Basicity of azoles
3.* The effect of annelation and substitution on the energy of nonbonding electrons of N-heterocycles

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According to the data of photoelectron spectroscopy, a linear dependence exists between the energies of nonbonding electrons in azoles and azines, on the one hand, and their benzoannelated derivatives, on the other hand. Substituents do not disturb this relationship; those in position 2 of N-heterocycles exert effects of the same type on the ionization potentials of the n-level of 1,3-diazole and pyridine.

Key words: azoles, azines, annelation; substitution; ionization potentials.

In the majority of the present-day papers concerning problems of basicity, the proton affinity (*PA*) or free energy of ionization in a gas ($\Delta G^{o}_{i,g}$) are used as the criteria for studying a selected series of compounds. In general, *PA* characterizes the addition of a proton and, therefore, is determined by the properties of both neutral molecules and cations. This statement can be easily justified in terms of thermodynamic formalism and can be written as the equation

$$PA = \text{const} + HA - IP, \qquad (1)$$

where *HA* is the energy of homolytic cleavage of an H—X bond in a cation (the affinity of the corresponding radical cation for a hydrogen atom), and *IP* is the ionization potential of a free base. In a narrow series of related compounds, Eq. (1) acquires a simpler form[2—5]

$$PA = a - bIP. \qquad (2)$$

This means that *HA* is either a constant characterizing the series ($b = 1$) or a linear function of *IP* or *PA* ($b < 1$).

The question arises as to whether the general and specific features observed for *PA* in a series of related bases holds for the *IP* values. To elucidate this, we considered the effect of annelation of nitrogen-containing heteroaromatic compounds (N-heterocycles) with an unsaturated carbocycle. The addition of a fused benzene ring to this type of organic σ-base is accompanied by an increase in *PA* (decrease in $\Delta G^{o}_{i,g}$); the *PA* ($\Delta G^{o}_{i,g}$) values of the starting compounds and their benzologs are related to each other by a linear dependence. The former of the above-mentioned regularities holds no matter which particular bond of the N-containing ring (*a*, *b*, or *c*) is involved in the annelation.[6,7] The latter has been established so far only for azoles,[7,8] however, it might be expected that a similar relationship would also be revealed for azines. This is also supported by the data presented by us that the effects of substituents on the energies of nonbonding electrons in pyridine and benzimidazole are of the same type.

Experimental

The photoelectron spectra of 1,3-diazoles were recorded on an ES-3201 electron spectrometer. The resonance radiation of He^{I} (21.21 eV) was used for excitation. The energy scale was calibrated using the first ionization potentials of Ar (15.76 eV) and chlorobenzene (9.06 eV). The error in the determination of the positions of the resolved bands was 0.05 eV. Full data on the orbital structure of the 1,3-diazoles under consideration obtained by photoelectron spectroscopy and by calculation of the single-particle Green function in the AM1 semiempirical approximation will be published in a separate communication.

Results and Discussion

The relationship of the *IP* values of five- and six-membered N-heterocyclic compounds (B) with the ionization potentials of annelated derivatives (BzB) presented in Fig. 1 is described by a linear function. The regression equation deduced from IP_n of bases for compounds **1—19** (Table 1) except compound **4** is written as follows:

$$IP_n(\text{BzB}) = 0.995\ IP_n(\text{B}) - 0.24\ (\text{eV}), \qquad (3)$$
$$n = 18,\ r = 0.993.$$

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* For part 2, see Ref. 1.

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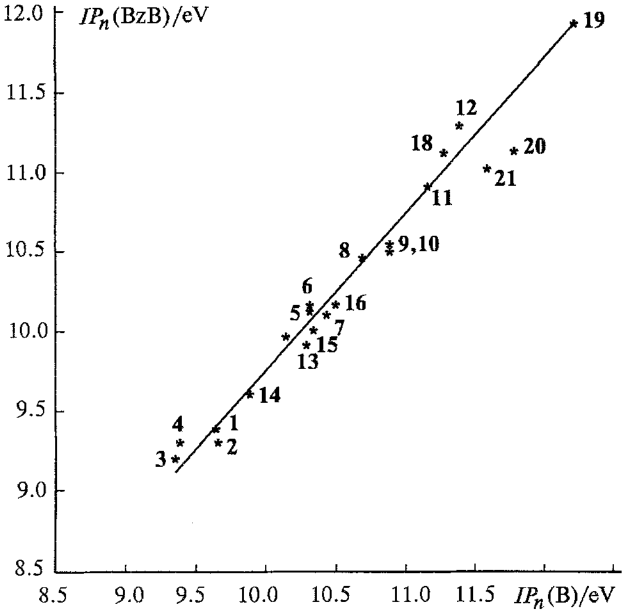
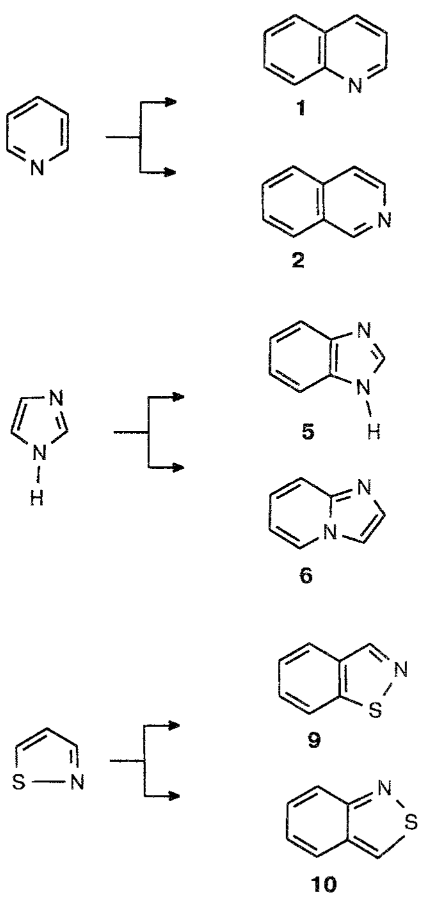


Fig. 1. The effect of annelation on the energies of the nonbonding electrons of azoles. The numbering of points corresponds to the numbers of compounds in Table 1.

Scheme 1



The results of the analysis of the chemical structure of compounds whose IP_n follow Eq. (3) indicate that the effect of annelation ($\delta_{an}IP_n$) depends neither on the number of atoms in the starting N-containing ring nor on the nature of these atoms, nor does it depend on which bond attach the unsaturated moieties to one another (Scheme 1).

Table 1. The energies of abstraction of nonbonding electrons from simplest N-heterocycles and their derivatives fused with a benzene ring

Azine, azole	$IP_n{}^a$ /eV	Benzolog	$IP_n{}^a$ /eV
Pyridine	9.66	Quinoline (**1**)	9.39
Pyridine	9.66	Isoquinoline (**2**)	9.3
Quinoline	9.39	Acridine (**3**)	9.20
Quinoline	9.39	Phenanthridine (**4**)	9.30
Imidazole	10.33	Benzimidazole (**5**)	10.12
Imidazole	10.33	Imidazo[1,2-*a*]pyridine (**6**)	10.1
Thiazole	10.45	Benzothiazole (**7**)	10.1
Pyrazole	10.70	1*H*-Indazole (**8**)	10.45
Isothiazole	10.90	1,2-Benzisothiazole (**9**)	10.53
Isothiazole	10.90	2,1-Benzisothiazole (**10**)	10.50
Oxazole	11.19	Benzoxazole (**11**)	10.9[b]
Isoxazole	11.4	1,2-Benzisoxazole (**12**)	11.27
1,2-Diazine	10.3[c]	Cinnoline (**13**)	9.9[c]
Cinnoline	9.9[c]	Benzo[*c*]cinnoline (**14**)	9.6[c]
1,3-Diazine	10.35[c]	Quinazoline (**15**)	10.0[c]
1,4-Diazine	10.5[c]	Quinoxaline (**16**)	10.15[c]
Quinoxaline	10.15[c]	Phenazine (**17**)	9.95[c]
1,2,3-Thiadiazole	11.3[c]	1,2,3-Benzothiadiazole (**18**)	11.1[c]
1,2,5-Oxadiazole	12.25[c]	2,1,3-Benzoxadiazole (**19**)	11.9[c]
1,2,5-Thiadiazole	11.8[c]	2,1,3-Benzothiadiazole (**20**)	11.1[c]
2*H*-1,2,3-Triazole	11.5[c]	1*H*-1,2,3-Benzotriazole (**21**)	11.0[c]

[a] Literature data[10—16]. [b] Data of the present work. [c] The mean ionization potential of two n_N-levels.

Thus, when a fused benzene ring (rings) is attached to an unsaturated σ-base, the energy of the nonbonding electrons is virtually insensitive to the π-electronic structure of the molecular system. It should be noted that the angular coefficients in Eq. (3) are similar to those in the expressions describing the relationship between the *PA* [7] and $G^0{}_{i,g}$ [8] of azoles:

$$PA(\mathrm{BzB}) = 0.93\ PA(\mathrm{B}) + 17.7\ (\mathrm{kcal\ mol^{-1}}), \quad (4)$$

$$\Delta[\Delta G(\mathrm{BzB})] = -0.96\Delta[\Delta G(\mathrm{B})] - 2.5\ (\mathrm{kcal\ mol^{-1}}). \quad (5)$$

Therefore, the linear dependence between the *PA* of N-heterocycles and their benzologs is qualitatively and quantitatively caused by the fact that a similar correlation exists for the energy of the nonbonding electrons of free σ-bases; the latter correlation (see below) involves fewer details and hence, is more general.

Unlike ionization potentials, the variation of the degree of proton affinity resulting from annelation of an N-containing ring with a benzene ring depends considerably on the above-listed structural factors. In fact, it has been found previously[7] that $\delta_{an}PA$ associated with

Table 2. The effect of annelation on the IP_n values of substituted azoles and pyridines

Azine, azole	$IP_n{}^a$ /eV	Benzolog	$IP_n{}^a$ /eV
4-Ethoxypyridine	9.6	4-Ethoxyquinoline (**22**)	9.3
1,5-Dimethylpyrazole	10.27	2,3-Dimethylindazole (**23**)	9.80
1-Ethylpyrazole	10.46	2-Ethylindazole (**24**)	10.0
1-Methylpyrazole	10.54	2-Methylindazole (**25**)	10.24
1-Methylpyrazole	10.54	1-Methylindazole (**26**)	10.15
1-Vinylpyrazole	10.71	1-Vinylindazole (**27**)	10.45
2,3-Dimethylpyridine	9.15	2,3-Dimethylquinoline (**28**)	9.11
2-Ethoxypyridine	9.64	2-Ethoxyquinoline (**29**)	9.6
2-Methyl-1-ethylimidazole	9.52[b]	2-Methyl-1-ethylbenzimidazole (**30**)	9.54[b]
1,2-Dimethylimidazole	9.79	1,2-Dimethylbenzimidazole (**31**)	9.68[b]
2-Methyl-1-vinylimidazole	9.81	2-Methyl-1-vinylbenzimidazole (**32**)	9.9
1-Ethylimidazole	9.85	1-Ethylbenzimidazole (**33**)	9.83
1-Methylimidazole	9.9	1-Methylbenzimidazole (**34**)	9.93
1-Vinylimidazole	10.10	1-Vinylbenzimidazole (**35**)	10.15
1-Acetylimidazole	10.9	1-Acetylbenzimidazole (**36**)	10.84

[a] Literature data[10,13,17]. [b] Data of the present work.

the transition from *N*-methylpyrazole to 2-methylindazole is much greater than would have been expected from Eq. (4). It is believed that this discrepancy is due to the fact that the set of compounds (see Table 1) is not complete and due to differences in the manifestation of the effect under consideration in the series of the simplest N-heterocyclic compounds and their derivatives.

In this connection, it seemed necessary to consider the regularities of the effect of annelation on IP_n of substituted azoles and pyridines (Table 2). Fusion of these bases with a benzene ring showed that according to the $\delta_{an}IP$ values they may be divided into two similar subgroups: substituted 1,2-diazoles and 1,3-diazoles. From the limited data on pyridines (see Table 2), one may infer that they are probably also divided into two subgroups, *viz.*, 2(3)- and 4-substituted pyridines.

The ionization potentials of substituted pyrazoles, 4-ethoxypyridine, and their benzologs obey the relationship

$$IP_n(\mathrm{BzB}) = 0.993\ IP_n(\mathrm{B}) - 0.29\ (\mathrm{eV}),$$

which differs insignificantly from Eq. (3). With the aid of dispersion analysis we found that the previously discussed N-heterocyclic compounds, substituted 1,2-diazoles and 4-substituted pyridine and quinoline, should in fact be treated as a uniform group of free σ-bases. This unification does not disturb the rather high accuracy of the correlation between IP_n:

$$IP_n(\mathrm{BzB}) = 1.002\ IP_n(\mathrm{B}) - 0.33\ (\mathrm{eV}),\quad n = 24,\ r = 0.991. \tag{6}$$

The angular coefficient of the general relationship (6) practically coincided with the angular coefficient (1.009)[7] of the correlation between pK_{H_2O} of a wide series of five-membered heterocycles, their benzologs, and derivatives. A peculiar feature of the two latter correlations is that the basicity of benzazole with the "quinoid" structure in an aqueous solution or in the gaseous phase does not follow the regularity found for compounds of the "benzoid" type.[7]

Taking into account the fact that the $\delta_{an}IP_n$ values are constant for the N-heterocycles listed, we attempted to apply the relationships that hold for *PA* and pK_{H_2O} of azoles directly to the description of the effect of annelation on the basicity of azines in the gaseous and liquid phases.[6,9] However, in both cases, this attempt was unsuccessful. Furthermore, according to the reported data,[9] the determination of the liquid-phase basicity of azines is complicated by the fact that fusion with one or two benzene fragments exerts a clearly nonadditive effect on the pK_{BH^+} value; this effect is also dependent on the final structure of the benzolog.[9] However, this was not observed (except for compound **4**) for the IP_n values. Thus, the regularities of the variation of the basicity of N-heterocyclic compounds resulting from their annelation with a benzene ring (or rings) cannot be completely determined by the properties of the free molecules and, therefore, their description requires invoking the data on the corresponding cations.

An examination of IP_n of substituted 1,3-diazoles leads one to the same conclusion. The ionization potentials of these compounds and of 2(3)-substituted derivatives of pyridine and quinoline obey the following linear equation:

$$IP_n(\mathrm{BzB}) = 0.991IP_n(\mathrm{B}) + 0.08\ (\mathrm{eV}),\ n = 9,\ r = 0.991. \tag{7}$$

The constant term of this equation differs from that of Eq. (3) (or (6)) in magnitude and sign. In principle, this may result from the fact that we use vertical, rather than adiabatic, ionization potentials due to the normally poor resolution of the photoelectron band assigned to n_N-MO.

However, the characteristics of the photoelectron spectra of substituted *N*-alkylbenzimidazoles (Alk =

Table 3. Vertical energies (eV) of the abstraction of nonbonding electrons from 2-substituted pyridines and benzimidazoles

Substituent	Py[a]	BzIm[b]	1-MeBzIm[c]
Me	9.4	9.86[c]	9.68
Ph	9.41	9.8	—
SMe	9.56	9.9	9.8
NH_2	9.6	10.0[c]	9.82
OEt_2	9.64	9.96[c]	—
H	9.66	~10.12	9.93
Cl	10.1	~10.5	10.29
CN	10.4	—	10.57
OMe	9.82	—	10.0

[a] Literature data[10,18,19]. [b] Data of the present work. [c] Literature data[10,20].

1,2-Me_2, 1,2-Et_2, 1-Et-2-Me, 1-Me-2-Et), in which the band in question is resolved and has a fine structure, make it possible to say with confidence that the shift in the regression lines caused by this factor must not exceed 0.15 eV (the shift observed in the achieved region of IP_n variation is ~0.3 eV). This is probably due to the fact that the effect of substitution somehow balances the effect of annelation. The slight influence of fused benzene rings on the ionization potentials of 2-substituted pyridines (see Table 2) is apparently due to the same fact. It is of interest that the IP_n(B) and IP_n(BzB) values for compound **4** also obey Eq. (7).

No matter what the detailed mechanism of the phenomenon observed may be, this phenomenon does not disturb the linear correlations between both IP_n and PA values. According to the data available,[7,8] there is no need to distinguish *N*-substituted 1,3-diazoles on the basis of the effect of annelation on their gas-phase or liquid-phase basicity. Thus, in the case of a limited array of bases, the properties of the cations derived from these diazoles do not reflect the differences in the properties of the free molecules.

It should be noted that relationship (3) is unsuitable for the description of $\delta_{an}IP_n$ for compounds like **20** (see Table 1). The variations in the structures of thiadiazoles **20** formally correspond to the transition from one stable tautomeric form to the other. Therefore, if annelation essentially disrupts the tautomeric equilibrium of each molecular system, this will result in the deviation of the observed IP_n(BzB) value from that predicted by Eq. (3). These deviations are in fact observed for tautomers of triazoles **21** (see Table 1).

In order to gain additional evidence that a correlation between PA of azines and benzologs exists, we analyzed the relationships between the ionization potentials of the n_N-levels of 2-substituted pyridines and benzimidazoles (Table 3). The following linear equations were found:

$$IP_n(\text{BzIm}) = 0.984\ IP_n(\text{Py}) + 0.52\ (\text{eV}),\ n = 7,\ r = 0.99;$$

$$IP_n(\text{1-R-BzIm}) = 0.913\ IP_n(\text{Py}) + 1.03\ (\text{eV}),\ n = 7,\ r = 0.99.$$

From these relationships it follows that azines, like azoles, tend to undergo normal annelation and the basicity of azines is more sensitive to a substituent in position 2 than that of 1,3-diazoles.

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