2-Diazo-2*H*-indoles

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2-Diazo-2*H*-indoles were prepared by diazotization of the corresponding 1*H*-indol-2-amines and subsequent neutralization. On the basis of NMR data and *ab initio* and semiempirical calculations, we suggest that the zwitterionic form **A** is the most representative structure for 2-diazo-2*H*-indoles. In fact, spectral data are compatible with a 1*H*-indole structure, and the fully optimized molecules gave distances in agreement with those reported for the anion obtained from 1*H*-indole. The calculated charges are compatible with a zwitterionic structure in which the negative charge is mainly located at the ring N-atom at variance with the case of diazopyrroles and 3-diazo-3*H*-indoles where the negative charge is essentially located on the *ipso* C-atom.

Introduction. – For a long time, diazoazoles have been very important key intermediates for the synthesis of molecules of biological interest. Among them, the most important is 5-diazo-5*H*-imidazole-4-carboxamide (Diazo-IC), which represents the precursor of dacarbazine (= 5-(3,3-dimethyltriaz-1-enyl)-1*H*-imidazole-4-carboxamide), the only triazene derivative used in anticancer chemotherapy and the most active drug available for treatment of malignant melanoma and *Hodgkin* tumors resistant to MOPP therapy [1][2]. Diazo-IC is also the precursor of temozolomide (= 3,4-dihydro-3-methyl-4-oxoimidazo[5,1-*d*][1,2,3,5]tetrazine-8-carboxamide), which is now on the market under the trade name *Temodal*® and is used against malignant melanoma, mycosis fungoides, and brain tumors [3].

The 3-diazo-3*H*-pyrroles were utilized for the synthesis of 3-triazenyl-1*H*-pyrroles, which showed *in vitro* antileukemic activity with IC_{50} 1.1 – 3.1 μM [4]. Benzo fusion led to the 3-triazenyl-1*H*-indoles, which turned out to be 20 – 40 times more active in *vitro* antileukemic assays [5].

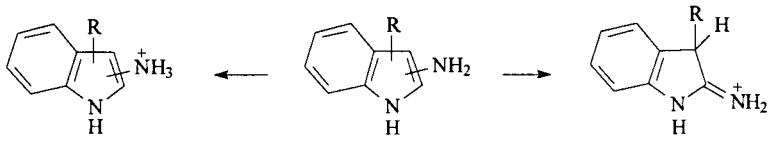
The 2-diazo-2*H*-pyrroles were employed for the synthesis of 2-triazenylpyrroles, which were shown to be cytotoxic against leukemic, lymphoma, and carcinoma cell lines, with IC_{50} 3.9 – 21 μM, and to inhibit Cox-B2 and VSV with EC_{50} 10 – 50 μM [6]. The same 2-diazo-2*H*-pyrroles reacted with alkyl or aryl isocyanates to give the pyrrolo[2,1-*d*][1,2,3,5]tetrazinone derivatives, which show the deaza skeleton of temozolomide [7] and had potent antiproliferative activity with IC_{50} 0.09 – 56 μM [8], whereas, by reaction with methylene active compounds, it was possible to isolate derivatives of the pyrrolo[2,1-*c*][1,2,4]triazine ring system [9]. These latter derivatives showed antiproliferative activity with IC_{50} in the range 5.5 – 88 μM [10].

Having in mind the promising biological activities shown by the compounds obtained from diazopyrroles and considering the increase in antiproliferative activity achieved by the benzo fusion as in the case of 3-triazenyl-1*H*-indoles, we planned to use also 2-diazo-2*H*-indoles as building blocks for the synthesis of derivatives with antineoplastic activity. But 2-diazo-2*H*-indoles were unknown, probably because

1*H*-indol-2-amines are not easily available since they are unstable and difficult to handle and auto-oxidize extremely rapidly [11].

However, as protonation studies carried out on pyrrolamines [12] contributed to the understanding of the behaviour of these derivatives towards electrophiles and to the isolation of 2-diazo-2*H*-pyrroles [13], some 1*H*-indol-2- and -3-amines have been prepared to study their tautomerism and behavior towards protonation, which provided information about the feasibility of the diazotization reaction of 1*H*-indol-2-amines leading to the unknown 2-diazo-2*H*-indoles [14] (see *Scheme 1*).

Scheme 1



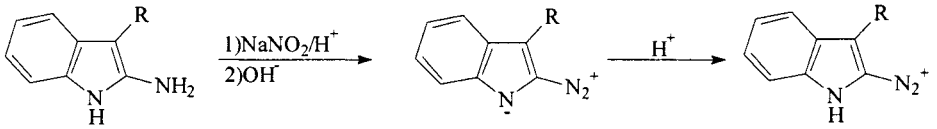
R=COOEt, COMe, Ph, H

An evaluation of the behavior of 1*H*-indolamines towards protonation allowed us to be confident of the feasibility of the diazotization reaction, at least for derivatives bearing electron-withdrawing substituents, and suggested weakly acid reaction conditions. In fact, 1*H*-indol-3-amines that undergo very easily diazotization to give isolable diazo compounds and diazonium salts are protonated at the exocyclic N-atom both in DMSO/CF_3COOH and in pure CF_3COOH. The 1*H*-indol-2-amines, instead, need an electron-withdrawing group at the position 3 to give exocyclic protonation [14].

Results and Discussion. – The 2-diazo-2*H*-indoles **2a**–**c** were obtained by diazotization of the corresponding 1*H*-indol-2-amines **1** under the reaction conditions employed for the preparation of the 2-diazo-2*H*-pyrroles, *i.e.* by treatment with $NaNO_2$ in AcOH at 0°, followed by neutralization with Na_2CO_3 (*Scheme 2*). Strict control of the temperature during diazotization and neutralization was crucial to achieve reasonable yields (50–60%). Diazotization of amine **1d** led to a very complex mixture from which it was impossible to isolate the corresponding diazo compound **2d**. The 2-diazo-2*H*-indoles **2a**–**c** are, as expected, light-sensitive and have to be stored at −20° under N_2. The 1*H*-indole-2-diazonium salts **3a**–**c** were prepared in quantitative yields by suspending the corresponding diazo compound **2** in dry Et_2O and heating it in the presence of gaseous HCl.

The structures of the 2-diazo-2*H*-indoles **2a**–**c** were confirmed by combustion analysis and by their spectral data (IR, ^{1}H- and ^{13}C-NMR). The presence of the diazo group was confirmed by IR spectroscopy, the only method that gives a direct diagnostic information about the presence of a diazo function, which appears as sharp and strong band at 2107–2150 cm^{-1}. This band is shifted to 2157–2216 cm^{-1} in the 1*H*-indole-2-diazonium salts **3a**–**c**. The ^{1}H-NMR spectra, except for the absence of the signal due to the indole NH proton, do not provide any significant information about the structure of compounds **2a**–**c** (*Table 1*).

Scheme 2



1a R = Ph
b R = COMe
c R = COOEt
d R = H

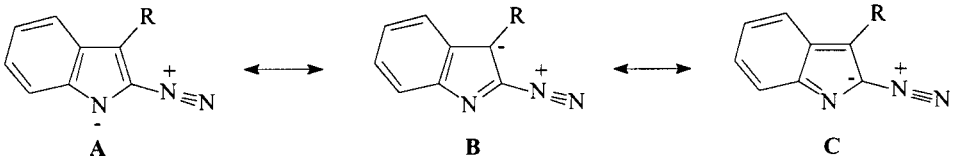
2a R = Ph
b R = COMe
c R = COOEt

3a R = Ph
b R = COMe
c R = COOEt

Table 1. *^{1}H-NMR Data* ((D_6)DMSO) *for 2-Diazo-2*H*-indoles* (**2**) *and 1*H*-Indole-2-diazonium Salts* (**3**). δ in ppm

	H–N(1)	H of R–C(3)	H–C(4)	H–C(5)	H–C(6)	H–C(7)
2a (R=Ph)		7.00–7.17 (*m*, 2 H); 7.32–7.40 (*m*, 2 H); 7.44–7.54 (*m*, 1 H)	7.74–7.93 (*m*, 1 H)	6.70–6.90 (*m*, 1 H)	6.70–6.90 (*m*, 1 H)	7.74–7.93 (*m*, 1 H)
2b (R=COMe)		2.51 (*s*, 3 H)	7.61 (*d*, 1 H)	6.95–7.09 (*m*, 1 H)	6.95–7.09 (*m*, 1 H)	7.34 (*d*, 1 H)
2c (R=COOEt)		1.34 (*t*, 3 H); 4.35 (*q*, 2 H)	7.80 (*dd*, 1 H)	7.27 (*dt*, 1 H)	7.33 (*dt*, 1 H)	7.58 (*dd*, 1 H)
3a (R=Ph)	10.21 (br. *s*, 1 H)	7.28–7.50 (*m*, 5 H)	7.82–7.80 (*m*, 1 H)	7.05–7.15 (*m*, 1 H)	7.05–7.15 (*m*, 1 H)	7.82–7.80 (*m*, 1 H)
3b (R=COMe)	10.53 (br. *s*, 1 H)	2.51 (*s*, 3 H)	7.88 (*d*, 1 H)	7.17–7.27 (*m*, 1 H)	7.17–7.27 (*m*, 1 H)	7.64 (*d*, 1 H)
3c (R=COOEt)	9.04 (br. *s*, 1 H)	1.35 (*t*, 3 H); 4.35 (*q*, 2 H)	7.87 (*d*, 1 H)	7.27 (*t*, 1 H)	7.33 (*t*, 1 H)	7.58 (*d*, 1 H)

The ^{13}C-NMR spectra of 2-diazo-2*H*-indoles **2a–c** (*Table 2*) did not show any upfield *s* attributable to the C-atom bound to the diazo function, as already observed in the 3-diazo-3*H*-indole and diazopyrrole series [13][15][1]); the spectra rather exhibited patterns comparable to those of other substituted 1*H*-indoles [16], which are very similar to the ^{13}C-NMR data of the 1*H*-indole-2-diazonium salts **3a–c** (*Table 2*). Thus, the 2-diazo-2*H*-indoles can be represented by zwitterionic structure **A**, where the negative charge is located at the ring N-atom.



[1]) ^{13}C-NMR Data of 3-diazo-2-phenyl-3*H*-indole in $CDCl_3$ (δ in ppm): 68.1 (*s*, C(3)); 117.7 (*d*, C(7)); 121.7 (*d*, C(6)); 123.6 (*d*, C(4)); 125.7 (*d*, C(5)); 127.0 (*d*, C(3′), C(5′)); 129.0 (*d*, C(2′), C(6′)); 130.1 (*d*, C(4′)); 130.8 (*s*, C(1′)); 133.1 (*s*, C(3a)); 147.0 (*s*, C(7a)); 160.2 (*s*, C(2)).

Table 2. *^{13}C-NMR Data* ((D$_6$)DMSO) *for 2-Diazo-2*H*-indoles* (**2**) *and 1*H*-Indole-2-diazonium Salts* (**3**). δ in ppm. F = found; C = calc.

		C(2)	C(3)	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7a)	R
2a (R = Ph)	F	112.9 (*s*)	120.7 (*s*)	126.5 (*s*)	130.4 (*d*)	127.1 (*d*)	126.9 (*d*)	115.6 (*d*)	143.4 (*s*)	128.3 (*d*), 128.5 (*d*), 128.7 (*d*), 130.3 (*s*)
	C	125.03	127.75	125.18	119.44	122.37	129.99	113.04	150.61	124.08 125.81, 128.94, 129.22, 130.20, 133.12
2b (R = COMe)	F	110.1 (*s*)	117.6 (*s*)	133.2 (*s*)	126.1 (*d*)	123.6 (*d*)	120.4 (*d*)	119.7 (*d*)	147.4 (*s*)	29.6 (*q*), 191.2 (*s*)
	C	155.59	112.50	128.00	116.96	127.91	129.11	114.86	150.76	28.70 210.29
2c (R = COOEt)	F	115.9 (*s*)	110.0 (*s*)	128.2 (*s*)	126.9 (*d*)	125.7 (*d*)	121.6 (*d*)	121.4 (*d*)	149.2 (*s*)	14.1 (*q*), 60.4 (*t*), 161.3 (*s*)
	C	162.28	125.95	128.27	116.71	127.85	128.28	115.85	149.65	18.03 53.60, 163.00
3a (R = Ph)	F	113.1 (*s*)	121.1 (*s*)	127.6 (*s*)	130.3 (*d*)	127.1 (*d*)	126.3 (*d*)	115.2 (*d*)	143.5 (*s*)	128.7 (*d*), 129.1 (*d*), 129.3 (*d*), 130.3 (*s*)
	C	105.95	164.33	142.96	133.15	128.38	130.22	130.20	148.82	127.67 131.47, 132.33, 133.54, 134.22, 141.66
3b (R = COMe)	F	111.3 (*s*)	115.6 (*s*)	132.9 (*s*)	124.7 (*d*)	123.3 (*d*)	122.3 (*d*)	121.2 (*d*)	143.7 (*s*)	21.2 (*q*), 192.0 (*s*)
	C	134.15	121.50	146.12	133.66	126.81	126.59	129.59	162.67	0.86 216.76
3c (R = COOEt)	F	113.2 (*s*)	109.6 (*s*)	136.2 (*s*)	127.5 (*d*)	125.5 (*d*)	121.8 (*d*)	121.4 (*d*)	148.4 (*s*)	14.1 (*q*), 60.6 (*t*), 161.3 (*s*)
	C	147.68	147.49	148.13	133.74	126.45	126.56	129.89	162.82	14.47 59.47, 163.03

To confirm the structure assignment based on the NMR analysis, we did semiempirical molecular-orbital calculations with the Vamp (V 6.5) software, supplied by *Oxford Molecular*. The structure of the diazo compounds and of the corresponding diazonium cations were fully optimized *in vacuo* by SCF calculation with different Hamiltonian (AM1, PM3, MNDO) methods. All the methods gave good results in evaluating the interatomic distances (*Table 3*), from which the bond orders could be derived; however, the best results in terms of charge were obtained from the PM3 Hamiltonian (*Table 4*). However, semiempirical methods, although being orders of

Table 3. *Interatomic Distances* [Å] *for 2-Diazo-2*H*-indoles* (**2**) *and 1*H*-Indole-2-diazonium Ions* (**3**) *as Obtained by Semiempirical Molecular-Orbital Calculations* (PM3)

	2a	**2b**	**2c**	**3a**	**3b**	**3c**
N(1)–C(2)	1.422	1.414	1.408	1.461	1.432	1.432
C(2)–C(3)	1.443	1.447	1.441	1.420	1.423	1.424
C(3)–C(3a)	1.394	1.401	1.401	1.429	1.414	1.412
C(3a)–C(4)	1.425	1.427	1.424	1.409	1.418	1.419
C(4)–C(5)	1.359	1.360	1.362	1.376	1.369	1.369
C(5)–C(6)	1.435	1.434	1.432	1.412	1.422	1.422
C(6)–C(7)	1.359	1.359	1.361	1.382	1.373	1.373
C(7)–C(7a)	1.432	1.431	1.429	1.401	1.412	1.411
C(7a)–C(3a)	1.453	1.452	1.449	1.425	1.433	1.435
C(7a)–N(1)	1.350	1.350	1.357	1.414	1.390	1.389
C(2)–N(2)	1.339	1.342	1.348	1.364	1.376	1.376
N(2)–N(3)	1.119	1.119	1.116	1.113	1.110	1.110
C(3)–R	1.453	1.471	1.462	1.446	1.494	1.485
N(1)–H				0.992	0.988	0.988

magnitude faster, are less accurate than *ab initio* calculations. Therefore, we decided to study these molecules also by *ab initio* methods employing *Hartree-Fock* SCF calculations and the *Breneman* model to generate potential-derived charges (see *Table 4*).

Analysis of the data reported in *Table 3* revealed that the calculated bond distances for 1*H*-indole-2-diazonium salts **3a**–**c** are compatible with those reported for 1*H*-indole structures [17]. The calculated structural parameters again suggest structure **A**, derived from 1*H*-indole, to be the most probable one for 2-diazo-2*H*-indoles, as evidenced by the difference in bond distances compared to the corresponding diazonium salts, which are in agreement with the geometrical changes brought about by anion formation from 1*H*-indole [18]. In particular, a shortening of the bonds N(1)–C(2) by 1.8–3.9 pm, C(3)–C(3a) by 1.1–3.5 pm, and C(7a)–N(1) by 3.2–6.4 pm and lengthening of the bonds C(2)–C(3) by 1.7–2.4 pm, C(3a)–C(7a) by 1.4–2.8 pm, and C(7)–C(7a) by 1.8–3.1 pm are observed. The geometrical changes in the benzene moiety of the diazoindoles **2a**–**c** are not in agreement with those observed in the indole anion. In fact, a double-bond fixation at the C(4)–C(5) and C(6)–C(7) positions is observed with shortening of the bond distances by 0.7–1.7 and 1.2–2.3 pm,

Table 4. *Charges for 2-Diazo-2*H*-indoles* (**2**) *and 1*H*-Indole-2-diazonium Ions* (**3**). *i.v.* = *in vacuo*

	2a				**2b**				**2c**				**3a**		**3b**		**3c**	
	PM3		*Ab initio*		PM3		*Ab initio*		PM3		*Ab initio*		PM3		PM3		PM3	
	i.v.	DMSO			*i.v.*	DMSO			*i.v.*	DMSO			*i.v.*	DMSO	*i.v.*	DMSO	*i.v.*	DMSO
N(1)	–0.723	–0.801	–0.6046	–0.6112	–0.661	–0.708	–0.5809	–0.6013	–0.718	–0.783	–0.5835	–0.6399	–0.373	–0.332	0.066	0.155	0.402	0.524
C(2)	–0.384	–0.410	0.4392	0.0453	–0.388	–0.428	0.4488	0.0573	–0.174	–0.145	0.4816	0.1779	–0.906	–0.910	–0.874	–0.838	–1.069	–1.003
C(3)	–0.088	–0.033	0.0004	–0.2486	–0.410	–0.331	–0.1035	–0.4013	–0.714	–0.731	–0.1328	–0.5035	0.518	0.481	0.105	0.074	0.035	–0.073
C(3a)	–0.223	–0.265	–0.1022	0.1127	0.013	–0.034	–0.0667	0.1737	0.042	0.008	–0.0599	0.1789	–0.153	–0.197	–0.145	–0.192	0.002	0.014
C(4)	0.048	0.065	–0.0946	–0.2298	0.048	0.053	–0.0961	–0.2646	–0.003	–0.004	–0.0979	–0.2830	0.002	0.015	–0.050	–0.030	–0.034	–0.063
C(5)	–0.239	–0.268	–0.1779	–0.1368	–0.273	–0.298	–0.1678	–0.1124	–0.213	–0.224	–0.1679	–0.0873	–0.097	–0.128	–0.043	–0.074	–0.042	–0.049
C(6)	0.011	0.026	–0.1588	–0.0707	0.027	0.040	–0.1612	–0.0516	–0.023	–0.023	–0.1641	–0.0821	0.065	0.039	0.070	0.016	0.069	0.008
C(7)	–0.286	–0.318	–0.1257	–0.2749	–0.292	–0.309	–0.1209	–0.3347	–0.278	–0.292	–0.1211	–0.3278	–0.180	–0.207	–0.195	–0.180	–0.166	–0.131
C(7a)	0.693	0.690	0.2370	0.4177	0.618	0.605	0.2207	0.4597	0.651	0.650	0.2110	0.4753	0.339	0.369	0.263	0.248	0.056	0.008
N(2)	1.502	1.604	0.0146	0.5389	1.480	1.583	0.0220	0.5548	1.456	1.533	0.0474	0.5157	1.663	1.777	1.643	1.752	1.682	1.780
N(3)	–0.699	–0.686	–0.0997	–0.1681	–0.670	–0.641	–0.0822	–0.1403	–0.645	–0.612	–0.0717	–0.1042	–0.580	–0.593	–0.518	–0.555	–0.523	–0.561

respectively, of the above mentioned positions, and lengthening of the C(3a)–C(4) and C(7)–C(7a) bonds by 0.5–1.6 and 1.8–3.1 pm, respectively. These figures, together with the short bond distances between C(7a)–N(1) and C(2)–N(2), indicate that also forms **B** and **C** can represent the actual structure. The diazo N≡N bond lengths, 111.6–111.9 pm, are close to X-ray values determined for 3-diazo-3*H*-indazole (111.0 pm) [19] and for 1-(4-diazo-2,5-diphenyl-4*H*-pyrrol-3-yl)ethanone (111.0 pm) [20].

Semiempirical and *ab initio* methods all predict a negative partial charge at the N(1) atom of **2a–c** and a less but still negative one at C(3), compatible with structures **A** and **B** (*Table 4*). The PM3 method gives a positive charge at N(2) (range 1.46–1.50 *in vacuo*), higher than that generated with potential-derived charges (range 0.52–0.55). The main discrepancy is observed for C(2) of **2a–c**, for which the two methods predict charges of opposite sign. In the case of the diazonium ions **3**, only the semiempirical methods give results compatible with the canonical structure generally accepted for diazonium salts.

Although there are discrepancies between the semiempirical and *ab initio* charges, the data obtained further support a major contribution of structure **A** to **2a–c** with the negative charge located on N(1), but also a substantial contribution from structure **B**, especially when electron-withdrawing groups are present at the C(3) position of the indole moiety.

Solvent effects were simulated with the PM3 method, which allowed also a prediction of the ^{13}C-NMR chemical shifts by the neural-net technique [21]. Data calculated for solutions in DMSO (*Table 4*) are in agreement with those obtained *in vacuo* for charges and interatomic distances as well. Moreover, we found a good linear correlation between the theoretical and experimental ^{13}C-NMR chemical shift values, especially in the case of **2b**,**c** ($r^2 = 0.878–0.873$) and for the corresponding diazonium species ($r^2 = 0.985–0.917$); the r^2 value was increased to 0.973–0.971 and 0.997–0.944, respectively, if the value obtained for C(2) is excluded. Evidently, the algorithm is not suitable for evaluating the solvent effect in the case of C-atoms more directly involved in this particular mesoionic structure.

In conclusion, the structure of 2-diazo-2*H*-indoles, as depicted in form **A**, with the negative charge mainly located at the indole N-atom, differs from those of diazopyrroles and 3-diazo-3*H*-indoles in which the negative charge is essentially located on the *ipso* C-atom [13][15][1]).

Experimental Part

1. *General.* Column chromatography: *Merck* silica gel 230–400 mesh ASTM. M.p.: *Büchi-Tottoli* capillary apparatus; uncorrected. IR Spectra: *Jasco FT/IR-5300* spectrophotometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: in (D_6)DMSO solns. with $SiMe_4$ as internal reference, at 200 and 50.3 MHz, resp.; *Bruker AC-200-MHz* spectrometer.

2. *3-Substituted 2-Diazo-2*H*-indoles* **2a–c**: *General Procedure.* To a stirred soln. of 1*H*-indol-2-amines **1a–c** [22] (10 mmol) in 80% AcOH (10 ml) at 0°, under inert atmosphere, was added a stoichiometric amount of $NaNO_2$ (690 mg) in H_2O (2 ml). The mixture was stirred for 3 h and, keeping the temp. at 0°, neutralized with 10% aq. Na_2CO_3 soln. The brown precipitated solid was filtered off and dried in a desiccator under vacuum and in the dark. The crude products, quickly shaken in cyclohexane and filtered off, gave 2-diazo-2*H*-indoles **2a–c**.

Diazotization of 1*H*-indol-2-amine (**1d**) [22] led to an intractable mixture.

*2-Diazo-3-phenyl-2*H*-indole* (**2a**): Yield 50%. M.p. 115–117° (dec.). IR: 2107 (N≡N). Anal. calc. for $C_{14}H_9N_3$ (219.25): C 76.70, H 4.14, N 19.17; found: C 76.41, H 4.31, N 19.38.

*1-(2-Diazo-2*H*-indol-3-yl)ethanone* (**2b**): Yield 50%. M.p. 105–108° (dec.). IR: 2150 (N≡N), 1636 (CO). Anal. calc. for $C_{10}H_7N_3O$ (185.19): C 64.86, H 3.81, N 22.69; found: C 65.04, H 3.64, N 23.00.

*Ethyl 2-Diazo-2*H*-indole-3-carboxylate* (**2c**): Yield 60%. M.p. 55° (dec.). IR: 2150 (N≡N), 1677 (CO). Anal. calc. for $C_{11}H_9N_3O_2$ (215.21): C 61.39, H 4.22, N 19.53; found: C 61.71, H 4.39, N 19.11.

3. *3-Substituted 1*H*-Indole-2-diazonium Salts* **3a**–**c**. Through a soln. of diazo compound **2a**–**c** (5 mmol) in dry Et_2O (50 ml) at 0° (100-ml flash, drying tube ($CaCl_2$)), dry gaseous HCl was bubbled until the brown suspension became yellowish-green (*ca*. 15 min for **2b** and **2c**, 2 h for **2a**). After the mixture had been allowed to reach r.t., the solid was filtered off, washed with dry Et_2O, and dried in a desiccator under vacuum, giving salts **3a**–**c** in quantitative yields.

*3-Phenyl-1*H*-indole-2-diazonium Chloride* (**3a**): M.p. 276–280°. IR: 3391 (very br. NH), 2157 (N≡N$^+$). Anal. calc. for $C_{14}H_{10}ClN_3$ (255.71): C 65.76, H 3.94, N 16.43; found: C 65.51, H 3.81, N 16.48.

*3-Acetyl-1*H*-indole-2-diazonium Chloride* (**3b**): M.p. 178–180°. IR: 3257 (very br. NH), 2190 (N≡N$^+$), 1680 (CO). Anal. calc. for $C_{10}H_8ClN_3O$ (221.65): C 54.19, H 3.64, N 18.96; found: C 54.28, H 3.69, N 18.81.

*3-(Ethoxycarbonyl)-1*H*-indole-2-diazonium Chloride* (**3c**): M.p. 186–188°. IR: 3175 (very br. NH), 2216 (N≡N$^+$), 1713 (CO). Anal. calc. for $C_{11}H_{10}ClN_3O_2$ (251.67): C 52.50, H 4.00, N 16.70; found: C 52.61, H 3.98, N 15.56.

4. Calculations. The semiempirical (AM1, PM3, MNDO) methods were employed with the Vamp (V 6.5) program running on an *Indigo-2-Silicon Graphics* work station. For *ab initio Hartree-Fock* SCF calculation, the 6-311G basis set, with p- and d-polarization functions, were employed. CHELPG was used to generate the potential-derived charges within the *Breneman* model [23]. Full geometry optimization was achieved by checking the eigenvalues of the *Hessian* matrix.

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