THE NATURE OF THE INTERACTION BETWEEN THE PHENYL AND IMIDAZOLE RINGS IN N-ARYLIMIDAZOLES.

IV. N-Phenylimidazoles with Substituents in the Benzene Ring*.

A. F. Pozharskii, L. M. Sitkina, A. M. Simonov, and T. N. Chegolya

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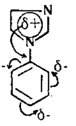
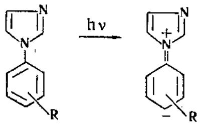
The interaction between the imidazole ring and substituents in the benzene ring in some N-arylimidazoles is examined with the aid of dipole moments, UV spectra, ionization constants, and rate constants for the Menshutkin reaction.

It has been shown previously that in N-phenylimidazole (I) there is a weak but definite interaction between the π-electron systems of the imidazole and benzene rings, resulting in a displacement of π-electron density in the direction of the latter (IA) [1–5].



IA



II III

This interaction affects the physical properties of the molecule of I, and the reactivity of the rings concerned. For example, I is less basic than N-alkyl(aralkyl)imidazoles, and undergoes the Menshutkin reaction with greater difficulty [3]. The very smooth nitration of I to 1-p-nitrophenylimidazole (**IIb**) [6] shows that the N-imidazolyl group possesses ortho-para orienting properties; π, π-conjugation of the phenyl and N-imidazolyl groups also appears in the dipole moments [1] and electronic absorption spectra [2, 5], and it is well known by molecular orbital calculations [4].

Our work has recently resulted in N-arylimidazoles of type II becoming readily accessible [7, 8]. This has enabled us to investigate further the mutual effects of the aryl and N-imidazolyl radicals, and to focus attention on the nature of the electron transfer effects between the substituents R in II, and the imidazole ring. The results are given in the present paper.

a) UV Spectra. In contrast to imidazole and its 1-alkyl derivatives, which do not absorb higher than 210–215 nm, the UV spectra of I are composed of two absorption bands; one intense band at short wavelength in the 240 nm region, and a low intensity band at long wavelength in the region of 260 nm. As in other substituted benzenes [9], the short wavelength band is assigned to the electron transfer involving both rings (the K-band), and the long wavelength band is associated with the forbidden B-band of benzene [2]. Some authors assign the K-band in N-phenylazoles to an aniline-like shift of type II → **III**. It appears, however, to be more correct to regard it as the result of the interaction of the π-electron system of the benzene ring with all the π-electron systems of the heterocyclic residue (IA), and not merely with the p-electrons of the pyrrole nitrogen atom [4, 5].

The results for II are given in Table 1. The introduction of electron-accepting substituents (p-NO_2, p-CHO, p-$COCH_3$) into the benzene ring of N-phenyl imidazole results in a marked bathochromic shift of the 240 nm band, with the result that it becomes superimposed on the B-band, and the latter does not appear in the spectrum. This indicates appreciable conjugation of the substituents R in **IIb–IId** (Table 1) with the N-imidazolyl group, which consequently assumes an electron-donor character (for example, **IIIb**).

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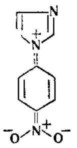
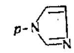
*For part III, see [3].



IIIb

The absolute values of this bathochromic shift in a series of imidazoles are, however, about 2.5 times less than in a corresponding series of dimethylanilines (Table 2). This is not surprising, since internal conjugation of the π-electrons in the imidazole ring reduces its ability to participate in conjugation with the π-electrons of the substituents.

Table 1. UV Spectra of N-Arylimidazoles (II)

Compound	R	K-Band		B-Band	
		λ_{max}, nm	lg ε	λ_{max}, nm	lg ε
IIa	H	238	3.93	264*	3.27
IIb	p-NO_2	295	4.08	—	—
IIc	p-CHO	276	4.25	—	—
IId	p-$COCH_3$	270	4.20	—	—
IIe	p- 	256	4.28	—	—
		Does not absorb above 220 nm			
IIf	o-CH_3	239	4.06	260*	3.66
IIg	m-CH_3	241	4.09	280*	3.32
IIh	p-OCH_3	238	4.05	278*	3.34
IIj	p-OH	236*	3.96	282	3.60
IIk	m-OH	232*	3.79	281	3.66
IIl	o-OH	245	4.19	—	—
IIm	p-Br				

*Shoulder

Introduction of electron-donor groups (OH, CH_3O, Br, CH_3) into the 1-phenylimidazole molecule has little effect on the position of the K-band. It is well known that the presence in the benzene ring of two substituents of a single type (noncomplementary) does not substantially affect the UV spectrum in comparison with that of the mono-substituted compound. Thus, in compounds IIf–IIm, the imidazolyl group behaves as an electron donor. In IIf, the K-band undergoes a substantial bathochromic shift as a result of the distortion of the coplanarity of the molecule.

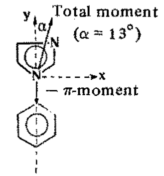
Table 2. Values of the Bathochromic Shift in the K-band (in mm) in p-Substituted Dimethylanilines ($\Delta\lambda_1$) and N-Phenylimidazoles ($\Delta\lambda_2$)

Substituent	$\Delta\lambda_1$[10]	$\Delta\lambda_2$	Ratio $\Delta\lambda_1/\Delta\lambda_2$
p-NO_2	+140	+57	2.46
p-CHO	+ 92	+38	2.42
p-$COCH_3$	+ 87	+32	2.72

The UV spectrum of IIe is of interest. The large bathochromic shift (+ 18 nm) of the K-band in comparison with the spectrum of I is due to the increased length of the conjugated chain in this compound. This is possible only if the second N-imidazolyl group assumes the unusual character of an electron-accepter (IIIe).

IIIe

b) **Dipole Moments.** The conjugational interaction of the rings in N-phenylimidazole results in the appearance of an increased π-moment directed along the $N-C_6H_5$ axis toward the phenyl group [1]. This π-moment, whose value was estimated to be 0.68 D, was calculated from the moment of the imidazole ring, which is accompanied by a reduction in the dipole moment of N-phenylimidazole in comparison with imidazole itself, and with its 1-alkyl derivatives. It was estimated that the total vector dipole moment of N-phenylimidazole is directed at an angle of 13° to the axis passing through the N_1-atom of the heterocycle and the p-carbon atom of the phenyl group (IV) [4].



IV

In this connection, it was interesting to examine the effect of the substituents R in **II** on the magnitude of the dipole moment of this molecule.

Table 3. Dipole Moments of N-Arylimidazoles (in Debye units) at 25°

Compound	R in II	Solvent	μ_{exp}	μ_{calc}
IIa	H	Benzene	3.50	3.52*
IIn	p-CH_3	"	3.90	3.86
IIg	m-CH_3	"	3.73	3.70 (3.76; 3.62)**
IIf	o-CH_3***	"	3.79	3.68 (3.76; 3.61)**
IIm	p-Br	"	2.20	2.01
IIj	p-OH	Dioxan	5.48	5.25
IId	p-$COCH_3$	Benzene	2.89	270 (2.01; 3.25)**
IIb	p-NO_2	Dioxan	1.55	1.00
IIo	m-NO_2	"	3.63	3.84 (3.04; 4.50)**

*Theoretical value, from molecular orbital calculations.

**The values in parentheses are those calculated for conformations A and B, respectively.

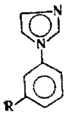
***The dipole moment of 1-phenyl-2-methylimidazole (4.19 D in benzene) was also measured. The theoretical value is 3.90 D.

Our experimental values for the dipole moments (Table 3) were compared with those calculated by the vector method. In the calculations, the N-arylimidazoles were regarded as planar, disubstitued benzenes, and their moments were calculated by the formula:

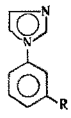
$$\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta)^{1/2},$$

where μ_1 is the dipole moment of 1-phenylimidazole (+3.50 D); μ_2 is the moment of the C_{ar}—R bond, taken to be equal to the moment of the corresponding monosubstituted benzene [11]; $\mu(C_6H_5\text{—}CH_3) = +0.37$ D; $\mu(C_6H_5\text{—}Br) = -1.57$D; $\mu(C_6H_5OH) = +1.78$D; $\mu(C_6H_5COCH_3) = -2.8$D, directed at an angle of 132° to the C_6H_5—R axis [12]; $\mu(C_6H_5\text{—}NO_2) = -4.03$D; θ is the angle between the vectors of the dipole moments of the substituents R and the imidazole residue.

Since the vector of the moment of 1-phenylimidazole is somewhat inclined to the N—Ph axis in the direction of the pyridine nitrogen atom, for compounds II substituted in the ortho and meta positions of the benzene ring, we took into account the nonequivalence of conformations A and B.



A



B

The total moments for these compounds were calculated from the formula:

$$\mu = \left(\frac{\mu_A^2 + \mu_B^2}{2}\right)^{1/2},$$

where μ_A and μ_B are the dipole moments of the conformations A and B. In 1-phenyl-2-methylimidazole and 1-(o-tolyl)imidazole, disturbance of the coplanarity of the molecule makes it necessary to reduce the value of the additional π-moment, according to Braude's law $\Delta\mu_{inter} = \Delta\mu_{inter}^0 \cos^2\theta$. Consequently, in calculating the vector dipole moments of these compounds, we introduced into the moment of 1-phenylimidazole the corresponding correction with a positive sign (+0.36 D), taking $\Delta\mu_{inter}^0 = 0.68$ D, $\theta = 46°$ (the angle of deflection of the phenyl group with respect to the N—Ph bond [5]).

A good correlation is observed, for most of the compounds, between the experimental values for the dipole moments and the vector values, thus confirming the validity of our assumptions concerning the direction of the total vector dipole moment of the imidazole ring. The results also indicate that the interaction of the substituents R with the imidazole ring in **II** is only weak. In those cases where the interaction is strong, as for example in 1-p-nitrophenylimidazole, a marked divergence is observed between μ_{exp} and μ_{calc}. This is explained by polarization of the imidazole ring, and the change in its dipole moment resulting from direct polar conjugation with the nitro group (**IIIb**).

Table 4. Ionization Constants (pK_a) and Reaction Constants with Ethyl Iodide (k) of N-Arylimidazoles

Compound	pK_a	$k \times 10^6$ ($l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$)	(Mach-Danielli and Brown)
IIa	5.10	15.7	0
IIj	5.35	22.6	−0.37
IIk	5.23	19.6	−0.268
IIn	5.24	19.0	−0.170
IIg	5.24	16.9	−0.069
IIm	4.91	11.0	+0.232
IId	4.54	10.8	+0.502
IIb	3.96	7.8	+0.778

c) **Reactivity of the pyridine N-atom.** Conjugation of the π-systems of the phenyl and imidazole rings in 1-phenylimidazole, as has already been point out, leads to a decrease in the basicity of the imidazole ring. The introduction of electron-donor substituents into the benzene ring of 1-phenylimidazole causes a modest increase in the basicity of the pyridine nitrogen atom, while electron-accepting substituents result in a decrease in basicity (Table 4). A satisfactory correlation exists between the σ-constants (Mach-Danielli and Brown) of electron-donor and weak electron-acceptor (e.g., Br) groups, and the values of the ionization constants. The relatively low values for the reaction constant $\rho(+0.753)$ indicates, however, the weakness of the electron transfer effects from the substituent R to the pyridine nitrogen atom in **II**. Strongly electron-accepting groups (p-NO_2 and p-$COCH_3$) behave as if their respective σ values were significantly greater than normal, viz., +1.25 and +0.65, respectively. These values are close to those for the σ- constant (1.27 for p-NO_2 and 0.87 for $COCH_3$), which itself shows that significant polar conjugation exists between the π-electrons of the heterocycle and the substituent R, **IIIb**, (**IIId**) [13].

The imidazole ring is still less sensitive to the effect of the substituents R in reactions involving alkylation at the pyridine N-atom to give quaternary salts. For the reaction between N-arylimidazoles and ethyl iodide in acetone at 50°, the constant has the general value of −0.395. The low sensitivity of this reaction to the nature of the substituent R results in an equally satisfactory correlation between the rate constants and the σ values, both for electron-donating and electron-accepting groups.

The correlation coefficients r and the standard deviation s are equal to, for the ionization constants, 0.958 and 0.033, and for the quaternization reaction, 0.949 and 0.041, respectively.

These investigations therefore show that the N-imidazolyl group of II usually exhibits electron-donor properties. The nature of the interaction between the imidazole ring and the substituent R depends to a large extent on the nature of the latter. The interaction appears very strongly in compounds with strongly electron-accepting substituents, and less clearly in those compounds where R is electron-donating or weakly electron-accepting.

EXPERIMENTAL

All the starting materials were obtained by direct arylation of imidazole with aryl halides, as described previously [7, 8].

UV Spectra were measured on an SF-4 instrument, in methanol solution. The dipole moments were measured by the resonance method, and the ionization constants (in 50% aqueous ethanol at 20°) and the rate constants for the reaction of the N-arylimidazoles with ethyl iodide (in acetone at 50°) were measured as described in [1, 3].

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Rostov-on-Don State University