σ,π COMPLEXING CAPACITIES OF HETEROAROMATIC COMPOUNDS (REVIEW)*

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The results of experimental studies and quantum-chemical calculations of pyrrole, methylpyridines, and azoles obtained in recent years make it possible to formulate the conditions for the manifestiation of π-complexing capacities by π-deficient compounds and compounds of a similar nature, viz., blocking of the σ-donor center in the case of ortho substitution by alkyl groups and primary H or v bonding.

Ambident ligands are compounds that contain two or more conjugated donor centers. The interest in the study of these compounds was stimulated by solution of the problems of competitive coordination and by the discovery of the conditions that are necessary for the manifestation of one or another donor function [2-4].

Heteroaromatic compounds — ambident cyclic systems that contain two or several potential donor centers — occupy an important position among ambident organic molecules [5-8]. These potential donor centers are the heteroatoms — chiefly elements of the major subgroups of group V and VI elements — and the π systems of primarily five- and six-membered heterorings.

Depending on the number of heteroring electrons, heteroaromatic compounds are divided by the Albert classification [9-11] into two types, viz., π-surplus compounds with a greater number of π electrons in the heteroring than the number of ring atoms (I) and π-deficient compounds, which have a depletion of π electrons (II, III).

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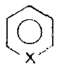

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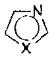

III

I X=O,S,Se,Te,NR,PR,AsR; II X=N,P,As,Sb; III X=O,S,Se,NR

The so-called fundamental heterocycles, viz., furan, thiophene, pyrrole, and their analogs, which are depicted by formula I, are compounds of the first type, whereas azines II are compounds of the second type.

Azoles III should formally be classified as π-surplus systems, since there are six π electrons and five atoms in them. However, as we will demonstrate below, they are more like π-deficient than π-surplus heterocyclic ligands in complexing reactions.

The indicated division was justified not only by different behaviors of π-deficient and π-surplus heterocycles with respect to nucleophilic (for example, sodium amide in the Chichibabin reaction) and electrophilic (for example, diazo coupling and nitration) agents but also, as assumed until recently, by different types of complexing.

In this review we examine the conditions under which π-deficient heteroaromatic ligands and compounds of a similar nature manifest not only the σ(n)-donor function peculiar to them but also π-complexing capacities. In order to arrive at a theoretical substantiation of the different behaviors of π-surplus and π-deficient heteroaromatic ligands we used quantum-chemical calculations to study the distribution of the σ- and π-electron densities in pyrrole, pyridine and its C-methyl-substituted homologs, and azoles (imidazole, pyrazole, and 1,2,4-triazole). The quantum-chemical calculations were made by the PNDO (partial ne-

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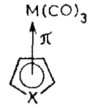
glect of differential overlap) method in connection with the necessity for taking into account the distribution of the σ-electron density, the examination of nonplanar molecules, and the reliable description of the energy characteristics of complexes of ambident ligands. The calculations were made with a BÉSM-6 computer with the aid of the CNINDO program [12, 13]. The optimal geometries of the molecules were found by minimization of the functional of the total energy with respect to all of the natural coordinates of the atoms [14, 15].

π-Surplus Heteroaromatic Ligands

Five-membered monoheterocyclic compounds of the I type act as π-donor ligands [16]. Let us examine individual examples of π complexes of π-surplus heteroaromatic ligands (IV-VI). Among these complexes one should particularly note azoferrocene (V) (X = N); however, it should be emphasized here that σ(n) complexes VI were obtained relatively recently for 2,3,4,5-tetraphenyl-substituted phospholes, arsoles, and stiboles [17]. An enormous number of various complexes of five-membered π-surplus heterosystems have been obtained [3, 16].



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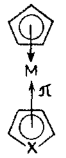

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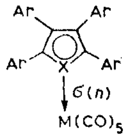
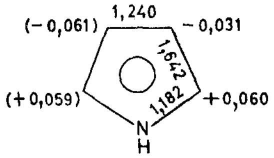


VI

IV X = NR, PR, AsR, SbR, O, S, Se, Te, M = Cr, Mo, W, Mn, Re;
V X = NR, S, M = Fe; VI X = P, As, Sb, M = Cr, Mo, W

Let us examine the σ,π-electron distribution in a π-surplus system, viz., the pyrrole molecule (VII). The π-electron charges are presented in parentheses. It follows from the scheme that the π-electron charges on the carbon atoms in the 3 and 4 positions are negative and are somewhat larger in absolute value than the analogous positive charges in the 2 and 5 positions of the pyrrole ring. Thus the overall π-electron charge in the pyrrole molecule is negative, which is in agreement with its classification as a π-surplus system.



VII

Let us note that the $C_{(2)}$—$C_{(3)}$ bond has the maximum bond order; this constitutes evidence for the manifestation of partially expressed diene character by the pyrrole molecule and for an increased probability of electrophilic attack or protonation at the $C_{(2)}$ or $C_{(3)}$ atoms, as well as coordination with the π heterosystem.

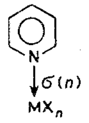
According to calculated data [18], the most stable complex is the 2-protonated complex of pyrrole and N-methylpyrrole. An analysis of the π-bond orders in the protonated forms showed that the degree of conjugation in the ligand increases as a result of complexing. Protonation at the nitrogen atom is less likely than at any of the carbon atoms, despite the negative charge of the nitrogen atom; this is in agreement with the experimental data [19, 20].

The following facts also provide evidence in favor of the preferableness of the π-donor function. In conformity with the assignment of the photoelectronic spectra [21], the high values of the parameters of asymmetry of the ionization bands of the spectrum of pyrrole [22], and the results of calculations with allowance for correlation of the electrons [23], the first and second bands correspond to ionization of the π molecular orbitals. In addition [23], substantial distortion of the unshared pair of electrons of the nitrogen atom was demonstrated under the condition of simultaneous localization of the σ and π orbitals.

In addition, according to Raman spectroscopic data [24], chiefly the pyrrole nitrogen atom participates in complexing with boron trichloride, bromine, and chlorine.

π-Deficient Heteroaromatic Ligands

π-Deficient ligands form primarily σ(n) complexes, i.e., complexes in which the heteroatoms participate [25]. They have been studied in detail in the case of pyridine and other azines (six-membered nitrogen-containing heterocycles such as quinoline, dipyridyl, and phenanthroline) and phosphorus analogs of azines (VIII, IX). Moreover, instances of the formation of π complexes are known for individual π-deficient systems, particularly complexes based on 2,4,6-triphenylphosphabenzene (X) [26].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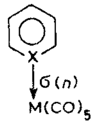
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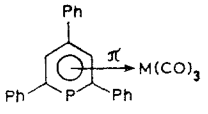
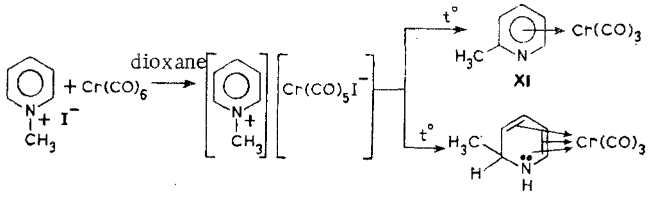

X

However, pyridine and its homologs were firmly considered to be σ(n) ligands, although attempts have been made to obtain complexes with π-bonded pyridine even by such prominent scientists as the Nobel laureate E. O. Fischer.

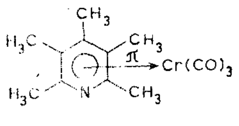
In 1959 Fischer [27] set out, one would think, on the surest path to π bonding of pyridine: By quaternization of the pyridine ring he eliminated the σ(n) donor center in the molecule, after which he obtained a methylpyridinium complex, heating of which yielded a compound corresponding, according to the results of elementary analysis, to complex XI of the tricarbonylchromiumbenzene type. A complex with a "π-bonded pyridine" was thus produced. However, in 1967 Fischer himself [28] demonstrated on the basis of data from the NMR spectrum of the compound that he synthesized that the latter is a π,σ derivative of aminomethylene system XII, which is formed by partial reduction of the pyridine ring during the synthesis.



XI
XII

The firm opinion that pyridine and azines, being π-deficient systems, are exclusively σ(n)-donor ligands was thus formed.

In 1975-1978, Biedermann in West Germany and Lagowski in the USA independently and virtually simultaneously obtained complexes of π-bonded methylpyridines, viz., chromium tricarbonyl complexes of pentamethylpyridine (XIII) [29, 30] and the complete sandwich bis-(2,6-dimethylpyridine)chromium (XIV) [31-33]. The structure of the latter compound was proved indisputably by the results of x-ray diffraction analysis. It was obtained under cryosynthesis conditions in the gas phase [33].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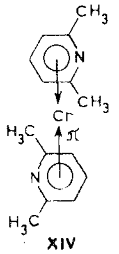

XIV

Anomalies in the donor properties of methylpyridines as compared with other π-deficient systems of the pyridine series were also observed in their reactions with typical v and σ acceptors, viz., metal-containing Lewis acids [34-36] and halogens [34].

The indicated facts led to a re-examination of some previously expressed ideas relative to the π- and σ-donor properties of π-deficient systems. In addition, the problem of the role of methyl groups in the 2 and 6 positions of the pyridine ring in reactions involving donor-acceptor interaction of π(n)-ambident systems of the pyridine series remained unanswered.

We studied the distribution of the π- and σ-electron densities in the pyridine ring and in its methyl-substituted derivatives and, on the basis of this study, explained the donor properties of pyridine systems with respect to Lewis v and σ acids.

TABLE 1. Experimental ($IP_{1,exp}$) and Theoretical ($IP_{1,th}$) Values of the Ionization Potentials of Methylpyridines, pK_a Values in the Gas Phase, and Charges on the Nitrogen Atom

No.	Compound	$IP_{1,exp}$, eV	$IP_{1,th}$, eV	pK_a	q_N
1	Pyridine	9,30	11,43	5,17	−0,197
2	2-Methylpyridine	9,02	11,20	5,97	−0,215
3	3-Methylpyridine	9,04	11,32	—	−0,195
4	4-Methylpyridine	9,04	11,26	—	−0,204
5	2,3-Dimethylpyridine	8,85	11,12	—	−0,213
6	2,4-Dimethylpyridine	8,85	11,03	—	−0,222
7	2,6-Dimethylpyridine	8,85	11,04	6,75	−0,233

TABLE 2. σ- and π-Atomic Populations (P) and Heats of Formation of Complexes of Methyl-Substituted Pyridines with Iodine (ΔH_{I_2}) and with Borane (ΔH_{BH_3})

No.	Molecule	σ-Components		$-\Delta H_{I_2}$, kcal/mole	π-Components		$-\Delta H_{BH_3}$, kcal/mole
		P_s	P_{pz}		P_{px}	P_{py}	
1	Pyridine	1,492	1,073	7,9	1,060	1,570	28,8
2	2-Methylpyridine	1,499	1,096	9,3	1,055	1,564	28,1
3	3-Methylpyridine	1,492	1,064	—	1,064	1,574	29,1
4	4-Methylpyridine	1,492	1,086	7,7	1,057	1,567	29,4
5	2,3-Dimethylpyridine	1,499	1,087	—	1,058	1,568	—
6	2,4-Dimethylpyridine	1,499	1,108	—	1,052	1,562	—
7	2,5-Dimethylpyridine	1,499	1,086	—	1,059	1,568	—
8	2,6-Dimethylpyridine	1,506	1,117	—	1,051	1,557	27,2
9	3,4-Dimethylpyridine	1,492	1,076	—	1,061	1,571	—
10	3,5-Dimethylpyridine	1,492	1,053	—	1,068	1,578	—
11	2,3,4-Trimethylpyridine	1,498	1,099	—	1,056	1,566	—
12	2,3,5-Trimethylpyridine	1,498	1,076	—	1,062	1,572	—
13	2,3,6-Trimethylpyridine	1,506	1,106	—	1,054	1,561	—
14	2,4,6-Trimethylpyridine	1,506	1,129	8,0	1,048	1,555	—
15	3,4,6-Trimethylpyridine	1,500	1,096	—	1,057	1,565	—
16	3,4,5-Trimethylpyridine	1,492	1,065	—	1,065	1,570	—
17	2,3,4,5-Tetramethylpyridine	1,498	1,088	—	1,059	1,569	—
18	2,3,4,6-Tetramethylpyridine	1,506	1,118	—	1,051	1,558	—
19	Pentamethylpyridine	1,506	1,103	—	1,055	1,563	—

To characterize the state of the nitrogen atom responsible for the formation of donor-acceptor complexes of the n(v), n(σ) and n(π) types we used the overall (σ + π) electron charge and the energy of the highest occupied molecular orbital (HOMO). The latter value, taken with the opposite sign, is, according to Koopman's theorem, the ionization potential (IP_1) [37] and may, to a first approximation, characterize the donor properties of the nucleophilic center responsible for coordination. Within the framework of the PNDO method, the IP_1 values, although they turn out to be appreciably overstated [38], accurately convey the relative trend of the change in this characteristic of the donor capacity (Table 1).

The data in Table 1 provide evidence for a symbatic relationship between the experimental [39, 40] and calculated values of the ionization potentials of methylpyridines, as well as the basicity constants in the gas phase (pK_a) [14] and the charges (q_N^{PNDO}) on the nitrogen atom. Consequently, the overall σ + π characteristics correctly reflect the influence of the +I effect of methyl groups on the physicochemical characteristics and donor capacity of the N heteroatom of the pyridine ring.

The steric effect of methyl substituents is observed in a separate examination of the σ and π components (Table 2). Thus, when 2-methyl or 2,6-methyl substituents are present (Table 2, compounds 2 and 8, respectively), a regular increase in the σ population and a decrease in the π population of the nitrogen atom are observed.

The indicated change in the σ and π populations finds confirmation in the experimental data on the heats of formation of σ(I_2) and v(BH_3) complexes (Table 2) taken from [42, 43]. According to the existing classification of donor-acceptor complexes [34, 44], iodine is a σ acceptor. Consequently, as the σ population on the nitrogen atom increases, the heat of formation of the complex of methylpyridine with iodine should also increase, and this is observed experimentally (Table 2). In principle, it would have been more correct to link

TABLE 3. Overall $\sigma(\Sigma\sigma)$- and $\pi(\Sigma\pi)$-Electron Densities of the Nitrogen Atom (N) and the Heteroring (C)*

No.	$\Sigma\sigma^N$	$\Sigma\pi^N$	$\Sigma\sigma^C$	$\Sigma\pi^C$	No.	$\Sigma\sigma^N$	$\Sigma\pi^N$	$\Sigma\sigma^C$	$\Sigma\pi^C$
1	−0,565	−0,630	−0,128	0,424	11	−0,597	−0,622	−0,094	0,378
2	−0,595	−0,619	−0,107	0,408	12	−0,574	−0,634	−0,111	0,388
3	−0,556	−0,638	−0,127	0,421	13	−0,612	−0,615	−0,090	0,377
4	−0,578	−0,624	−0,112	0,408	14	−0,635	−0,603	−0,078	0,370
5	−0,586	−0,626	−0,107	0,397	15	−0,596	−0,622	−0,118	0,380
6	−0,607	−0,614	−0,096	0,386	16	−0,557	−0,635	−0,119	0,390
7	−0,585	−0,627	−0,107	0,398	17	−0,586	−0,628	−0,096	0,427
8	−0,624	−0,609	−0,093	0,392	18	−0,624	−0,609	−0,077	0,354
9	−0,568	−0,632	−0,115	0,440	19	−0,615	−0,618	−0,076	0,343
10	−0,545	−0,646	−0,134	0,411					

*The numbering of the molecules corresponds to the numbering adopted in Table 2.

the population with the energy of formation of the complex rather than with the heat of formation [45]; however, the entropy factor evidently does not play a decisive role in complexing in this series of ligands, as evidenced by the calculated values (Table 2). In contrast to iodine, borane is a v acceptor and gives complexes of the nv type. For borane complexes one should therefore examine the correlation of the heat of formation with the populations of the p_x and p_y orbitals of the nitrogen atom. It is apparent from the data in Table 2 that the populations in the p_x and p_y orbitals decrease in the case of methylpyridines that contain substituents in the ortho positions (compounds 2 and 8) and that the heats of formation of complexes with borane consequently decrease. Whereas in the first case the increase in the heats of formation of complexes with iodine can be explained by the +I effect of the methyl groups, which leads to an increase in the σ population of the nitrogen atom, in the second case the decrease in the heat of formation is associated with the effect of a steric factor that gives rise to a decrease in the π populations of the p_x and p_y orbitals. On the other hand, when methyl groups are absent in the ortho positions (methyl groups in various combinations are located in the 3, 4, and 5 positions), one observes an increase in the π-components and a decrease in the σ components of the atomic populations on the nitrogen atom (Table 2). This result is in agreement with the corresponding data on the heats of formation: The $-\Delta H$ values for the iodine complexes decrease on passing from 2- to 4-picoline (compounds 2 and 4) and increase in the same order in the case of borane complexes. The heat of formation of the iodine complex of 2,4,6-trimethylpyridine (Table 2, compound 14) is in agreement with the discussion presented above and also with the data in [46] from a study of the hydrogen bonding of pyridine and alkylpyridines with phenol by NMR spectroscopy.

The σ- and π-overall electron densities of the nitrogen atom and the heteroring were calculated in order to study the effect of methyl substituents on the change in the distribution of the electron density in the heteroring of methylpyridines as compared with unsubstituted pyridine. The latter may be a sufficiently satisfactory criterion for the evaluation of the manifestation of the π-donor properties of a system. Calculations provide evidence (Table 3) that methyl substituents decrease the π components and increase the σ components of the electron densities of the heteroring carbon atoms, which, as we demonstrated above, should increase the tendency of a nucleophilic system to undergo complexing with v acceptors.

This effect is manifested particularly distinctly in the case of 2-picoline, 2,6-lutidine, and other more complex derivatives for the carbon atoms bonded directly to the pyridine nitrogen atom; it is apparent from the data in Table 4 that an increase in the π components of the atomic populations and a decrease in the σ components are characteristic for these compounds. This effect is not exerted so distinctly on the remaining carbon atoms, but the pattern can be averaged out in the case of perturbation of the corresponding ligands by π acceptors.

Thus the data presented in this review provide evidence that o-methyl substituents decrease the ability of the pyridine ring nitrogen atom to undergo complexing with v acceptors and simultaneously promote an increase in the π-donor capacity of the heteroring. Both of the indicated effects, which include the steric and electronic effect of the o-methyl groups, also explain the successful synthesis of π complexes of six-membered nitrogen heterocycles, viz., methylpyridines [29-33].

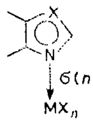
TABLE 4. Atomic Populations at the $C_{(2)}$ Atom

No.	Compound	P_s	P_{pz}	P_{px}	P_{py}
1	Pyridine	1,040	0,961	0,896	0,957
2	2-Methylpyridine	1,024	0,943	0,909	0,968
3	2,6-Dimethylpyridine	1,025	0,936	0,911	0,970

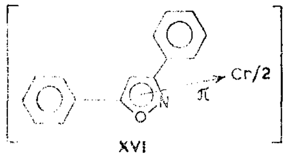
Azoles

We and a number of other researchers have shown in numerous examples that azoles are primarily ligands of the σ(n) type (XV) [6, 47]; in this case acceptors of the v type (halides and other salts of elements of all groups), of the σ type (H donors, halides, and interhalogens), and of the π type (tetracyanoquinodimethane, nitrobenzenes, and chloranil) were used as complexing agents. Acceptors that are extremely inclined to undergo π complexing such as salts of soft platinum metals [48] and hexacarbonyls of Group VI elements [49] were also among them.

However, attempts to obtain π complexes on the basis of azoles were successful. They they were isolated in the case of aryloxazoles (XVI) [50].



XV



XVI

It is known that the stability constants of complexes of azoles with phenols decrease as the difference in the acid-base properties of the partners decreases. Low-basicity benzannelated azoles (benzo- and naphthotriazoles) and, to some degree, triazole, for which the stability constants change antibatically with respect to their basicities but symbatically with respect to the accumulation of benzene rings, which is usually characteristic for π,π complexing, since the π-donor properties are not regulated by the pK_a values of azoles [51, 52], constitute an exception. The pK_a value of triazole and its π-donor capacity are apparently limiting values, inasmuch as both types of interactions are displayed for it, depending on the nature of the phenol. The anomalously high stabilities of H complexes of benz- and naphthannelated azoles vis-à-vis their relatively weak polar properties, which were determined by dielcometry, is explained precisely by π interaction.

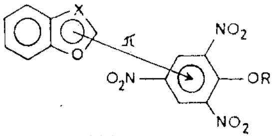
Low-basicity benzannelated azoles also form π,π complexes with trinitroanisole [53]. Structural confirmation for this was obtained in solutions from data on the Kerr effect on the basis of negative deviations from additivity in isomolar series of components. In fact, the dipole moment of the interaction of the components deviates from the plane of the maximum polarizability of the complex only in the case of the sandwich structure of XVII complexes.

π,π Complexing of thiazole with a π acceptor, viz., tetracyanoethylene, was proved by theoretical calculations (see [54] and the literature cited therein).

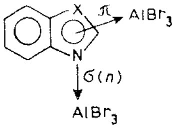
For the same benzannelated azoles, viz., benzothiazole, benzoxazole, and their methyl-substituted derivatives, two compositions in their complexes with aluminum bromide — $L \cdot AlBr_3$ and $L \cdot 2AlBr_3$ — were detected by calorimetry [41]. The heats of formation of these complexes calculated from the experimental data show that the first heat of formation changes symbatically with respect to the basicity of the complex and is close in order of magnitude to the heats for typical n,v complexes with coordination at the nitrogen atom rather than at the bridge heteroatom. However, the heat of formation of the second complex remains approximately constant (61 ± 2 kJ/mole) and coincides with the heat of π,v interaction of typical π donors (substituted benzenes) with aluminum bromide. The close values of the heats of formation of the π,v complexes of azoles with aluminum bromide constitute evidence for approximately identical states of the π systems of the indicated heterocycles. For these complexes the unshared pair of electrons of the pyridine nitrogen atom is blocked by one of the aluminum bromide molecules, and coordination of the second bromide molecule takes place not only with the π system of the heteroring but apparently with the entire branched π system of XVIII, including the annelated aryl ring.

TABLE 5. Theoretical (μ_{th}) and Experimental (μ_{exp}) Dipole Moments of Azoles

Compound	μ_{th}, D	μ_{exp}, D
Pyrazole [55]	2,29	2,21
Imidazole [56]	3,96	3,8±0,4
1,2,4-Triazole [57]	2,73	2,64



XVII



XVIII

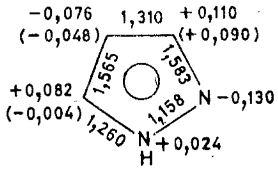
Our quantum-chemical calculations of pyrazole, imidazole, and 1,2,4-triazole made it possible to pose the problem of the possibility of the synthesis of new π complexes, the ligands in which may be ambident azole systems.

The authenticity and sufficient reliability of the calculations can be judged from the closeness of the experimental and theoretical dipole moments (Table 5) and also from the agreement of the regularities of the electron-density distributions in the ligands with the results of known calculations (see, for example, [11, 58]).

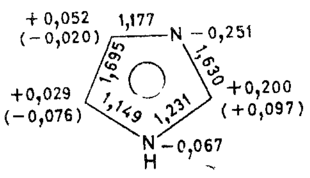
In the Albert classification system azoles occupy an intermediate position that is characterized by the absence of clearly expressed π-surplus or π-deficient character. Heteroatoms of both the pyrrole and pyridine type are included in the compositions of the azole molecules. This is reflected in the nonuniform electron distribution in these molecules [57]. The principles of the change in the charges on the atoms in pyrazole and imidazole are regulated by the π-donor and σ-acceptor properties of the nitrogen atom of the pyrrole type. As a result, this atom bears a low negative or even positive charge. The nitrogen atoms of the pyridine type are characterized by the highest positive charge.

The electron-density distribution in the pyrazole ring (XIX) reflects the peculiar geometrical structure of this heteroring. According to Raman spectral data [59], the plane of symmetry of the pyrazole molecule is perpendicular to the plane of the ring. This fact permits the equivalence of both nitrogen atoms and equal affiliation of the proton with each of them. The two adjacent nitrogen atoms, by virtue of their electronegativities, become a source of a strong negative inductive effect. The carbon atoms adjacent to the nitrogen atom, by experiencing their effect on them, bear a certain excess amount of positive charge [6, 58]. The carbon atom in the 4 position experiences virtually no such effect and is polarized to only a slight extent. As a result, this atom bears a negative overall charge. The results of the calculations show that the equilibrium between the electron-donor capacity of the pyrrole nitrogen atom and the electron-acceptor capacity of the pyridine nitrogen atom is shifted to favor the latter. In conformity with the influence of the mesomeric effect, the highest electron density on the carbon atoms is retained in the 4 position, and the lowest electron density is manifested in the 3 and 5 positions. The same theory is also observed in the case of superimposition of the inductive and mesomeric effects, since the negative effects coincide.

In conformity with this, the overall π charge on the carbon atoms is positive (+0.038), and pyrazole has an overall π deficiency.



XIX



XX

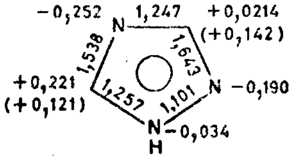
The imidazole ring consists of three carbon atoms and two nitrogen atoms, which form a five-membered ring with two conjugated double bonds [60]. The nitrogen atoms participate differently in π-electron conjugation. One of the nitrogen atoms has a relatively free electron pair and is a nucleophilic center; the other nitrogen atom, which participates in conjugation of the ring system, is characterized by an electron-density deficit. The pyridine nitrogen atom is the center of electrophilic attack. This electron pair can be used for the addition of a proton (to give a conjugate acid) and for the acid of Lewis acids (to give the corresponding complexes).

At the same time, the electron distribution in imidazole (XX) shows that the π-donor effect of the pyrrole nitrogen atom prevails over the σ-acceptor effect of the pyridine nitrogen atom or that these effects compensate one another. This is evidenced by the fact that the π-electron charges on the carbon atoms in the 4 and 5 positions are negative, despite the overall positive charge of all of the carbon atoms. The overall π charge on the carbon atoms is therefore either negative [10] or, as in our calculations, close to zero (+0.001). In this respect, imidazole is of interest as a potential ambident system. In addition, condensed imidazoles, thiazoles, and oxazoles have an overall π deficiency [61].

The problem as to whether azole systems are π-surplus or π-deficient systems can also be solved on the basis of calculations of the radical forms. Ground states of both the π and σ types (XXI) can be examined for 1-imidazolyl and 1-pyrazolyl radicals. It is known [62] that phenyl radicals have an unpaired electron in the σ-type orbital. However, in the case of 1-imidazolyl or 1-pyrazolyl radical there is a possiblity that the π-surplus system (six π electrons for five centers) will give rise to the formation of a radical with π symmetry. The literature data dealing with this problem are extremely contradictory. A study by EPR spectroscopy [63] made it possible to propose that the 1-imidazolyl radical has a $B_1(\pi)$ ground state. On the other hand, on the basis of PNDO calculations [64], a ground state of the σ type is likely for it. The experimental data for the 1-pyrazolyl radical led to the conclusions that it has a σ ground state [65]. Nonempirical calculations of the described radicals in the 4-31G basis, according to which the imidazolyl and pyrazolyl radicals are $B_1(\pi)$ radicals, were performed in [66, 67]. Two low-lying π states (B_1 and A_2) and one σ state are observed. The results show that the 1-pyrazolyl radical may have a rather long life in the σ state and may participate in reactions as a σ radical; this was confirmed experimentally [65]. In the case of the 1-imidazolyl radical, however, the σ state is metastable.

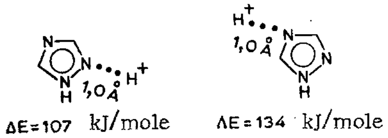
XXI

The character of the electron distribution for the 1,2,4-triazole system (XXII) is not disrupted qualitatively, although in this case the π-electron charge is distributed between two sp^2-hybridized nitrogen atoms [68].



XXII

Ambident character of a somewhat different nature is displayed in 1,2,4-triazole: Coordination with the pyridine nitrogen atom in the 2 or 4 position is observed. According to our calculations, protonation takes place in the 4 position (XXIII).



XXIII

1,2,4-Triazole and its methyl-substituted derivatives form complexes with σ (iodine and interhalogens) and v (MX_3, where M = Al, Ga, and In; X = Cl, Br, and I; shift reagents) acceptors. The results of determination of the dipole moments, the PMR spectra obtained with the aid of lanthanide shift reagents, and the results of calculations of the vibrational spectra showed that coordination is realized only in the 4 position [51]. Quantum-chemical analysis of the charge-transfer complex (CTC) of triazole with iodine as compared with other azoles made it possible to evaluate the favorability (490 kJ/mole) of coordination of 1,2,4-triazole in the 4 position as compared with the 2 position. The explanation of such a significant difference follows from the substantial reverse transfer of the electron density in the complex through the system of π bonds from the acceptor to the heteroring (a dative bond, "reverse donation"). It follows from an analysis of the AO population that in the coordination of iodine in the 2 position both processes, viz., direct donor-acceptor interaction, which takes place through the system of π bonds, and "reverse donation," lead to the result that the order of the $N_{(2)}$—I bond remains approximately equal to zero, whereas the order of the $N_{(4)}$—I bond is 0.31.

Thus our data make it possible to establish the general principles of the donor-acceptor interaction of five- and six-membered heterocycles. In the case of π-deficient systems their n-donor properties are most clearly expressed — coordination of all types of acceptors, including those of the π type, generally takes place at the pyridine nitrogen atom of the heteroring. However, the ability of pyridines and azoles to undergo complexing is not exhausted by their n-donor properties — they are only the prevailing properties. π-Donor properties, which are manifested when a number of conditions are observed, are also possible for pyridines and azoles. The chief such π-donor property is blocking of the stronger (than the π-donor center) n-donor center either in the case of ortho substitution by alkyl groups or by primary H or v bonding. Benz- or naphthannelation of the heterorings leads to considerable branching of the π system, i.e., to more pronounced π-donor properties.

The accumulated experimental and calculated data may serve as a basis for the prediction and specific creation of ligands with prevailing σ(n)- or π-donor properties. Thus the introduction of π-acceptor substituents into π-surplus systems apparently may make it possible to obtain σ(n) complexes with the participation of the heteroatoms of fundamental five-membered heterocycles. On the other hand, the introduction of electron-donor substituents and groups that block the nucleophilic center, as has already been demonstrated experimentally, will make it possible to obtain π-bonded complexes on the basis of π-deficient heterocycles.

In addition, in solving the problems of the specific preparation of σ or π complexes in series of heteroaromatic ligands one must take into account the nature of the acceptors. It should also be taken into account in quantum-chemical substantiations of the reactivities of ambident ligands by introduction of the molecular orbitals of the corresponding acceptors into the calculations. We are currently performing calculations of this sort, and their realization will apparently provide a rigorous approach to the specific synthesis of π and σ complexes in series of heteroaromatic compounds.

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RESEARCH ON THE CHEMISTRY OF 2-HETARYLBENZIMIDAZOLES.

5.* ACYLATION OF 1-METHYL-2-(2'-HETARYL)BENZIMIDAZOLES

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and L. Ya. Oleinikova

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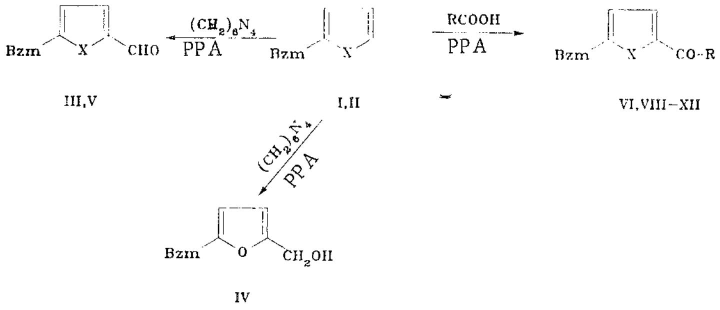
542.951.1:543.422

The acylation of 1-methyl-2-(2'-furyl)- and 1-methyl-2-(2'-thienyl)benzimidazoles was studied. A convenient method for the formylation of the furan and thiophene rings by the action of urotropin in polyphosphoric acid (PPA) was found. Acylation of the furan and thiophene rings was realized by the action of acetic acid and aromatic carboxylic acids in PPA.

It has been previously shown [2] that, despite the acidophobic properties of the furan ring, electrophilic-substitution reactions in 1-methyl-2-(2'-furyl)benzimidazole proceed smoothly to give the products in high yields even under rather severe conditions. It seemed of interest to study the behavior of 1-methyl-2-(2-furyl)- (I) and 1-methyl-2-(2-thienyl)-benzimidazole (II) in reactions with weaker electrophilic reagents.

The formylation of five-membered heterocycles and their derivatives has been realized by the Vilsmeier reaction [3, 4]. We attempted to introduce a formyl group by means of this reaction into I and II by the action of the dimethylformamide (DMF)—$POCl_3$ complex. However, the compounds proved to be inert, and we therefore used formylation with urotropin in polyphosphoric acid (PPA) [5].

Compound I forms a 5'-formyl-substituted derivative (III) in no higher than 31% yield. In addition, 5'-hydroxymethyl derivative IV was also obtained in 49% yield. In contrast to I, II forms 1-methyl-2-(5'-formyl-2'-thienyl)benzimidazole (V) smoothly and in high yield.



I X=O; II X=S; III X=O; V X=S; VI X=O, R=CH_3; VIII X=S, R=CH_3; IX, X X=O, S, R=C_6H_5; XI, XII X=O, S; R=*o*-Cl—C_6H_4; 1-methyl-2-benzimidazolyl

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*See [1] for communication 4.

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