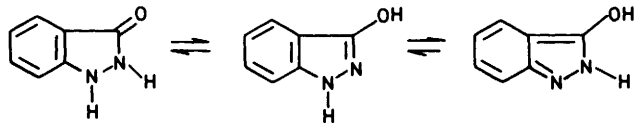
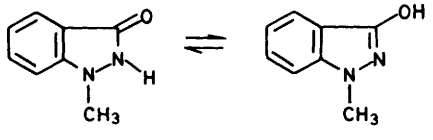
The structure of indazolinone and some of its derivatives was obtained by the combined use of crystallography, ^{13}C CP/MAS, and ^{15}N n.m.r. It was concluded that indazolinone exists as such in the solid state but only as a minor tautomer (15%) in DMSO solution, where the 3-hydroxyindazole tautomer predominates (85%). The result of bromination of indazolinone is reported. Two acylhydrazines, as open analogues of indazolinone, were studied as model compounds.

Among the simple heterocycles, indazolinones remain one of the last unresolved problems of tautomerism.[1,2] Although indazolinone is a much studied compound,[3] the structure of its major tautomer is still a matter of controversy. While structure (**1c**), a 2*H*-indazole, is very unlikely considering present knowledge of indazole tautomerism,[4] (**1a** and **b**) are reasonable and have been postulated by different authors.[1] When the indazolinone carries a substituent on the nitrogen, such as a methyl group [(**2**) and (**3**)], the possibility of tautomerism is reduced to two structures. Here, there is general agreement: tautomers (**2b**) and (**3a**) are the most stable in the solid state and in solution.[1]

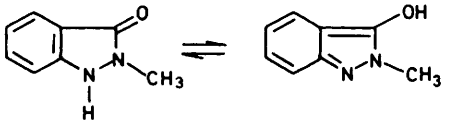
To settle this problem and to establish the tautomeric structure of (**1**)—(**3**) in the solid state and in DMSO solution, we have used *X*-ray crystallography and ^{13}C and ^{15}N n.m.r.



(**1a**) (**1b**) (**1c**)



(**2a**) (**2b**)



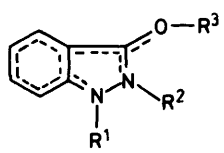
(**3a**) (**3c**)

Experimental

3-Hydroxyindazole (**1**),[3] 1-methyl-3-hydroxyindazole (**2**),[5] δ_H 10.52 (OH),[7] 2-methylindazolinone (**3**),[6] 3-methoxyindazole (**4**),[7] δ_H 11.90 (NH), 1-methyl-3-methoxyindazole (**5**),[5] 1,2-dimethylindazolinone (**6**),[5] 1-ethoxycarbonylindazolinone (**7**),[6] benzoylhydrazine (**11**),[8] and β-acetylphenylhydrazine (**12**)[9] were prepared according to literature procedures.

1-*Acetyl*-3-*methoxyindazole* (**8**).—3-Methoxyindazole (**4**) (0.88 g, 0.006 mol) was heated under reflux for 1 h with acetic anhydride (1 ml). The excess of acylating agent was removed under vacuum and the *residue* (**8**) was analytically pure, m.p. 85—86 °C, yield 95%, δ_H ($CDCl_3$) 2.60 (s, 3 H), 4.10 (s, 3 H), 7.10—7.75 (m, 3 H), and 8.35 (m, 1 H) (Found: C, 62.9; H, 5.5; N, 14.5. $C_{10}H_{10}N_2O_2$ requires C, 63.2; H, 5.3; N, 14.7%).

Bromination of Indazolinone (**1**).—Indazolinone (2 g, 0.015 mol) was dissolved in glacial acetic acid (100 ml) and bromine (3.2 g, 0.02 mol) in acetic acid (20 ml) was added dropwise. After 1 h of heating under reflux the mixture was neutralized with a saturated solution of potassium carbonate and a green solid (2.4 g) precipitated. This was a mixture of two compounds which were separated by column chromatography on silica gel (Merck 60; 70—230 mesh ASTM), using chloroform–ethanol (7:3) as eluant. The first eluted product was 5,7-*dibromo*-3-*hydroxy*-



(**1**) $R^1 = R^3 = H$
(**2**) $R^1 = Me$, $R^3 = H$
(**3**) $R^2 = Me$, $R^1 = H$
(**4**) $R^3 = Me$, $R^1 = H$
(**5**) $R^1 = R^3 = Me$
(**6**) $R^1 = R^2 = Me$
(**7**) $R^1 = CO_2Et$, $R^2 = H$
(**8**) $R^1 = COMe$, $R^3 = Me$
(**9**) $R^3 = H$: 5-Br
(**10**) $R^3 = H$: 5,7-Br_2

R^1NHNHR^2

(**11**) $R^1 = COPh$, $R^2 = H$
(**12**) $R^1 = COMe$, $R^2 = Ph$

indazole (**10**), m.p. 235—237 °C (decomp.), yield, 10%, *m/z* 291, 293, and 295, δ_H ([$^2H_6$]DMSO) 12.24 (NH), 10.94 (OH), 7.84 (d, H-4), and 7.71 (d, H-6, $J_{4,6}$ 1.4 Hz) (Found: C, 28.8; H, 1.5; N, 9.4. $C_7H_4Br_2N_2O$ requires C, 28.8, H, 1.4; N, 9.6%). The second product was *5-bromo-3-hydroxyindazole* (**9**), m.p. 269—272 °C, yield 32% *m/z* 212 and 214, δ_H ([$^2H_6$]DMSO) 11.75 (NH), 10.67 (OH), 7.80 (d, H-4), 7.39 (q, H-6, $J_{4,6}$ 1.4 Hz), and 7.28 (d, H-7, $J_{6,7}$ 8.8 Hz) (Found: C, 39.3; H, 2.1; N, 13.3. $C_7H_5BrN_2O$ requires C, 39.5; H, 2.4; N, 13.2%).

^{13}C N.m.r. spectra in solution were recorded at 50.32 MHz using a Bruker AM-200 spectrometer (Marseille). Samples were dissolved in [$^2H_6$]DMSO or $CDCl_3$, the deuterium signal providing field–frequency lock; the concentration was 20—30% (w/v). Chemical shifts are expressed in p.p.m. from tetramethylsilane. Typical conditions were as follows: pulse width, 8 μs (*ca.* 60°); repetition time, 2 s; spectral width, 12 kHz; data points, 16 384.

^{15}N N.m.r. spectra were recorded at 20.28 MHz using the same spectrometer with nitromethane as external standard. No corrections for bulk differences were applied. The ^{15}N spectra of (**2**), (**4**) (for N-1), (**5**), (**6**), and (**9**)—(**11**) were obtained using the INEPT pulse sequence.[10] The width of a nitrogen 90° pulse was 26 μs and the width of a proton 90° pulse was 28 μs. The delay time τ between the pulses was set at 0.003 and 0.125 ms which correspond to $J_{NH}/4$ values[11] for, respectively, direct and long-range NH couplings. Traces of $Cr(acac)_3$ were added to compounds (**1**), (**3**), (**4**) (for N-2), and (**8**) to shorten the relaxation times T_1. In this case a typical delay between pulses was 5 s and the pulse angle, *ca.* 70°, 20 μs.

^{13}C Cross-polarization magic angle spinning (CP/MAS) n.m.r. spectra were obtained at 50.31 MHz on a Bruker CXP-200 spectrometer (Grénoble) using 3.2—3.5 kHz MAS. Chemical shifts were measured with regard to linear polyethylene mixed with the samples and reported to the tetramethylsilane signal using the relationship $\delta_{Me4Si} = \delta_{obs} + 33.6$.[12] In the case of indazolinone itself (**1**), as the spectra were not well resolved, another experiment was carried out at 100.63 MHz and the chemical shifts thus determined are used subsequently.*

Crystal Structure Determination.—Crystals of indazolinone were obtained by leaving a saturated solution in dimethylsulphoxide to stand at room temperature (the product being insoluble in water). Crystal data are given in Table 1. A sample, 0.50 × 0.17 × 0.07 mm, was put into a Lindemann capillary and used to collect the data on a Philips PW 1000 diffractometer, with graphite-monochromated radiation, bisecting geometry, and 1.5° scan width in the ω/2θ mode. Two reflections were monitored every 90 min, showing no significant variation in the crystal nor in the experimental conditions. Unit-cell parameters were refined by least-squares from the 2θ values of 48 reflections up to 45° in θ. The structure was solved by direct methods and refined by least-squares based on F_{obs} only.[13–15] All hydrogen atoms were unambiguously obtained in a difference synthesis and included isotropically in the final cycles of refinement, where two strong low-angle reflections were excluded as they suffered from extinction. Weights were chosen so as to give no trends in $<\omega\Delta^2F>$ *versus* $<|F_{obs}|>$ and $<\sin\theta/\lambda>$, by the use of functions of the $\omega = K/[f(F_{obs})]\cdot[g(\sin\theta/\lambda)]$ type, K being a scale factor to ensure that $<\omega\Delta^2F> \sim 1$. The final shift over error was 0.02 for 115 variables, with a maximum thermal factor of 0.072 (2) Å^2 for U_{33} (C6). The highest final residual electron density was 0.18 e Å^{-3}. Final atomic co-ordinates are given in Table 2.

* The spectra were recorded on a Bruker MSL-400 spectrometer by Drs. D. Müller and G. Hermann (Bruker Analytische Messteknik GmbH, Karlsruhe) to whom we are greatly indebted: spinning rate, 4.1 kHz; spectral width, 31.25 kHz.

Results and Discussion

Crystal and Molecular Structure of Indazolinone (**1**).—The molecules in the crystal pack in a network of hydrogen bonds, as shown in the Figure and, in greater detail, in the Scheme. They are of two types, one forming 'classical' dimers [N(2)(i)–O(9)-(ii)] around the symmetry centres at (0,0,0), (1/2,1/2,1/2), and equivalents. These dimers pack in a infinite helix (hydrogen bond between O(9)(i)–N(1)(iii) around the two-fold screw axis at (1/4, *y*, 1/4), the least-squares planes between two-consecutive dimers, symmetry-related by the axis, as shown in the Figure, forming an angle of 58.4(1)°. The six-membered ring [formed by N(2)C(3)O(9) and their symmetry atoms] around the symmetry centres has a slightly puckered chair conformation, with a maximum deviation of 0.034(2) Å from the least-squares plane which is at 5.1(1)° from the corresponding one through the nine atoms of the fused system, excluding O(9).

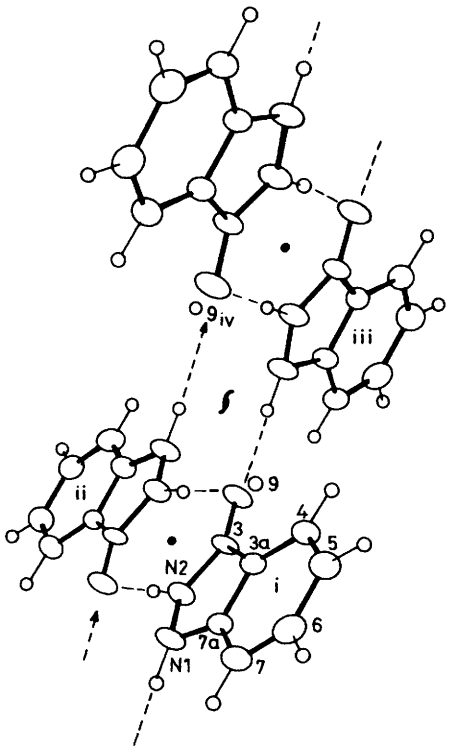
The benzene ring is planar, with the same bond length and angle ranges (see Table 3) as in the structure of 2-acetylindazolinone,[17] with the lowest values at C(6)–C(7) and at C(6)–C(7)–C(7a) and C(5)–C(4)–C(3a). The five-membered ring is not planar but slightly puckered with an envelope flapping at N(1). The angles around this atom add up to 353(3)°, while in the acetyl derivative the situation is more tetrahedral, the angles adding to just 330(2)°. The shortening in N(1)–C(7a), N(1)–N(2) and N(2)–C(3) with respect to the acetyl derivative may involve some degree of delocalization from the benzene

Table 1. Crystal analysis parameters at room temperature

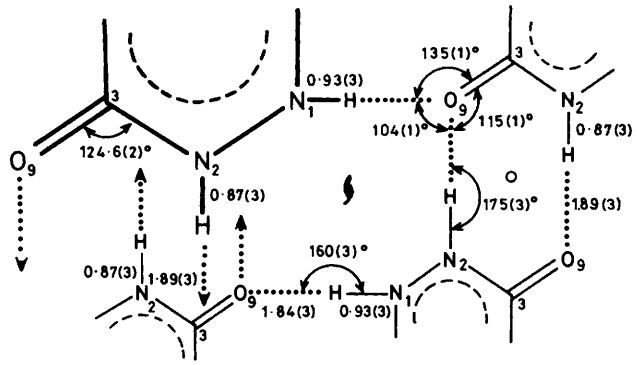
Formula	$C_7H_6N_2O$
System	Monoclinic
Space group	$P2_1/n$
Unit-cell dimensions	11.091 1(6), 6.847 4(3), 8.597 5(4) Å 107.514(4)°
U (Å^3)	622.67(5)
Z	4
D (g cm^{-3})	1.815
F (000)	352
$\theta_{max.}$ (°)	65° (Cu-K_α)
Total independent data	1 051
Observed data	774, $I > 3\sigma(I)$
Final R, R_w	0.042, 0.040

Table 2. Final atomic co-ordinates

Atom	*x*	*y*	*z*
N(1)	−0.194 4(2)	0.333 9(3)	−0.084 9(2)
N(2)	−0.107 4(2)	0.186 9(3)	−0.023 3(2)
C(3)	−0.024 0(2)	0.237 8(3)	0.118 4(3)
C(3a)	−0.065 3(2)	0.427 3(3)	0.158 2(2)
C(4)	−0.019 5(2)	0.550 2(4)	0.292 5(3)
C(5)	−0.085 4(2)	0.720 9(4)	0.295 1(3)
C(6)	−0.193 5(2)	0.767 3(4)	0.166 5(3)
C(7)	−0.239 3(2)	0.648 7(4)	0.034 0(3)
C(7a)	−0.171 9(2)	0.474 9(3)	0.032 1(3)
O(9)	0.070 3(1)	0.136 0(2)	0.194 6(3)
H(1)	−0.274(3)	0.312(4)	−0.159(3)
H(2)	−0.098(3)	0.090(5)	−0.083(4)
H(4)	0.054(3)	0.517(4)	0.387(4)
H(5)	−0.057(3)	0.812(5)	0.387(4)
H(6)	−0.238(3)	0.894(5)	0.167(4)
H(7)	−0.312(3)	0.679(5)	−0.053(4)



An ORTEP[16] view showing the helical packing of the dimers, together with the numbering system and the symmetry operations involved: i = x,y,z; ii = $-x,-y,-z$; iii = $1/2 + x,1/2 - y,1/2 + z$; and iv = $1/2 - x, -1/2 + y,1/2 - z$. The arrowed bond H(1;ii) ····· O(9) indicates its connection with the iv-(010) molecule, below the one depicted



Scheme.

ring and from the ketone bond, which is also lengthened by the presence of a hydrogen bond.

The precise location of the hydrogen atoms bonded to heteroatoms, even more the 'ketone' length of the C(3)–O(9) bond, prove conclusively that the tautomer present in the crystal is indazolinone (**1a**). In addition, the strong hydrogen bonds explain the difficulty in interpreting the i.r. spectra of indazolinones in the solid state.[18]

Carbon-13 Chemical Shifts of Indazolinones in the Solid State (CP/MAS) and in DMSO Solution.—The assignment of chemical shifts (Table 4) was based on those of indazole[19] and its *N*-methyl derivatives.[20] The chemical shifts of C(3a) and C(7a) of hydrazides (**11**) and (**12**) are consistent with those of

Table 3. Bond lengths (Å) and angles (°)

N(1)–N(2)	1.384(3)	N(1)–C(7a)	1.362(3)
N(2)–C(3)	1.335(3)	C(3)–C(3a)	1.451(3)
C(3)–O(9)	1.264(2)	C(3a)–C(4)	1.395(3)
C(3a)–C(7a)	1.381(3)	C(4)–C(5)	1.382(4)
C(5)–C(6)	1.401(3)	C(6)–C(7)	1.366(4)
C(7)–C(7a)	1.408(4)	N(1)–N(2)–C(3)	111.8(2)
N(2)–N(1)–C(7a)	106.3(2)	C(2)–C(3)–C(3a)	105.5(2)
C(2)–C(3)–O(9)	124.6(2)	C(3)–C(3a)–C(7a)	106.4(2)
C(3a)–C(3)–O(9)	129.9(2)	C(4)–C(3a)–C(7a)	121.3(2)
C(3)–C(3a)–C(4)	132.3(2)	C(4)–C(5)–C(6)	120.7(3)
C(3a)–C(4)–C(5)	114.4(2)	C(6)–C(7)–C(7a)	116.5(2)
C(5)–C(6)–C(7)	122.6(3)	N(1)–C(7a)–C(7)	128.9(2)
C(3a)–C(7a)–C(7)	121.5(2)	C(7a)–N(1)–H(1)	123(2)
N(1)–C(7a)–C(3a)	109.6(2)	N(2)–N(1)–H(1)	124(2)
N(1)–N(2)–H(2)	122(2)		
C(3)–N(2)–H(2)	124(2)		

indazolinones, with the exception of the strongly deshielded C(3a) in benzoylhydrazine (**11**). This deshielding (*ca.* 14 p.p.m.), which can be observed for C(7) [from δ 112.0 in (**6**) to 128.3 p.p.m. in (**11**)], corresponds to the breaking of the N(1)–C(7a) bond and is of the same order as the *ortho* effect of the NH_2 group in aromatic compounds (13 p.p.m.). The most difficult problem was the assignment of the two signals near δ 120 p.p.m. to C(4) and C(5). For this purpose we carried out the bromination of indazolinone (**1**). A study of the brominated derivatives (**9**) and (**10**) allowed us to solve this problem. Habraken *et al.*[21] described similar substituent chemical shifts in 5-bromo- and 5,7-dibromo-2-phenylindazoles. The assignment of carbon atoms C(4) and C(5) in compounds (**2**), (**5**), (**7**), and (**8**) was made by analogy with (**1**). In the case of compounds (**3**) and (**6**), the assignment is only tentative.

The most remarkable feature in Table 4 is the similarity between the chemical shifts in the solid state and those in DMSO solution. However, that does not necessarily imply that the tautomeric structure is the same. The most sensitive carbons to oxo ⇌ hydroxy tautomerism are C(6) (oxo, δ 131—132 p.p.m.; hydroxy, δ 127—129 p.p.m.) and, above all, C(4) (oxo, δ 123—124 p.p.m.; hydroxy, δ 119—122 p.p.m.). It is worthy of note that the heterocyclic C(3), C(3a), and C(7a) are totally useless in the study of the tautomerism of indazolinones. As we know from the *X*-ray structure, indazolinone (**1**) exists in the solid state as such [(**1a**)] and thus the chemical shifts obtained from the CP/MAS spectra are representative of this tautomer. From these values it can be deduced that 2-methylindazolinone (**3**) also exists in the oxo form (**3a**), whereas 1-methylindazolinone (**2**) is the 3-hydroxy tautomer (**2b**) both in solution and in the solid state. Model compounds (**4**)—(**6**) agree with these conclusions. The 1-ethoxycarbonyl group in (**7**) introduces perturbations that preclude the use of carbon-13 chemical shifts to determine its tautomeric structure.

Some signals are split in the ^{13}C-CP/MAS n.m.r. spectra: C(7a) in (**3**) and (**12**) and the methyl groups of the ethyl ester in (**7**). For carbons, and C(7a), directly bound to a nitrogen atom the most reasonable explanation is the quadrupole moment of ^{14}N.[22] The behaviour of (**7**) in the solid state could correspond to a mixture of two conformations of the 1-ethoxycarbonyl group.

Even if we have been unable to prepare the still unknown 2-methyl-3-methoxyindazole [from (**8**) and methyl fluorosulphonate],[23] the indazole annular tautomerism (**1b**) ⇌ (**1c**) in DMSO solution can be determined from the study of indazole itself.[20] In particular, C(7a) in compound (**1**) appears at δ 143 p.p.m. (Table 4), whereas in 2-methylindazole it appears at δ 148 p.p.m.[20] By comparing the chemical shifts of (**1**) in DMSO with

Table 4. Carbon-13 chemical shifts of indazolinones and related compounds

Compound	Solvent		C(3)	C(4)	C(5)	C(6)	C(7)	C(3a)	C(7a)	Substituents
(1)	[$^2H_6$]DMSO		156.8	120.5	118.9	127.6	110.5	113.0	143.0	—
	None		160.8	123.8	120.3	131.3	111.4	114.0	144.3	—
(2)	[$^2H_6$]DMSO		154.7	120.3	118.7	127.3	109.4	112.8	142.2	NCH_3(1):35.0
	None		155.8	121.7	118.1	127.3	109.3	112.1	140.2	NCH_3(1):34.1
(3)	[$^2H_6$]DMSO		160.7	122.8	120.8	131.1	112.0	117.5	145.9	NCH_3(2):30.3
	None		158.5	124.1	121.6	131.4	110.1	116.5	144.8[b]	NCH_3(2):30.4
(4)	[$^2H_6$]DMSO		156.5	119.1	119.0	127.0	110.1	111.2	142.1	OCH_3(3):55.8
	None		158.6	121.0	121.0	128.6	109.6	112.4	143.0	OCH_3(3):55.2
(5)[a]	[$^2H_6$]DMSO		155.2	119.2	118.8	127.0	109.1	111.4	141.7	NCH_3(1):34.8; OCH_3(3):55.8
(6)	[$^2H_6$]DMSO		161.7	122.8	121.7	131.8	112.0	117.8	150.0	NCH_3(1):36.9; NCH_3(2):28.4
	None		161.4	123.7	119.5	132.2	115.0	117.5	153.2	NCH_3(1):38.1; NCH_3(2):28.3
(7)	[$^2H_6$]DMSO		158.6	123.3	120.4	129.9	114.1	117.3	140.4	CO:150.0; CH_2:62.8; CH_3:14.1
	None		159.8	122.2	120.4	130.6	113.3	117.3	139.8	CO:150.0; CH_2:65.8; CH_3:12.9[c]
(8)	$CDCl_3$		159.8	124.0	119.6	130.2	115.9	117.6	140.6	CO:170.3; CH_3:22.9; OCH_3(3):56.4
(9)	[$^2H_6$]DMSO		154.5	122.0	110.2	129.3	112.0	113.7	140.5	—
(10)	[$^2H_6$]DMSO		154.9	121.7	109.8	130.9	103.7	114.8	139.4	—
(11)	[$^2H_6$]DMSO		166.0	131.0	128.3	127.0	128.3	133.4	131.0	—
12)[d]	[$^2H_6$]DMSO	*E*	n.o.	129.0	118.9	129.0	111.7	111.7	148.8	CH_3:19.2
		Z	169.0	128.6	118.4	128.6	112.2	112.2	149.4	CH_3:20.6
	None	*Z*	n.o.	131.0	120.3	131.0	115.4	109.8	150.9[e]	CH_3:18.5

[a] An oil. [b] Two signals at δ 144.6 and 145.0 p.p.m. [c] Two signals at δ 12.2 and 13.6 p.p.m. [d] 85% Of *Z* conformation in [$^2H_6$]DMSO. [e] Two signals at δ 150.3 and 151.5 p.p.m.

those of (**3**) and (**4**) it can be deduced that tautomer (**1b**) predominates.

Nitrogen-15 Chemical Shifts of Indazolinones in DMSO Solution.—Nitrogen-15 chemical shifts are far superior to carbon-13 ones for tautomeric studies.[1,2] Nevertheless, there is only one reference to its use for the study of pyrazolone tautomerism.[24] Amongst the compounds of Table 5 only two have been described, benzoylhydrazine (**11**)[8] [N(1), δ 324.6 (^1J 68 Hz) and N(2), 251.4 p.p.m. (^1J 101 Hz)] and β-acetylphenylhydrazine (**12**).[25] As some anomalies were found in the chemical shifts of the most abundant conformer (85% *Z*, the only one observable at natural abundance), doubly labelled β-acetylphenylhydrazine was studied (INEPT) confirming the values in Table 5. In addition, the chemical shifts of the less abundant conformer (15% *E*) were N(1), δ −286.8 and N(2) −243.8 p.p.m.* The acylhydrazines (**11**) and (**12**) and antipyrine [N(1) (Me), δ −244.5; N(2) (Ph) −197.0 p.p.m.][26] confirm the assignment of nitrogen atoms in Table 5.

With regard to indazole and 1-methylindazole[27] the introduction of a hydroxy or a methoxy group in position 3 produces upfield shifts in both nitrogen signals, δ −53.8 [N(2)] and −33.9 p.p.m. [N(1)] [from (**2**), OH effects]; δ −47.4 [N(2)] and −29.5 p.p.m. [N(1)] [from (**4**), OMe effects]; δ −47.4 [N(2)] and −29.0 p.p.m. [N(1)] [from (**5**), OMe effects]. The fact that the substituent chemical shifts of the hydroxy group are somewhat larger probably indicates a small amount of the oxo tautomer. The remarkable agreement of the methoxy substituent chemical shifts proves that compound (**4**) is an N(1)H tautomer.

Considering the *N*-methyl effects on the nitrogen chemical shifts [pairs (**3**), (**6**) and (**4**), (**5**)] it is possible to have a rough estimation for tautomers (**1a**) {δ −267.5 [N(1)] and −225.5 p.p.m. [N(2)]} and (**1b**) {δ −228.5 [N(1)] and −120.0 p.p.m. [N(2)]}.

From the experimental values of compound (**1**) (Table 5), an interpolation gives 85% of OH tautomer (**1b**) and 15% of NH tautomer (**1a**). Compounds (**2**) and (**7**) both exist predominantly as the 3-hydroxyindazole tautomer.

Table 5. Nitrogen-15 chemical shifts (p.p.m.) of indazolinones and related compounds in [$^2H_6$]DMSO

Compound	N(1)	N(2)	Coupling constants
(**1**)	−233.6[a]	−136.1[a]	
(**2**)	−236.7[b]	−110.4[b]	
(**3**)	−269.0[a]	−216.4[a]	
(**4**)	−223.9[b]	−113.0[a]	$^1J(N_1H)$ 107.1 Hz
(**5**)	−231.8[b]	−104.0[b]	
(**6**)	−259.8[b]	−217.5[b]	
(**7**)	−210.3[a]	−125.7[a]	
(**11**)	−324.5[b]	−251.8[a]	$^1J(N_1H)$ 100.4 Hz
(**12**)	−291.6[b]	−245.3[b]	$^1J(N_1H)$ 90.8 Hz; $^1J(N_2H)$ 101.7 Hz

[a] In the presence of $Cr(acac)_3$. [b] INEPT sequence.

Conclusions.—It is now possible to summarize the tautomerism of indazolinones in the solid state and in DMSO solution:†

Compound	Solid state	DMSO solution
(**1**)	(**1a**) *X*-ray	85% (**1b**) + 15% (**1a**) ^{15}N
(**2**)	(**2b**) ^{13}C	≥90% (**2b**) ^{13}C, ^{15}N
(**3**)	(**3a**) ^{13}C	≥95% (**3a**) ^{13}C, ^{15}N
(**4**)	(**4b**)[a] ^{13}C	≥95% (**4b**)[a] ^{13}C, ^{15}N
(**7**)	(**7b**)[b,c] ^{13}C	Mostly (**7b**)[b] ^{15}N

[a] N(1)H tautomer. [b] 3-Hydroxy tautomer. [c] Tentative.

The ^{13}C n.m.r. spectra of 1-ethoxycarbonylindazolinone is very similar in the solid state and in DMSO solution (Table 1). As we have concluded from the ^{15}N study [N(2) at δ −125.7 p.p.m.] that tautomer (**7b**) predominates, the same structure has been tentatively assigned to the solid.

* If a 346 p.p.m. correction ($^{15}NH_4Cl$ *versus* nitromethane) is applied to the published data,[25] the chemical shifts for N(2) are correct (*Z*, δ −244.9; *E* −244.3 p.p.m.) but those of N(1) are erroneous by −36.5 p.p.m. (*Z*, δ −255.0; *E* −250.3 p.p.m.).

† A recent publication[28] on the tautomeric equilibria of some 3-hydroxyindazole derivatives by ^{15}N n.m.r. spectroscopy came to similar conclusions. In DMSO there is 75 ± 3% of (**1b**) and 94 ± 3% of (**2b**).

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