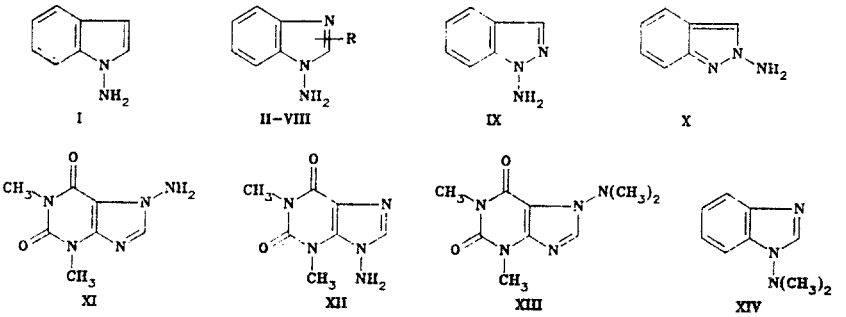
MUTUAL EFFECT OF THE N-AMINO GROUP AND THE HETERORING IN N-AMINOBENZAZOLES

A. F. Pozharskii, V. V. Kuz'menko, A. A. Bumber, É. S. Petrov, M. I. Terekhova, N. L. Chikina, and I. M. Nanavyan

UDC 547.857.4'785.4'779'772.04: 541.132.3:543.257.1

The basicity constants, NH acidities, and anode oxidation potentials of N-amino derivatives of a number of heteroaromatic systems, viz., indole, benzimidazole, indazole, and 1,3-dimethylxanthine, were measured for the first time. The results obtained provide evidence for the inductive character of the interaction of the N-amino group and the benzazole ring vis-à-vis the almost complete absence of π interaction between them; the heteroring has a very strong electron-acceptor effect on the properties of the amino group, while the amino group changes the properties of the heteroring to only a small extent.

Despite the vigorous development of the chemistry of N-amino derivatives of heteroaromatic systems, including azoles also [1], data in the principal physicochemical characteristics of these compounds and, consequently, the character of the electronic interaction of the N-amino group with the heterocyclic ring have been almost unavailable up to this time. In this connection in the present research we measured the basicity constants, NH acidities, and electrochemical oxidation potentials of N-amino derivatives of indole (I), benzimidazoles II-VIII, indazoles IX and X, and theophyllines XI and XII. N-Methyl derivatives of the same heterocycles were subjected to a similar study.



II R=H, III R=2-CH_3, IV R=2-NH_2, V R=2-$NHCH_3$, VI R=2-$N(CH_3)_2$, VII R=2-Cl, VIII R=5,6-$(CH_3)_2$

Basicity Constants

The basicity constants were measured by potentiometric titration in acetonitrile (Table 1). An analysis of the pK_a values logically begins with 1-aminoindole, since the only protonation center in it is the amino group (the constant of C protonation of indole in acetonitrile is not recorded). The basicity of 1-aminoindole (pK_a 6.55) is an order of magnitude lower than the basicity of hydrazine (pK_a 16.55); this indicates the very strong electron-acceptor effect of N-indolyl fragment on the amino group. Although comparable data on the σ constants of the 1-indolyl and other N-azolyl groups investigated in the present research are not available, one can scarcely doubt that the basicities of the amino groups in II-XII should be of the same order of magnitude as in 1-aminoindole or even lower. Since the pK_a values of all

Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov state University, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 221-227, February, 1989. Original article submitted July 1, 1987; revision submitted November 23, 1987.

 0009-3122/89/2502-0180$12.50

TABLE 1. Basicity Constants, pK_a Values, and Characteristics of the Cyclical Voltamperograms of the Oxidation of the Investigated Compounds

Compound	pK_a (CH_3CN, 20 °C)	E_{pa}, V	$E_{pa}/2$, V	i_a, μA
Hydrazine	16,55	—	—	—
1-Methylindole	—*	1,18	1,00	66
I	6,55	0,95	0.84	53
Benzimidazole	13,22	1,62	—	38
1-Methylbenzimidazole	13,50	1,68	1,48	54
II	12,83	1,44	1,20	48
III	14,24	1,46	1,18	47
IV	15,60	0,94; 1,78	0,76; 1,66	21; 7
V	15,83	0,90; 1,78	0,75; 1,68	51; 16
VI	15,67	0,81; 1,78	0,70; 1,70	57; 17
VII	9,04	1,54	1,38	63
VIII	13,72	1,34	1,12	48
1-Methylindazole	6,85	1,62	—	55
2-Methylindazole	9,26	1,42	1,30	63
IX	6,70	1,12	0,98	65
X	8,64	1,42	1,24	67
Theophylline	7,55	—	—	—
7-Methyltheophylline	7,60	1,62	—	75
9-Methyltheophylline	9,91	1,46	—	58
XI	7,20	1,40	1,25	28
XII	9,30	1,47	1,32	26
XIII	6,30	1,56	—	36
XIV	12,40	1,38	—	16
XVa	9,05; 6,00	1,40†	—	9

*Not protonated in acetonitrile.
†The reduction potential.

TABLE 2. NH Acidities of N-Aminobenzazoles (DME, 20°C)

Compound	pK^*	Indicator †	pK_{ind}	K_{eq}	n ‡
II	28,4	PX	28,65	2,0±0,4	3
IX	28,6	BDM	30,25	45±5	2
	28,3	PX	26,65	2,2±0,2	4
XI	23,3	F	22,95	0,5±0,1	2

*$pK = PK_{ind} - \log K_{eq}$; the pK values were determined relative to the pK value of 9-phenylfluorene and the pK_{DME,Cs^+} values presented in [7].
†Abbreviations: PX is 9-phenylxanthine, BDM is p-biphenylyl-diphenylmethane, and F is fluorene.
‡Note that n is the number of independent determinations of K_{eq}. For II and XI the K_{eq} values were evaluated only with respect to the direct reaction of the Cs salt of the indicator acid with N-aminoazole; the reprotonation cannot be carried out in the reverse direction because of side processes.

1-aminobenzimidazoles II-VIII, 9-aminotheophylline XII, and 2-aminoindazole (X) are considerably higher than the pK_a value of indole I, the protonation of these compounds most likely proceeds at the nitrogen atom of the heteroring. This conclusion is indirectly confirmed by the fact that the reaction of 1-aminobenzimidazole with methyl iodide leads to the 1-amino-3-methylbenzimidazolium salt [2].

In the case of 1-aminoindazole IX and 7-aminotheophylline XI one cannot completely exclude the probability of at least their partial protonation at the N-amino group. The fact, established by us, that the only product is 7-dimethylaminotheophylline XIII when XI is heated with methyl iodide in a neutral medium constitutes indirect evidence in favor of this assumption. This reaction pathway is associated first and foremost with steric factors, i.e., the strong shielding of the $N_{(9)}$ atom by the 3-methyl group, but to a certain extent this result also constitutes evidence for the apparent nucleophilicity of the N-amino group in XI. At the same time, 9-aminotheophylline XII is converted to caffeine under the same conditions

[3]; this can be explained only by the initial occurrence of the reaction at the ring $N(_7)$ atom with subsequent deamination of the quaternary salt.

The basicities of benzimidazole (pK_a 13.22), 1-methyl-benzimidazole (pK_a 13.50), and 1-aminobenzimidazole (pK_a 12.83) constitute evidence that the N-amino group has a very weak electron-acceptor effect with respect to the heteroring. The same also applies to the N-amino derivatives of other azoles.

One of the side results of this research was the possibility, on the basis of pK_a values of the N-methyl derivatives of indazole and theophylline, to evaluate the position of the tautomeric equilibrium in indazole and theophylline in solution in acetonitrile. Using the formula $K_T = K_1/K_2$ [4], where K_1 and K_2 are the basicity constants of fixed tautomeric forms, we calculated that the concentration of the 1H tautomer of indazole exceeds the concentration of the 2H form by a factor of 260, while the amount of the 7H tautomer of theophylline is greater than the amount of the 9H tautomer by a factor of 200. When the pK_a values of N-amino derivatives of indazole and theophylline are used, the difference in the concentrations of the two tautomers turns out to be somewhat lower: 87 for indazole and 125 for theophylline. This disparity is evidently associated with the fact that the interaction of the N-amino group with the π-system of the heteroring is manifested somewhat differently in each of the tautomers.

NH Acidities

We used the indicator method to measure the equilibrium NH acidities of II, IX, and XI (Table 2). The measurements were made in 1,2-dimethoxyethane (DME), since in DMSO, for which an absolute NH acidity scale has been worked out [5], the N anion of the investigated amines are unstable and undergo rapid secondary processes. In order to reconcile the pK_{DME} values on the acidity scale in DMSO with respect to the pK_{DME} values one must add 1.5 pK units [5, 6]. The pK values presented in Table 2 were established with the Cs^+ gegenion and were assigned to the pH value of 18.5 for 9-phenylfluorene, which was selected as the reference compound.

Since the literature does not contain reliable data on the NH acidity of hydrazine, it is expedient to evaluate the acidifying effect of the N-azolyl groups relative to ammonia. According to the data in [5], the pK of ammonia on the DMSO scale is 41. Thus the acidifying effect of the N-benzimidazolyl and 1-indazolyl substituents is ∿11 pK units. This value almost coincides with the acidifying effect of the phenyl group, since the pK of aniline on the DMSO scale is 30.7 [5]. It is known that the electron-acceptor effect of the phenyl group in aniline, which is manifested, in particular, in a decrease in its basicity and an increase in the NH acidity as compared with ammonia, is the net result of approximately equal contributions from the resonance and inductive effects [8]. There is no doubt that the −I effect of N-benzazolyl groups should significantly exceed the −I effect of the phenyl group. It hence follows that the acidifying effect of N-benzazolyl substituents on the acidity of the NH_2 group is primarily due to the inductive effect. This conclusion is in agreement with data on the geometry of N-aminobenzazoles (see below), as well as with the conclusion drawn on the basis of a study of their basicities.

The NH acidity of 7-aminotheophylline XI is 5 units higher than the acidities of amines II and IX. It is interesting that the acidity of theophylline itself is higher than the acidities of benzimidazole and indazole [9] (data for aqueous solutions) by a factor of the same magnitude. This is explained by the higher positive charge on the nitrogen atoms of theophylline as a consequence of the electron-acceptor effect of the carbonyl groups.

We were also able to approximately characterize the NH acidity of 2-aminoindazole (pK ∿ 24), since in its reaction with the Cs salt of 9-tert-butylfluorene (pK 24.7) a short-lived equilibrium was observed. The value obtained is entirely likely if one considers that in indazole the electron density on the $N(_2)$ atom is lower than on the $N(_1)$ atom (see the data on the basicities).

The magnitudes of the NH acidities of the investigated N-aminobenzazoles enabled us to hope for the possibility of their alkylation at the amino group through the corresponding N anion. In fact, 1-dimethylaminobenzimidazole (XIV) was obtained in 52% yield by the action of KNH_2 in liquid ammonia on II with subsequent methylation with excess methyl iodide. However, the reaction proceeded with the formation of a complex mixture of substances and much less smoothly than the alkylation of 2-aminobenzimidazoles under the same conditions [10]. The apparent reason for this is the above-noted instability of the N anion of II.

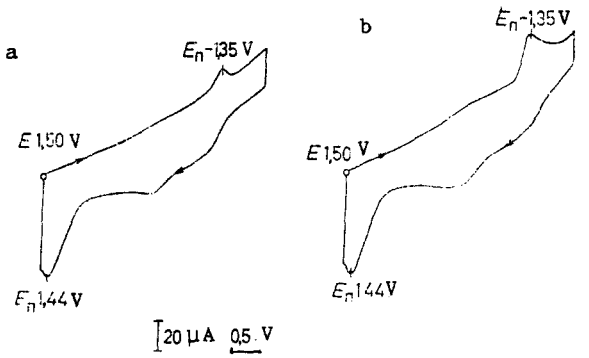
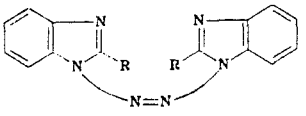


Fig. 1. Cyclical voltamperogram: a) 1-aminobenzimidazole (II); b) 1-aminobenzimidazole with added 1,1'-azobenzimidazole XVa.

Anode Oxidation Potentials

The oxidation potentials (Table 1) of the investigated compounds were determined by means of cyclical voltamperometry in acetonitrile. Clearly expressed cathode peaks are absent in the cyclical voltamperograms of all of the compounds (the difference $E_{pa} - E_{pa}/2$ is extremely significant). This constitutes evidence that the oxidation process is virtually irreversible in all cases. The initially formed cation radicals are evidently unstable and undergo fast subsequent reactions. Almost all of the compounds give one oxidation wave, which, judging from the maximum currents, corresponds to the detachment of one electron. 1,2-Diaminobenzimidazoles IV–VI, for which there is a small second oxidation wave at 1.78 V, constitute exceptions.

In the oxidation of benzimidazoles II and III peaks corresponding to products of transformation of the primary cation radicals are observed on the cathode branches of the cyclical voltamperograms. These products are evidently the recently obtained [11], 1,1'-azobenzimidazoles XV. In fact, the addition of authentic XV to the investigated solutions confirms this assumption: The peak with a potential of 1.35 V increases when the dimer is added (Fig. 1).



XVa,b
XV a R=H; b R=CH_3

For the interpretation of the oxidation potentials it is important to know the fragment of the N-aminoazole molecule from which the electron is detached. We have previously shown by means of x-ray diffraction analysis that the N-amino group in the 1-methyl-9-aminoxanthine molecules is situated almost perpendicularly to the plane of the heteroring [3]. In a geometry of this sort the π interaction between the unshared pair of electrons of the amino group and the aromatic heterosystem should be small. This conclusion also seems valid for the N-amino-azoles investigated in the present research. Although accurate data on the geometry of these compounds are not available, their electronic absorption spectra, which are virtually identical to the UV spectra of the corresponding N-methyl derivatives (Table 3), indicate minimal conjugation of the heteroring and the N-amino group. If this corresponds to reality, the ionization potentials (IP) of the amino group and the heterocyclic fragment should change relatively little as compared with the ionization potentials of ammonia and the corresponding heterocycles. Thus the IP_1 of indole (7.75 eV) [2], benzimidazole (8.31 eV), and caffeine (7.94 eV) [13] are considerably lower than the IP of ammonia (10.15 eV) or hydrazine (8.74 eV) [14]. This may constitute evidence that the oxidation potentials presented in Table 1 for 1-aminoindole, 1-aminobenzimidazoles, and 7- and 9-aminotheophyllines characterize the ease of detachment of an electron from the heterocyclic ring, most likely from the π orbital [12].

The literature contains no data on the ionization potential of indazole. Using the IP_1 of benzimidazole, imidazole (8.67 eV), and pyrazole (9.15 eV) [12], by extrapolation we obtain an IP_1 for indazole of ∿8.6 eV. Thus for both amines IX and X in the case of electrochemical oxidation the electron is most likely removed from the π orbital of the ring.

TABLE 3. Electronic Absorption Spectra of N-Methyl- and N-Aminobenzazoles (in methanol)

Compound	λ_{max}, nm (lg ε)
1-Methylbenzimidazole	248 (3,28), 254 (3,29), 267 (3,12), 274 (3,20), 282 (3,19)
1-Aminobenzimidazole (I)	249 (3,81), 266 (3,73), 273 (3,78), 279 (3,70)
1-Methylindazole	256 (3,71), 262 (3,70), 286* (3,79), 292 (3,85), 295 (3,83)
1-Aminoindazole (IX)	256 (3,55), 262 (3,53), 286* (3,60), 293 (3,66), 304* (3,53)
2-Methylindazole	273 (3,71), 291 (3,68)
2-Aminoindazole (X)	276 (3,83), 290 (3,81)
7-Aminotheophylline	272 (3,91)
7-Aminotheophylline (XI)	272 (4,11)
9-Methyltheophylline	239 (3,95), 268 (4,01)
9-Aminotheophylline (XII)	240 (3,85), 266 (3,94)

*Shoulder.

According to the data in Table 1, 1-aminoindole (E_{pa} = 0.95 V) undergoes electrochemical oxidation most readily. The oxidation potentials of the N-amino derivatives of benzimidazole, theophylline, and 2H-indazole are ∿1.4 V and differ little from one another (one exception that is not completely understood is 1-aminoindazole, for which E_{pa} = 1.12 V). These values correspond, in general, to the relative π-donor character of these heteroaromatic systems and do not contradict the assumption made above that the electron is detached from the π orbital in the oxidation of N-aminobenzazoles.

On comparing the relative oxidation potentials of N-amino- and N-methylbenzazoles one's attention is directed to the fact that the N-amino group decreases the E_{pa} value by an average of 0.2 to 0.25 V. This is evidently explained by the existence of slight overlapping of the π orbitals of the heteroring with the unshared electron pair of the nitrogen atom of the amino group, which should promote a certain degree of stabilization of the cation radical formed in the oxidation.

The oxidation potentials of N-aminobenzimidazoles III–VIII vary in correspondence with the electronic nature of the substituents. In particular, 1,2-diaminobenzimidazoles IV–VI are oxidized particularly easily; this is in agreement with the known very strong + M effect of the 2-amino group in the benzimidazole series. In the case of XIII and XIV it is apparent that the effect of an N-dimethylamino group on the oxidation potentials of the investigated heterosystems is approximately the same as the effect of the unsubstituted N-amino group.

EXPERIMENTAL

The basicity constants wre measured by potentiometric titration in acetonitrile by the method in [15]. The NH acidities were measured in 1,2-dimethoxyethane (DME) at 20°C by the method in [7]. The cyclical voltamperograms were recorded with a P 5827 M potentiostat with a source of triangular pulses [16] at a frequency of 0.1 Hz on a platinum electrode with a diameter of 2 mm. The inert electrolyte was 0.1 M tetraethylammonium perchlorate, and the reference electrode was an aqueous saturated calomel electrode with an asbestos–aluminum hydroxide diaphragm [17]. The depolarizer concentration was $5 \cdot 10^{-3}$ mole/liter. The IR spectra of solutions in chloroform were recorded with a UR-20 spectrometer. The UV spectra of solutions in methanol were obtained with a Specord M 40 spectrophotometer. The PMR spectra were obtained with a Tesla BS-487 spectrophotometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The results of elementary analysis for C, H, and N were in agreement with the calculated values.

1-Aminobenzimidazole (II). A solution of 20 g (0.16 mole) of 95% hydroxylamine-O-sulfonic acid (HASA) in 50 ml of water neutralized with dry $NaHCO_3$* was added in portions in the course of 3-5 min at 40-45°C to a solution of 11.8 g (0.1 mole) of benzimidazole and 16.8 g (0.3 mole) of KOH in 80 ml of water. The reaction is very exothermic, and the reaction is therefore carried out by cooling the flask with a cold-water bath. After 5-10 min, a colorless precipitate began to come out of the solution. The mixture was stirred for 30 min at 50-55°C and cooled, and the precipitate was removed by filtration and washed with

*One must neutralize the HASA very rapidly, and the resulting solution must be used without delay, since the sodium salt of this acid decomposes rapidly.

cold water to give 10.6 g (80%) of colorless needles with mp 156-157°C (from water), in agreement with the data in [18].

1-Amino-2-dimethylaminobenzimidazole (VI, $C_9H_{12}N_4$). A solution of 2.13 g (0.01 mole) of 1-aminobenzimidazole-2-sulfonic acid [19] and 10 ml of a 33% aqueous solution of dimethylamine was heated at 140°C for 4 h, after which it was cooled and treated with 50 ml of water. The precipitate was removed by filtration to give 0.95 g (54%) of colorless leaflets with mp 141-142°C (from water). IR spectrum: 1585, 1620, 3220, 3370 cm^{-1} (NH_2). UV spectrum, λ_{max} (log ε): 255 (4.36), 289 (4.39).

1-Amino-2-chlorobenzimidazole (VII, $C_7H_6ClN_3$). A solution of the sodium salt of HASA, obtained by neutralization of 4 g (0.032 mole) of HASA with sodium bicarbonate in 10 ml of water, was added in portions in the course of 2-3 min at 60-70°C to a solution of 3 g (0.02 mole) of 2-chlorobenzimidazole and 3.5 g (0.05 mole) of KOH in 20 ml of water, after which the mixture was stirred with spontaneous cooling for 20 min, and chromatographically pure precipitated amine VII was removed by filtration at 30°C. The yield was 0.8 g (24%). The colorless needles had mp 132-133°C (from water). IR spectrum: 3385 cm^{-1} (NH_2). UV spectrum, λ_{max} (log ε): 249 (3.93), 275 (3.97), 280 (3.84). Neutralization of the filtrate gave 2.05 g (67%) of the starting compound.

7-Dimethylaminotheophylline (XIII, $C_9H_{13}N_5O_2$). A suspension of 3.0 g (0.015 mole) of 7-aminotheophylline [20] in 10 ml (0.16 mole) of methyl iodide and 20 ml of alcohol was heated in a sealed ampul for 3 h at 100-110°C, after which the dark-red solution was evaporated, and the residue was triturated with acetone to give 1.07 g (25%) of product. The latter was purified by chromatography with a column packed with Al_2O_3 (elution with chloroform) with collection of the first fraction in the form of colorless crystals with mp 199-200°C (from alcohol). IR spectrum: 1680, 1725 (C=O), 3145 cm^{-1} (C_8–H). PMR spectrum ($CDCl_3$): 3.01 [6H, s, $N(CH_3)_2$], 3.40 (3H, s, N_1–CH_3), 3.54 (3H, s, N_3–CH_3), 7.65 ppm (1H, s, 8-H).

1-Dimethylaminobenzimidazole (XIV, $C_9H_{10}N_3$). A 4-g (0.03 mole) sample of amine II was added at −70°C to a solution of potassium amide obtained from 2.5 g (0.064 mole) of potassium in 50 ml of liquid ammonia at −70°C, and 4.0 ml (0.06 mole) of methyl iodide was added dropwise after 20 min. The mixture was stirred for 30 min at −70°C, the ammonia was evaporated (2 h 30 min), and the oily residue was extracted with chloroform (three 30-ml portions) and purified by chromatography with a column packed with Al_2O_3 (elution with chloroform) with collection of the fraction with R_f 0.6. The chloroform was removed by distillation under reduced pressure, and the residual yellowish oil was dried in vacuo over KOH to give 2.5 g (52%) of a product with n_D 1.485. UV spectrum, λ_{max} (log ε): 213 (4.16), 249 (3.45), 287 nm (3.44). PMR spectrum (CCl_4): 2.96 [6H, s, $N(CH_3)_2$], 7.06 (2H, q, 5,6-H), 7.35 (1H, m, 4-H), 7.60 (1H, m, 7-H) and 7.87 ppm (1H, s, 2-H). PMR spectrum (CF_3COOH): 2.57 [6H, s, $N(CH_3)_2$], 7.20 (4H, m, 4-7-HO, 8.55 ppm (1H, s, 2-H).

The hydrazine (99.5%) was obtained by the method in [21], the 1-aminoindole was obtained by the method in [22], the 1-methylindole was obtained by the method in [23], the 1-amino-2-methylbenzimidazole was obtained by the method in [19], the 1-amino-5,6-dimethylbenzimidazole was obtained by the method in [26], the 1-methylbenzimidazole was obtained by the method in [27], the 1-amino- and 2-aminoindazole were obtained by the method in [28], the 1-methyl- and 2-methylindazole were obtained by the method in [29], the 7-aminotheophylline was obtained by the method in [20], the 9-aminotheophylline was obtained by the method in [3], the 7-methyltheophylline was obtained by the method in [30], and the 9-methyltheophylline was obtained by the method in [31].

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