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The reaction of **1** with hydrazines provided hydrazinium-4,7-dioxo-4,7-dihydroindazol-3-olates **2a-e** and 4,7-indazolequinones **3f,g** depending upon the nature of the substituent present in the reactants. Compounds **3a-g** were obtained by treatment of **2a-e** with sodium hydroxide. Fixed tautomers **4a-b** and **5c-f** were synthesized by methylation of the corresponding **3a-f** or **2a-2e** with diazomethane. Migration of a methyl group of **5c-f** from the oxygen at C_3 to N_1 on heating afforded **6c-f**. The tautomerism of **2a-e** and **3a-g** has been studied by comparing ir, uv, ^1H nmr and ^{13}C nmr spectra with those of the fixed tautomers.

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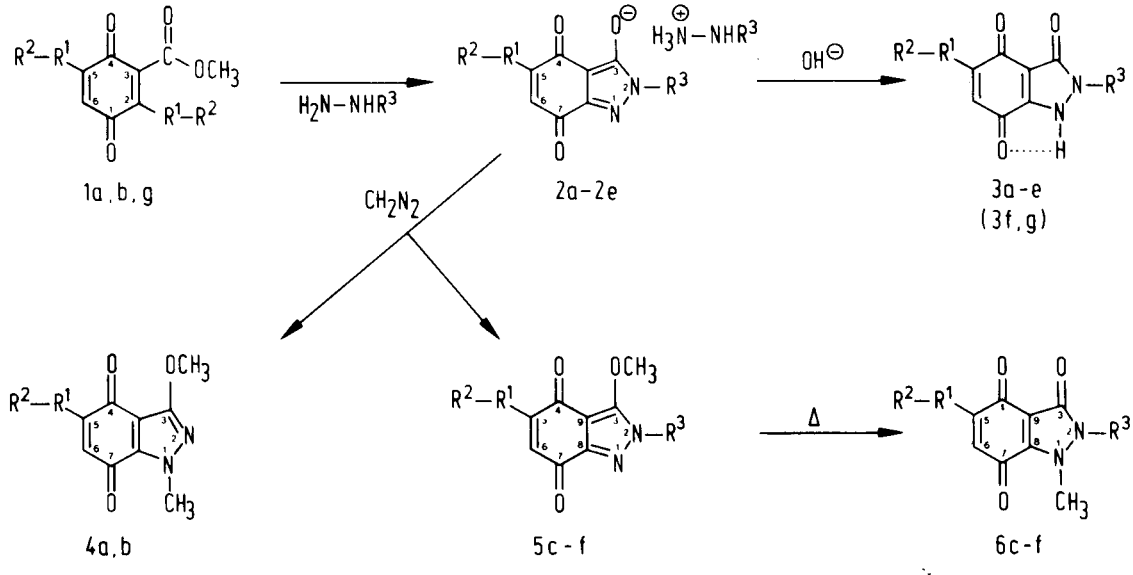
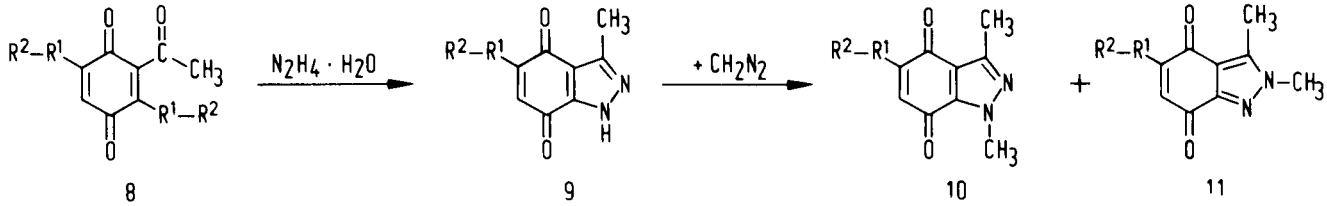
Synthesis [1,2] and tautomerism [3,4] of indazolones ⇌ hydroxyindazoles has attracted considerable interest in recent years because these heterocyclic systems are widely used in dyestuff and pharmaceutical research. Here we describe a simple, novel and convenient method for the preparation of substituted 4,7-indazolequinones in high

SCHEME I



R^2/R^3	H/H	Br/H	H/CH_3	Br/CH_3	H/C_6H_5	Br/C_6H_5	NO_2/H
	2a	2b	2c	2d	2e	–	–
	3a	3b	3c	3d	3e	3f	3g
	4a	4b	5c	5d	5e	5f	–
			6c	6d	6e	6f	–

R^1 = $-NH-C_6H_4-P-$, 7b = 4b, but H instead of CH_3 on N-1



yields [3]. Tautomerism in these heterocyclic quinones has been examined using spectroscopic techniques.

Compounds **1** were obtained by oxidative amination of 2-carbomethoxy-1,4-hydroquinone with arylamines in presence of sodium iodate [5]. The reaction of **1** with hydrazines (Scheme I) provided hydrazinium-4,7-dioxo-4,7-dihydroindazol-3-olates **2**. These hydrazinium salts **2** on treatment with sodium hydroxide afforded the corresponding 4,7-indazolequinones **3**. Only **3f** and **3g** were obtained by direct reaction of **1** with hydrazines. The reaction starts with a nucleophilic attack of the amino group of hydrazine on the C-2 atom of **1** followed by the cyclization with the elimination of methanol. The hydrazine present in the reaction mixture combines with the indazolequinone to give the hydrazinium salt **2**. The fixed tautomers **4a-b** and **5c-f** were obtained by alkylation of the corresponding **2a-e** or **3a-f** with an excess of diazomethane using different solvents. Methylation with diazomethane is predominating over the oxygen atom. However, adding equimolar amount of diazomethane in ether slowly to a suspension of **2b** in tetrahydrofuran leads mainly to **7b** (methylation at the oxygen) whereas **4b** was only a byproduct.

All attempts to alkylate **3a-e** and their salts **2a-e** with methyl iodide/potassium carbonate, or potassium hydroxide or sodium methoxide were unsuccessful. The other possible fixed tautomers **6c-f** were not obtained by direct methylation of **3c-f**. But when **5c-f** were heated in a high boiling solvent or alone, they rearrange to **6c-f** in good yields. Migration of the methyl group from oxygen to nitrogen is favoured in the solid state and was found to be hindered by the presence of a bulky group at N-2. Such thermal rearrangements of a methyl group are also reported for other heterocycles and for 3-methoxy-4,7-dioxo-4,7-dihydroisoxazoles [6]. With the latter the transformation of the methyl group from oxygen to nitrogen in these quinones was proved to be an intermolecular rearrangement [6]. Taking into account the close similarity in the structure of indazolequinones and isoxazolequinones, this rearrangement of the methyl group appears to proceed intermolecularly in both cases. The driving force for the OMe → NMe rearrangement is certainly the greater stabi-

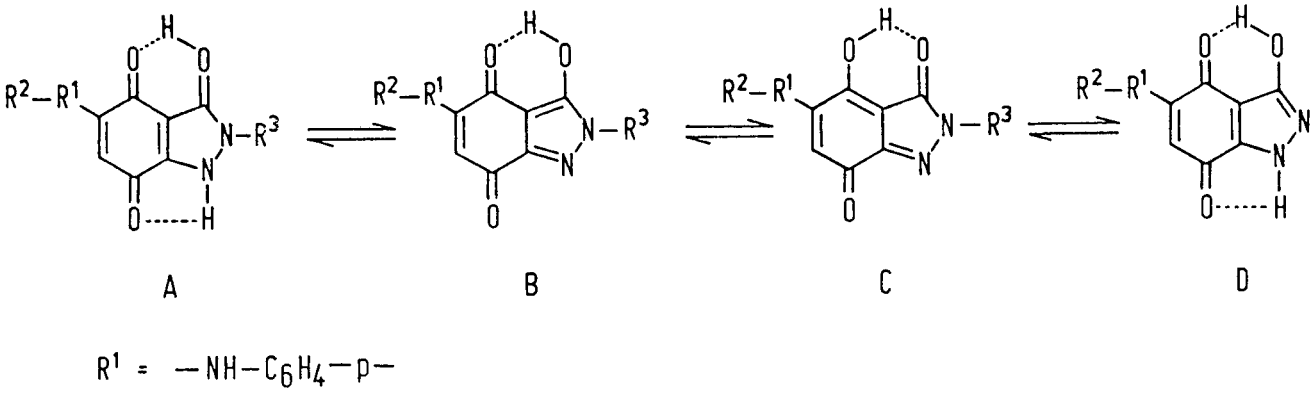
Table 1

UV and IR-Data of 4,7-Indazolequinone

		UV-Data						IR-Data (Potassium Bromide, cm^{-1})		
	Solvent	λ max		log ε				C=O	C=N/C=C	NH/OH
3a	[a]	444.5	(4.08)	297	(3.92)	251	(4.21)	1660, 1618		3285, 3190
3b	[b]	466	(3.81)	356	(3.77)	261	(4.29)	1650, 1617	1590	3564, 3430, 3200
3c	[a]	429	(4.09)	309	(3.99)	246	(4.26)	1670	1600	3318, 3200
3d	[a]	432	(3.95)	308	(3.87)	257	(4.22)		1610, 1592	3275
3e	[a]	440	(4.00)	325	(3.99)	258	(4.47)	1660		3140
3f	[b]	438	(3.85)	322.5	(4.05)	269.5	(4.51)	1670	1588, 1580	3260, 3240
3g	[c]	439	(3.92)	360.5	(4.04)	259	(4.13)	1679, 1634	1606	3320, 3260, 3060
5c	[b]	444	(3.71)	[332	(3.79)]	263	(4.40)	1665, 1629	1600	3320
5d	[a]	445	(3.91)	[327	(3.92)]	265	(4.50)	1660, 1627	1590, 1574	3305
5e	[b]	446	(3.72)	280	(4.46)	[260	(4.39)]	1670, 1627	1604, 1578	3305
5f	[a]	452	(3.86)	[316	(4.02)]	276	(4.51)	1670, 1632	1593, 1580	3300
6c	[a]	[519	(3.47)]	400	(4.11)	247	(4.25)	1700, 1637, 1618	1600, 1588	3264
6d	[a]	[520	(3.61)]	403	(4.26)	254	(4.46)	1690, 1635, 1612	1583	3255
6e	[a]	[510	(3.79)]	399.5	(4.41)	252.5	(4.81)	1700, 1641	1610	3310
6f	[b]	[519	(3.62)]	413	(4.65)	251.5	(4.82)	1715, 1640	1609	3200
4a	[a]	481.5	(3.72)	359	(3.89)	246	(4.26)	1675, 1612	1590	3230
4b	[b]	470	(3.76)	358	(3.94)	259	(4.29)	1672, 1625	1592	3280
7b	[b]	473	(3.71)	[353	(3.76)]	262	(4.21)	1671, 1623	1580	3280, 3160
9		458	(3.67)	314	(3.86)	261	(4.29)	1661, 1635		3318, 3170-2860
10								1668, 1620		3260, 3059-2920
11	[a]	461	(4.67)	310	(4.86)	264	(4.35)	1660, 1635		
2a	[a]	417	(4.07)	294	(3.94)	251	(4.27)	1655	1598	3250
2b	[a]	418	(4.02)	297	(3.88)	258	(4.21)	1670	1590	
2c	[a]	426	(4.09)	309.5	(4.01)	244	(4.27)	1657	1597	3264
2d	[a]	429.5	(4.09)	309	(4.00)	254	(4.27)	1650	1590	3322
2e	[a]	441	(4.19)	329	(4.14)	258	(4.68)	1658, 1635	1584	3318, 3220

[a] Ethanol. [b] Dioxane. [c] Dimethylsulfoxide. Numerical data for shoulders are surrounded by square brackets [ ].

SCHEME II



lity of the *para*-quinonic structure of the indazolequinone compared with the non *para*-quinonic form **5c-f**. Compound **9** was synthesized by the reaction of 2,5-bisarylamino-3-acetyl-1,4-benzoquinone (**8**) with hydrazine. Methylation of **9** with diazomethane predominates at 2-substitution of pyrazolone ring in comparison to N-1 substitution and yields **10** and **11**.

Tautomerism.

For 2-substituted 5-arylamino-4,7-indazolequinones **3c-f** the tautomeric forms **A, B** and **C** (R^3 = CH_3, C_6H_5) have to be discussed if one assumes that the proton of the arylamino group on C-5 is not involved. The unsubstituted quinones **3a, b** and **g** may contribute in addition to form **D**. From the fixed tautomers **5** stands for form **B** while compounds **6** represent **A**. Such tautomeric forms are energetically favourable and usually found in heterocycles [3].

UV-Spectra.

The uv data of the indazolequinones **3a-f** and their fixed tautomers **5c-f, 6c-f, 4a, b** and **7b** are listed in Table 1. Tautomer **A** is represented by a main absorption band of **6c-f** in the region 399-413 nm (log ϵ 4.2) with a characte-

Table 2

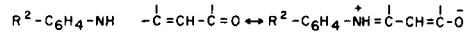
^{1}H NMR-Data of 4,7-Indazolequinones [a]

	Substituent on				Arylring				
	1-N	2-N	3-C	5-NH	H-2',H-6'	H-4'	H-3',H-5'	6 H	Solvent
3a	—	—	11.8 (br)	8.90 (s)	7.0		7.6 (m)	5.70 (s) [h]	[e]
3b	—	—	11.05 (s)	8.60 (s)	7.30 (d)	Jo = 8.8 Hz	7.56 (d)	5.69 (s) [h]	[e]
3c	—	3.28 (s)	—	8.50 (s)	7.0		7.6 (m)	5.66 (s) [h]	[e]
3d	—	3.31 (s)	—	8.66 (s)	7.32 (d)	Jo = 8.8 Hz	7.55 (d)	5.69 (s) [h]	[e]
3e	—	7.1-8.1 (m)	—	8.68 (s)	6.9-7.4 (m, 8H)		8.0-8.1 (m, 2H)	5.75 (s) [h]	[e]
3f	—	7.1-8.0 (m)	—	9.07 (s)	7.1		8.0 (m)	5.82 (s) [h]	[e]
3g	—	7.1-8.0 (m)	—	9.40 (s)	7.66 (d)	Jo = 8.8 Hz	8.26 (d)	6.14 (s) [h]	[e]
4a	4.07 (s)	—	4.09 (s)	7.78 (br)	7.1		7.5 (m)	5.99 (s)	[b]
4b	4.08 (s)	—	4.11 (s)	[g]	7.44 (d)	Jo = 8.5 Hz	7.58 (d)	6.10 (s)	[c]
5c	—	3.74 (s)	4.48 (s)	7.65 (br)	7.1		7.55 (m)	6.20 (s)	[b]
5d	—	3.74 (s)	4.48 (s)	7.60 (br)	7.12 (d)	Jo = 8.5 Hz	7.51 (d)	6.16 (s)	[b]
5e	—	7.2-7.8 (m)	4.48 (s)	7.7 (br)	7.2		7.8 (m)	6.27 (s)	[d]
5f	—	7.1-7.8 (m)	4.50 (s)	7.7 (br)	7.14 (d)	Jo = 9.0 Hz	7.53 (d)	6.24 (s)	[b]
6c	4.14 (s)	3.55 (s)	—	8.07 (s)	7.1		7.45 (m)	6.04 (s)	[b]
6d	4.07 (s)	3.42 (s)	—	9.47 (s)	7.32 (d)	Jo = 9.0 Hz	7.62 (d)	5.76 (s)	[e]
6e	3.86 (s)	7.24-7.7 (m)	—	8.14 (br)	7.24		7.7 (m)	6.10 (s)	[b]
6f	3.76 (s)	7.31-7.7 (m)	—	9.58 (s)	7.36 (d)	Jo = 8.8 Hz	7.65 (d)	5.86 (s)	[e]
7b	[g]	—	4.12 (s)	[g]	7.34 (d)	Jo = 9.0 Hz	7.54 (d)	5.73 (s)	[e]
9	13.8 (br)	—	2.53 (s)	9.05 (br)	7.6		7.98 (m)	5.81 (s)	[b]
10	4.04 (s)	—	2.43 (s)	[g]	7.26		7.77 (m)	5.70 (s)	[e]
11	—	3.86 (s)	2.59 (s)	9.02 (br)	7.11		7.55 (m)	5.80 (s)	[e]

[a] Data given in parts per million from TMS. [b] Deuteriochloforom. [c] Perdeuteriopyridine. [d] Deuteriochloroform + perdeuteriomethanol. [e] DMSO-d_6. [f] Signal exchangeable in deuterium oxide. [g] Signal not visible. [h] Partially exchangeable in deuterium oxide.

ristic long wave shoulder at 510-520 nm (log ε 3.6), whereas quinones **5c-f** (tautomer **B**) show two absorption bands in the area 280-332 nm (log ε 4.1) and 444-452 nm (log ε 3.8). Compounds **4a, b** and **7b**, representing tautomer **D** have two intensive absorption bands at 353-359.5 nm (log ε 3.9) and 473-481.5 (log ε 3.8).

Comparing the main absorption bands of **3a-g** with the above data we learn: a) 2-Substituted quinones **3c-f**, having absorption maxima in the region 309-325 nm (log ε 4.0) and 429-438 nm (log ε 4.0) are of type **B**. Small differences may be attributed to the necessity of measuring the spectra in different solvents. b) The spectrum of **3b** is, concerning the type and absorption maxima, very similar to that of compounds **4a, b** and **7b** (tautomer **D**). c) Compound **3a** with a long wave maximum of 414.5 nm is surely not of type **D**. One has also to keep in mind that the influence of the substituted arylamino group on C-5 on the carbonyl group on C-7 may be interpreted in terms of a merocyanine



and this effect again may influence the tautomerie of the indazole ring and the contribution of the hydrogen bridge in **3a-3b**.

IR-Spectra (Table 1).

The indazolequinones show strong NH-stretching vibration bands of the 5-arylamino group at 3240-3320 cm^{-1}. Compounds **3c-f** and the fixed tautomers **5c-f** (**B**-form) show strong bands in the region 1627-1675 cm^{-1} attributed to quinone carbonyls. Compounds **6c-f** (**A**-form), having a C=O group in the pyrazolone ring are characterized by a broad band at 1670-1715 cm^{-1} which is typical for five membered lactams. Because **3c-f** show no band in this region the tautomer **A** has to be excluded. The prevailing form for these compounds in the solid state seems to be **B**, because their ir spectra are mutually similar to those of the fixed **5c-f** (**B**-form) and this is in close agreement with studies on the tautomeries of indazolones and pyrazolones [3,7].

^{1}H NMR Spectra.

The ^{1}H nmr spectra data (Table 2) confirm, together with the uv and ir data, fully the structure of the fixed tautomers **4, 5, 6, 7b, 9, 10** and **11**. The H-6 protons of the compounds, measured in deuteriochloroform, apears at δ 6.04-6.70, whereas values at δ = 5.76-5.86 are found for substances, measured in DMSO-d_6. This is a solvent effect and does not indicate different tautomeric forms. It is of diagnostic value that, due to an anisotropic effect of the C-7 carbonyl group, 1-N methyl protons appear at lower field about 0.5 ppm compared to 2-N methyl protons. Compounds **3a** and **3b** showed a broad OH signal at 11.05-11.8, indicating a strong hydrogen bond to the C-4 carbonyl group. All assignment of the protons agrees with the data reported for other indazolones [2] but the data allow no decision between different tautomeric forms.

^{13}C-NMR Spectra.

The ^{13}C nmr spectral data are listed in Table 3. The assignments were established in the following way. The carbon atoms of the 5-arylamino ring appear in a definite position and are easily rationalized comparing with data from other arylaminoquinones. The quinonoid signal C-4 and C-7 in the region δ 171.5-179.8 occur at high field compared with the other C-signals of the heterocyclic system. The assignment of the other carbon atoms C-5 to C-9 has been

Table 3

^{13}C NMR-Data of 4,7-Indazolequinones [a]

No.	Solvent	1-N	Substituent on 2-N				C-3	C-3 subst	C-4	C-5	C-6	C-7	C-8	C-9	Aryl ring at C-5 C-1′	C-2′/C-6′	C-3′/C-5′	C-4′
			C-1′	C-2′/C-6′	C-3′/C-5′	C-4′												
3a	[b]	—	—	—	—	—	161.8	—	178.9	149.3	99.8 [f]	171.6	[e]	99.8 [f]	138.9	123.3	129.2	124.2
3b	[b]	—	—	—	—	—	158.1	—	177.4	148.1	101.1 [f]	174.8	142.9	100.1 [f]	137.8	125.7	132.1	117.3
3c	[b]	—	—	—	33.4	—	153.6	—	178.8	148.4	100.7	173.9	[e]	100.1	138.2	123.9 [f]	129.2	125.2 [h]
3d	[b]	—	—	—	33.4	—	153.7	—	179.0	147.9	101.4	173.7	144.5	101.1	137.8	125.6	132.1	117.0
3e	[b]	—	138.2	120.9	128.8 [g]	125.9 [f]	157.6	—	178.2	150.7	100.0	171.5	145.4	99.9	138.6	123.8 [h]	129.3 [g]	125.5 [h]
3f	[b]	—	137.9	126.9 [f]	128.7 [g]	120.6	158.7	—	179.0	149.5	101.0	171.3	145.4	99.7	139.0	125.0	132.0	116.9
3g	[b]	—	—	—	—	—	159.2	—	178.5	146.7	103.9 [f]	173.4	142.5	103.9 [f]	145.4	125.0	121.9	142.5
4a	[c]	38.1	—	—	—	—	160.5	56.3	177.0	149.0	100.3 [f]	175.5	142.4	100.5 [f]	139.0	124.6 [g]	129.9	126.2 [g]
5c	[d]	—	—	—	34.8	—	154.8	63.0	179.8	147.2	101.8	174.4	146.0	101.1	137.6	122.8	129.6	125.1
5d	[b]	—	—	—	34.6	—	154.2	62.2	178.6	117.2	101.7	174.2	145.1	101.5	137.6	125.6	132.1	117.2
5e	[b]	—	137.0 [f]	123.0 [g]	129.7 [h]	128.6	154.0	63.8	179.8	147.5	102.7	174.9	151.2	102.3	137.6	123.6 [g]	129.1 [h]	126.0
5f	[b]	—	136.7 [f]	123.0 [g]	129.0 [h]	128.6	154.7	63.6	179.6	146.9	103.0	174.5	[e]	102.2	136.9	124.9 [g]	132.9 [h]	118.7
6c	[b]	26.9	—	—	33.6	—	172.0	—	175.3	149.2	98.9	172.5 [g]	[e]	[e]	137.1	124.1 [f]	129.3	126.0 [f]
6d	[b]	27.1	—	—	33.2	—	171.8	—	175.3	149.3	99.1 [f]	172.7	141.0	99.8 [f]	137.0	125.8	132.0	117.8
6e	[b]	35.1	131.3 [f]	129.3 [g]	130.0 [f]	129.9 [g]	157.5	—	175.4	149.3	100.5	173.4	140.8	99.5	137.6	124.0 [h]	129.0 [f]	126.0 [h]
6f	[b]	35.2	131.3 [f]	128.9 [g]	129.9 [f]	129.5 [g]	157.3	—	175.5	148.8	100.5	172.7	141.2	99.7	137.1	126.0 [f]	132.0	118.0
7b	[b]	—	—	—	—	—	160.7	56.4	175.7	148.1	99.8 [f]	174.5	141.0	98.8 [f]	137.5	125.8	132.1	117.7

[a] In parts per million relative to TMS. [b] DMSO-d_6. [c] Perdeuteriopyridine. [d] Deuteriochloroform. [e] Signal not detectable. [f,g,h] Assignments may have to be reversed.

Table 4

Synthesis of Substituted 4,7-Indazolequinones **3a-f**

Compound	Mp °C dec	Yield %	Color	Molecular Formula	Calcd. % C	Calcd. % H	Calcd. % N	Found % C	Found % H	Found % N
3a	230	66	light brown	$C_{13}H_9N_3O_3$	61.17	3.55	16.46	61.01	3.66	16.31
3b	215	88	red	$C_{13}H_8BrN_3O_3$	46.73	2.41	12.58	46.82	2.64	12.49
3c	207	72	orange	$C_{14}H_{11}N_3O_3$	62.45	4.12	15.61	62.18	4.01	15.78
3d	232	43	red	$C_{14}H_{10}BrN_3O_3$	48.29	2.90	12.07	48.47	3.03	12.21
3e	350	26	light red	$C_{19}H_{13}N_3O_3$	68.88	3.95	12.68	68.59	3.62	12.82
3f	255	73	red	$C_{19}H_{11}BrN_3O_3$	55.63	2.95	10.24	55.80	3.16	10.28
3g	185	82	brown	$C_{13}H_8N_4O_5$	52.00	2.69	18.66	51.99	2.58	18.61

done by comparing their chemical shifts with those of the corresponding carbon atoms of reported indazole derivatives and their fixed tautomers [8-10]. The remaining signal was assigned to C-3 carbon atom.

The ^{13}C chemical shifts of all C-atoms except C-3 and C-8 are similar and cannot be used for discussion of tautomeric forms. In **5c-f** (**B**-form) chemical shifts for C-3 and C-8 are 154.0-154.8 and 145.1-151.2 respectively, **6c-f** (**A**-form) show the corresponding resonances at δ 157.3-172.0 and 140.8-141.2 and similar values are found for **4a** and **7b** (**D**-form). The spectra for **4b** could not be measured because of its low solubility. Chemical shifts for the N-2 substituted indazolequinones **3c-f** C-3/153.6-158.7 and C-8/-144.5-145.5 are similar to the values of **5c-f** (**B**-form), so the ^{13}C nmr measurements in dimethylsulfoxide support the assignment done by uv in ethanol and dioxane and by ir for the solid state. The predominating tautomer for the N-2 unsubstituted **3a,b,g** seems to be **D** because the chemical shifts C-3/158.1-161.8 and C-8/142.5-142.9 are nearly superimposable with the values of the fixed tautomer **4a**. This tautomeric form also seems to be energetically favourable because of the *para*-quinoid ring and furthermore this form may be stabilized by hydrogen bonding of the OH and NH-groups to the quinone carbonyls. However, the tautomeric form **A** cannot be totally ignored for **3a,b,g** because there is no appreciable difference in the position of C-3 and C-8 compared with **6c-f**.

EXPERIMENTAL

Melting points were determined in an open capillary tube apparatus and are uncorrected. The following spectroscopic apparatus were used: for ir spectra the spectrometer Model EM 250 from Perkin Elmer, for ^1H nmr spectra Varian HA 100 and Bruker WH 90 spectrometers, for ^{13}C nmr spectra the Bruker WH 90, operating at 22.63 MHz equipped with a Nicolet TT data system and a frequency synthesizer, for mass spectra the Varian CH 7A and 312 machines coupled with the data system Varian SS 200, for uv spectra the Gilford 240 spectrophotometer. Microanalyses were conducted by the Peptide Chemistry Division of Max-Planck-Institute of Biochemistry, Munich. All thin layer chromatographic separations were performed on Merck precoated silica gel F-254 plates with fluorescent backing. Data for ^1H nmr are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet, mc = multiplet center), integration, coupling constants and assignment. 5-Anilino-2,3-dimethyl-4,7-indazolequinone (**11**) was synthesized by the reported methods [11]. For all compounds except **2** structure proofing mass spectra will be published in detail elsewhere.

2,5-Bis-(4-bromoanilino)-3-carbomethoxy-1,4-benzoquinone (**1b**) and 2,5-Bis-(4-nitroanilino)-3-carbomethoxy-1,4-benzoquinone (**1g**).

To a stirred solution of 2,5-dihydroxybenzoic acid methyl ester (0.33 mole) in 2.1 ℓ of methanol and 4.1 ℓ of water was added *p*-bromoaniline (0.45 mole) and a hot solution of 120 g sodium iodate in 1.1 ℓ of water. After stirring overnight the precipitate was collected and dried and 34.8 g (48%) of **1b** was obtained as shining brown plates (methanol), mp 265° dec; ir (potassium bromide): 3240 (NH), 1730 (C=O), 1630 (C=O) cm^{-1}; uv (ethanol): λ max nm (log ϵ) 256 (4.32), 268 (4.24), 377 (4.29); ^1H nmr (DMSO-d_6): 3.08 (s, 3H, OCH_3), 5.87 (s, 1H, H_3), 9.6 (s, 1H, 2-NH, deuterium oxide exchangeable), 7.1-7.62 (m, 8H, 2 and 5 aryl H).

Anal. Calcd. for $C_{20}H_{14}Br_2N_2O_4$: C, 47.46; H, 2.79; N, 5.54. Found: C, 47.23; H, 2.73; N, 5.59.

By the same procedure **1g** was prepared and 37.8 g (58%) of red brown crystals (ethyl acetate) was obtained, mp 260° dec; ir (potassium bromide): 3265 (NH), 3240 (NH), 1713 (C=O), 1640 (C=O) cm^{-1}; uv (dioxane): λ max nm (log ϵ) 223.5 (4.41), 264.5 (4.18), 381 (4.49); ^1H nmr (DMSO-d_6): 3.12 (s, 3H, OCH_3), 6.28 (s, 1H, H_3), 9.77 (s, 1H, 5-NH, deuterium oxide exchangeable), 10.12 (s, 1H, 2-NH, deuterium oxide exchangeable), 7.4-8.28 (m, 8H, 2 and 5-aryl H).

Anal. Calcd. for $C_{20}H_{14}N_4O_8$: C, 54.80; H, 3.22; N, 12.78. Found: C, 54.52; H, 3.22; N, 12.61.

Hydrazinium-5-anilino-4,7-dioxo-4,7-dihydroindazol-3-olate (**2a**) and Hydrazinium-5-(4-bromoanilino)-4,7-dioxo-4,7-dihydroindazol-3-olate (**2b**).

A suspension of **1a** (2.78 g, 8.0 mmoles) of 50 ml of methanol was treated with 5 ml of hydrazine hydrate (99%) and stirred for 12 hours, the precipitate was collected and washed with 90% methanol and 2.76 g (96%) of **2a** as yellow crystals (water), mp 208° dec were obtained.

Anal. Calcd. for $C_{13}H_{13}N_5O_3$: C, 54.35; H, 4.56; N, 24.20. Found: C, 54.27; H, 4.49; N, 23.98.

Methylhydrazinium-5-anilino-2-methyl-4,7-dioxo-4,7-dihydro-2*H*-indazol-3-olate (**2c**).

A stirred suspension of 2,5-bis-anilino-3-carbomethoxy-1,4-benzoquinone **1a** (348 mg, 1 mmole) in 30 ml of methanol was treated with 1.5 ml of methylhydrazine (98%) at room temperature. It was warmed for 15 minutes in a boiling water bath, more 15 ml of methanol was added, and stirred at room temperature for 2 hours. The precipitate was collected by filtration, washed with methanol and dried to give 208 mg (66%) of **2c** as red crystals, mp 173° dec.

Anal. Calcd. for $C_{15}H_{17}N_5O_3$: C, 57.13; H, 5.43; N, 22.21. Found: C, 57.12; H, 5.41; N, 22.21.

Methylhydrazinium-5-(4-bromoanilino)-2-methyl-4,7-dioxo-4,7-dihydro-2*H*-indazol-3-olate (**2d**).

Five ml of methylhydrazine was added to a suspension of **1b** (4.0 g, 7.9 mmoles) in 50 ml of methanol at room temperature. After stirring overnight, the red precipitate was collected by filtration, washed with 80% methanol and dried over phosphorus pentoxide to give 0.72 g (59%) of **2d** as orange needles (methanol-ether), mp 153° dec.

Anal. Calcd. for $C_{15}H_{16}BrN_5O_3$: C, 45.70; H, 4.09; N, 17.77. Found: C, 45.42; H, 3.88; N, 17.94.

Phenylhydrazinium-5-anilino-2-phenyl-4,7-dioxo-4,7-dihydro-2*H*-indazol-3-olate (**21**).

Ten ml of phenylhydrazine was added to a suspension of **1a** (1.74 g, 5.0 mmoles) in 50 ml of methanol. The reaction mixture was stirred at room temperature for 1.5 hours, the orange-red precipitate was collected, washed with methanol and dried to yield 1.23 g (56%) of **2e** as orange needles (dimethylformamide-methanol), mp 198° dec.

Anal. Calcd. for $C_{22}H_{21}N_5O_3$: C, 68.32; H, 4.82; N, 15.94. Found: C, 68.53; H, 5.09; N, 15.92.

General Procedure for the Preparation of Substituted 4,7-Indazolequinones (**3a-e**) From **2a-e**.

The hydrazinium-4,7-dioxo-4,7-dihydro-2*H*-indazol-3-olate (12 mmoles) was dissolved in the appropriate volume of 1*N* sodium hydroxide and methanol and warmed on the water bath until only some substance was still undissolved. It was filtered and the filtrate was neutralized with 2*N* hydrochloric acid keeping the temperature below 20°. The product was isolated by filtration, washed with cold water and dried over phosphorus pentoxide. It was crystallized from methanol-ether to afford an analytically pure sample of the 4,7-indazolequinones **3a-e** (Table 4).

5-(4-Bromoanilino)-2-phenyl-4,7-indazolequinone (**3f**).

To a suspension of **1b** (4.05 g, 8 mmoles) in 50 ml of methanol was added dropwise 10 ml of phenylhydrazine and stirring was continued at room temperature overnight. The orange-red precipitate was collected, washed with methanol and dried. It was boiled in 50 ml acetone, the undissolved precipitate was collected by filtration and dried to give 2.40 g (73%) of **3f** as a dark red powder, mp 255° dec (Table 4).

5-(4-Nitroanilino)-4,7-indazolequinone (**3g**).

To an ice cold solution of **1c** (3.0 g, 6.8 mmoles) in 50 ml of methanol was added 5 ml of hydrazine hydrate and the mixture was stirred for 6 hours at room temperature. The light brown precipitate was collected and washed with methanol, it was purified by boiling it in ethyl acetate to give 1.68 g (82%) of **3g** (Table 4).

5-Anilino-3-methoxy-1-methyl-4,7-indazolequinone (**4a**) and 5-(4-Bromoanilino)-3-methoxy-1-methyl-4,7-indazolequinone (**4b**).

A suspension of 250 mg (0.87 mmole) of **2a** in 100 ml tetrahydrofuran was treated with 10 ml of an ether solution of diazomethane and stirred overnight at room temperature. Filtration gave starting material (150 mg). The filtrate was concentrated and column chromatographed (silica gel, 10% water deactivated) with chloroform-ethyl acetate (2:1) to afford firstly 70 mg (28%) of **4a** as dark red crystals, mp 218-219°.

Anal. Calcd. for $C_{15}H_{13}N_3O_3$: C, 63.59; H, 4.63; N, 14.84. Found: C, 63.78; H, 4.71; N, 14.48.

By the same procedure **2b** gave **4b** as light red crystals: yield 87%, mp 278° dec.

Anal. Calcd. for $C_{15}H_{12}BrN_3O_3$: C, 49.74; H, 3.34; N, 11.60. Found: C, 49.81; H, 3.28; N, 11.60.

Compound **4b** and 5-(4-Bromoanilino)-3-methoxy-1*H*-4,7-indazolequinone-3-one (**7b**).

To a stirred suspension of 300 mg (0.82 mmole) of **2b** in 300 ml of tetrahydrofuran was added 4 ml of ether solution of diazomethane (approximately equivalent amount of diazomethane in ether) over a period of 1 hour and stirring was continued for 8 hours. The mixture was filtered and the filtrate column chromatographed (silica gel, 10% deactivated) with chloroform-ethyl acetate (5:1) to give three fractions. The first portion yielded 89 mg (30%) of **4b** mp 278° dec. The second fraction of impurities was discarded and the third fraction afforded 125 mg (44%) of **7b** as dark red crystals (methanol-ether), mp 254-260° dec.

Anal. Calcd. for $C_{13}H_{10}BrN_3O_3$: C, 48.29; H, 2.90; N, 12.02. Found: C, 48.29; H, 2.94; N, 11.72.

5-Anilino-3-methoxy-2-methyl-4,7-indazolequinone (**5c**).

To a stirred suspension of 200 mg (0.63 mmole) of **2c** in 140 ml of chloroform was added 8 ml of an ether solution of diazomethane. The resulting dark green solution was stirred for 3 hours at room temperature. It was column chromatographed (silica gel, 10% water deactivated) with ethyl acetate. The first fraction afforded **5c** which after crystallization from chloroform-hexane provided 120 mg (67%) of yellow prisms. It starts to change the color at 130° and where it melts is not certain. Compound **5c** is quite stable at 0°. At room temperature within two weeks it partially rearranged to **6c**.

Anal. Calcd. for $C_{15}H_{13}N_3O_3$: C, 63.59; H, 4.63; N, 14.81. Found: C, 63.80; H, 4.53; N, 15.08.

5-(4-Bromoanilino)-3-methoxy-2-methyl-4,7-indazolequinone (**5d**) and 5-(4-Bromoanilino)-1,2-dimethyl-3*H*-4,7-indazolequinone (**6d**).

To a stirred suspension of 200 mg (0.51 mmole) of **2d** in 70 ml of tetrahydrofuran was added 6 ml of an ether solution of diazomethane after two hours of stirring the solvent was evaporated. The residue was column chromatographed (silica gel, 10% water deactivated) using chloroform-acetone (3:1). The first orange zone furnished 119 mg of **5d** as orange-red crystals, which after one week changed to fine yellow crystals. Recrystallization from benzene gave dark yellow needles, 96 mg (47%), mp 185° dec.

Anal. Calcd. for $C_{15}H_{12}BrN_2O_3$: C, 49.74; H, 3.34; N, 11.60. Found: C, 49.91; H, 3.42; N, 11.59.

The second small fraction afforded 7 mg (4%) of **6d**, mp 240° dec. Its structure was confirmed by comparing the ir, ^1H nmr spectrum and mixed melting point with the sample prepared by the thermal rearrangement of **5d** described below.

5-Anilino-3-methoxy-2-phenyl-4,7-indazolequinone (**5e**).

To a stirred suspension of 250 mg (0.57 mmole) of **2e** in 200 ml of dioxane was added 8 ml of an ether solution of diazomethane during 15 minutes. The mixture was evaporated to dryness, 20 ml of methanol and 30 ml of ether were added, the precipitate was isolated, washed with ether and dried to give 120 mg (61%) of **5e** as orange colored crystals (dichloromethane-hexane) mp 175-176°.

Anal. Calcd. for $C_{20}H_{15}N_3O_3$: C, 69.55; H, 4.38; N, 12.17. Found: C, 69.31; H, 4.28; N, 12.14.

5-(4-Bromoanilino)-3-methoxy-2-phenyl-4,7-indazolequinone (**5f**).

To a stirred suspension of 0.5 g (1.2 mmoles) of **3f** in 200 ml of tetrahydrofuran was added 12.8 ml of an ether solution of diazomethane within 15 minutes and stirring was continued for 1.5 hours. The solvent was evaporated from the wine red solution, the residue was dissolved in 30 ml of hot ethyl acetate-chloroform (4:1) and cooled. Dark brown crystals were collected, washed with little amount of ethyl acetate, dried to give 193 mg of **5f**. The filtrate on column chromatography (silica gel, 10% water deactivated) with ethyl acetate-chloroform (4:1) afforded additional 90 mg of **5f**, total yield (55%) of yellow needles (chloroform) of mp 193°.

Anal. Calcd. for $C_{20}H_{14}BrN_3O_3$: C, 56.62; H, 3.33; N, 9.90. Found: C, 56.82; H, 3.45; N, 9.80.

Thermal Rearrangements. 5-Anilino-1,2-dimethyl-3*H*-4,7-indazolequinone-3-one (**6c**).

A.

Two hundred mg (0.7 mmole) of **5c** was heated in an open glass capillary tube at 100° in an electric oven for 10 hours. After cooling the material was purified by column chromatography (silica gel, 10% water deactivated) with chloroform-acetone (1:1) to yield 180 mg (45%) of **6c** as dark orange-red crystals (from acetone-hexane), mp 254° dec.

Anal. Calcd. for $C_{15}H_{13}N_3O_3$: C, 63.59; H, 4.63; N, 14.84. Found: C, 63.68; H, 4.77; N, 14.67.

B.

Twenty-five mg (0.09 mmole) of **5c** was dissolved and heated in 25 ml of chlorobenzene at 120° for 8 hours. After cooling the solvent was evaporated under reduced pressure and the residue was purified as above to give 20 mg of **5c** and 4 mg (16%) of **6c**, mp 254° dec. Both samples were identical in every respect (ir, ms, mp).

5-(4-Bromoanilino)-1,2-dimethyl-3*H*-4,7-indazolequinone-3-one (**6d**).

Seventy-five mg (0.2 mmole) of **5d** was heated in an open glass tube at 170° for 24 hours. The material was suspended in 50 ml of boiling methanol, filtered and gave on evaporation 60 mg (80%) of **6d** as dark crystals (methanol ether), mp >200°.

Anal. Calcd. for $C_{15}H_{12}BrN_3O_3$: C, 49.74; H, 3.34; N, 11.60. Found: C, 49.92; H, 3.57; N, 11.40.

5-Anilino-3-methyl-2-phenyl-3*H*-4,7-indazolequinone-3-one (**6e**)

A.

One hundred mg (0.29 mmole) of **5e** was heated as above at 150° for 24 hours. The reaction product was subjected to column chromatography (silica gel, 10% water deactivated) and eluted with chloroform-ethyl acetate (1:1) to give 60 mg (60%) of **6e** as orange red crystals (chloroform-hexane), mp 287°.

Anal. Calcd. for $C_{20}H_{15}N_3O_3$: C, 69.55; H, 4.38; N, 12.17. Found: C, 69.45; H, 4.40; N, 12.15.

B.

Sixty mg (0.17 mmole) of **5e** was heated in 20 ml of chlorobenzene for 45 hours at 165°. After cooling the solvent was evaporated under reduced pressure, the residue was column chromatographed as described above to yield 28 mg (47%) of **5e**, mp 175-176° dec and 14 mg (23%) of **6e**, mp 285-287°.

5-(4-Bromoanilino)-1-methyl-2-phenyl-3*H*-4,7-indazolequinone-3-one (**6f**).

Ninety mg (0.21 mmole) of **5f** was heated as above at 180° for 20 hours. The resulting dark brown-red substance was dissolved in 200 ml of boiling acetone and filtered from insoluble material. The acetone was evaporated *in vacuo* to yield 60 mg (67%) of **6f** as dark brown crystals (acetone-hexane), mp 245-248° dec.

Anal. Calcd. for $C_{20}H_{14}BrN_3O_3$: C, 56.62; H, 3.33; N, 9.91. Found: C, 56.62; H, 3.22; N, 9.84.

5-Anilino-3-methyl-1*H*-4,7-indazolequinone (**9**).

To a stirred suspension of 1.5 g (4.3 mmoles) of 2,5-bisanilino-3-acetyl-1,4-benzoquinone (**8**) in 75 ml of methanol was added 1.5 ml of hydrazine hydrate and stirring was continued at ambient temperature for 24 hours. The orange red colored precipitate was collected by filtration, washed with aqueous ethanol and ether and dried to give 0.7 g (64%) of **9** (methanol), mp 252° dec.

Anal. Calcd. for $C_{14}H_{10}N_3O_2$: C, 66.11; H, 4.37; N, 16.50. Found: C, 66.28; H, 4.43; N, 16.32.

5-Anilino-1,3-dimethyl-4,7-indazolequinone (**10**) and 5-Anilino-2,3-dimethyl-4,7-indazolequinone (**11**).

To a stirred suspension of 200 mg (0.79 mmole) of **8** in 30 ml of tetrahydrofuran was added 3 ml of an ether solution of diazomethane and stirring was continued for 6 hours. After filtration to remove some starting material, the filtrate was column chromatographed (silica gel, 10% water deactivated) with dichloromethane-acetone (9:1) to give with the first band 55 mg (26%) of **10** as orange-red needles (methylene-chloride-hexane), mp 214°.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.19; H, 4.86; N, 15.61.

The second band afforded 21 mg (10%) of **11**, mp 238° and was found to be similar in every respect with an authentic sample prepared by a reported method [10].

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