CONCEPT OF π-SURPLUS CHARACTER IN THE CHEMISTRY OF HETEROAROMATIC COMPOUNDS (REVIEW)

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Problems in the classification of π-surplus heteroaromatic compounds and the criteria of their π-donor character are examined in the review. The results of quantum-mechanical calculations, the ionization potentials, the tendency to form charge-transfer complexes with various electron-acceptors, the oxidation potentials, etc., are singled out as criteria of π-donor character. It is shown that although high π-donor character is a consequence of π-surplus character, there is no quantitative relationship between these concepts, and they must be clearly distinguished.

According to the classification proposed by Albert in 1958, heteroaromatic compounds are divided into π-surplus and π-deficient systems [1]. The π-surplus category includes systems in which the total number of π electrons entering into the aromatic ensemble exceeds the number of atoms in the ring. As a result, the ring carbon atoms acquire surplus π-electron density, and this makes them readily accessible to attack by electrophilic reagents. Five-membered heterocycles — pyrrole, furan, thiophene, and selenophene (type I) — serve as a typical example of π-surplus systems. A fundamental feature of heterocycles of this sort is the presence of a heteroatom that supplies two π electrons to the aromatic system. We will subsequently call this type of heteroatom a "pyrrole" heteroatom.

I X = NH, O, S, Se

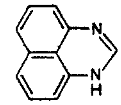
π-Surplus structures

II Y = N, O, S

π-Deficient structures

III X = NH, O, S

Azoles (absence of clearly expressed π-surplus or π-deficient character)



IV

Perimidine (chemically amphoteric structure having simultaneously clearly expressed π-surplus and π-deficient character)

π-Deficient heterocycles such as, for example, pyridine, pyrylium salts, thiapyrylium salts, and condensed systems based on them contain a heteroatom that furnish the π system with one electron. It is usually called a heteroatom of the "pyridine" type. Strictly speaking, heterorings of the II type should be considered to be π-equivalent systems, since the number of π electrons in them is equal to the number of atoms in the ring.* However, when

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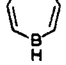
*Heterorings such as borepine (V), borirene (VI), and their aluminum, gallium, and other analogs with a heteroatom that has a vacant p orbital can also be classified as truly π-deficient systems. Some of them have been obtained, and a certain amount of aromatic character has been detected [2, 3].



V

VI

Rostov State University, Rostov-on-Don 344006. Translated from Khimiya Geterotsikliches-kikh Soedinenii, No. 6, pp. 723-740, June, 1977. Original article submitted July 13, 1976.

TABLE 1. Electron-Density Distribution in the Pyridine and Pyrrole Molecules According to the Results of Quantum-Mechanical Calculations

Compound	Hückel MO (π charges)*				*Ab initio*[5,6]†			
	N	2-C	3-C	4-C	N	2-C	3-C	4-C
Pyrrole	+0,280	−0,035	−0,105	—	π+0,34 σ−0,75	−0,08 −0,03	−0,10 −0,16	— —
Pyridine	−0,195	+0,077	−0,004	+0,050	π−0,11 σ−0,52	+0,05 +0,20	−0,04 −0,14	+0,07 −0,11

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*Here and subsequently, the calculations by the Hückel MO method were made with the parameters in [4].

†The negative σ charge on the 3-C and 4-C atoms in the pyridine molecule is due to polarization of the C_3-H and C_4-H bonds, which compensates the acceptor effect of the remote heteroatom.

Albert called them π-deficient systems, he had in mind the fact that the C atoms in them are connected by π electrons and bear an effective positive π charge, since the pyridine heteroatom has a greater degree of π-acceptor character than π-donor character. Calculations made with allowance for all the valence electrons (Table 1) have shown that the pyridine heteroatom is both a π acceptor and a σ acceptor. A heteroatom of the pyrrole type also accepts σ electrons; however, this is more than compensated by its high π-donor character, which is also reflected in the reactivity. Thus, even in the case of a considerable σ-electron effect, the behavior of the π electrons is the decisive factor with respect to the reactivities of heterocycles. π-Deficient rings readily undergo nucleophilic attack, whereas electrophilic substitution reactions are uncharacteristic for them.

It might have been supposed that when heteroatoms of both the pyrrole and pyridine type are present in the molecule, the compounds should also react readily with both electrophilic and nucleophilic agents. However, in most cases this assumption is unwarranted. Thus, in the case of azoles (of the III type), because of the different directions of the effects of the heteroatoms, the reactivities are reduced with respect to both electrophilic and nucleophilic agents. For example, 1-methylimidazole, in contrast to pyrrole, is extremely difficult to nitrate [7] (partly because of protonation in acidic media) and, in addition, in contrast to pyridine, does not react with strong nucleophiles such as sodium amide [8].

Nevertheless, heterorings that have simultaneously both high π-surplus character and high π-deficient character have been discovered. The clearest example is perimidine (IV) [9], which, in accordance with the Albert classification, is a π-surplus compound, since there are 14 π electrons among the 13 atoms of its peri-cyclic system. However, in addition to its exceptionally high π-surplus character, perimidine also has distinctly expressed π-deficient character in that it reacts readily with diverse nucleophiles [9]. Amphoteric character of this type is a consequence of pronounced migration of the π-electron density from the heteroring of perimidine to the naphthalene portion of the molecule. As a result, high positive charge, which is also attacked by nucleophiles, is concentrated on the μ carbon atom of perimidine, while a high negative charge develops on the o- and p-carbon atoms of the naphthalene ring and makes them active even with respect to very mild electrophiles [9]. See [10-12] for the results of calculation of the perimidine molecule.

Unfortunately, the concepts of π-surplus character and π-deficient character, as formulated by Albert, are only qualitative in nature. In this connection, two fundamental questions arise: 1) can more quantitative character be imparted to the entire concept in order to compare the π-surplus character and π-deficient character of different systems, and 2) are these two parameters related to some more fundamental properties of the molecules? Properties of the latter type might include, for example, the π-donor character and π-acceptor character of heterocycles. In this connection, the aim of the present review was to discuss, on the basis of the available literature data, possible approaches to the quantitative evaluation of the π-surplus and π-donor character of heteroaromatic compounds and to establish more clearly the relationship between these parameters. We note that there is evidently a relationship between the π-donor character of heterocycles and their antioxidant activity and effect on the central nervous system [13]. Consequently it is desirable to have an objective criterion of π-donor character for the specific synthesis of substances with a given effect.

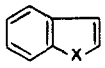
The problem of π-deficient and π-acceptor character may become the subject of an independent review.

Classification of π-Surplus Heterocycles

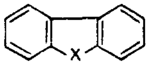
From the point of view of the author of this review, it is convenient to divide π-surplus heteroaromatic systems into five fundamental groups:

I. Monocyclic systems, for example, five-membered heterocycles or azonines [14].

II. Condensed systems with an unbridged heteroatom of the pyrrole type. Annelated structures based on five-membered heterorings (VII, VIII), perimidine (IV), compounds of the phenothiazine group (IX), etc. can be assigned to this category.



VII



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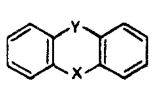
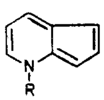


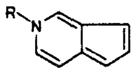
IX

The assignment of condensed heterocycles to a separate group is due to the fact that the benzene rings in them also become π-surplus rings because of migration of the π-electron density from the heteroring, in which case their reactivities may change markedly as compared with benzene. Thus, for example, the benzene rings of phenothiazine and perimidine are readily acylated, are nitrated by nitric acid, and couple with diazonium salts [9, 15, 16].

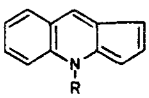
III. Compounds with a quinoid system of bonds of the type involved in pyridines (Xa, b), quinindines (XI), isoindole (XII), etc.



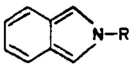
Xa



Xb

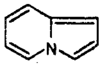


XI

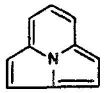


XII

IV. Bridged heterorings in which a heteroatom of the pyrrole type is affiliated with two (XIII) or three (XIV, XV) rings.



XIII



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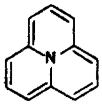
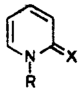
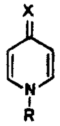


XV



XVIa



XVIb

X = O, S, NH

V. Rings containing a septet of π electrons, i.e., oxo, thio, and imino derivatives of aza aromatic systems (XVIa, b).

Methods for the Evaluation of π-Surplus Character

If the π-equivalent model of benzene, the carbon atoms of which have zero π charge, is taken as the standard, the average negative charge on each carbon atom of the heterocycle system may serve as a measure of the π-surplus character. Consequently, even a simple calculation shows that in pyrrole each ring atom, including the nitrogen atom, has an average of 6/5 π electrons, as compared with 10/9 π electrons in indole, and 14/13 π electrons in carbazole, i.e., the π-surplus character decreases in this series. This picture is also confirmed by quantum-mechanical calculations (diagram 1), regardless of whether we examine the entire molecule in the case of indole and carbazole or only the pyrrole ring atoms. Thus, the average effective π charges on all of the carbon atoms of pyrrole, indole, and carbazole are −0.040, −0.015, and −0.008, as compared with −0.040, −0.024, and −0.013, respectively, for the carbon atoms of the pyrrole ring [17].

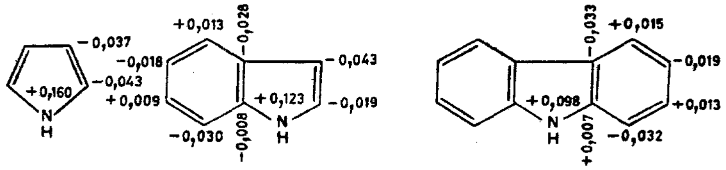


Diagram 1. Effective π charges (SCF MO method) [17].

Similar regularity is observed in the furan, benzofuran, and dibenzofuran series. Although the numerical values of the charges and even the order of their change on the 2-C and 3-C atoms depend markedly on the computational method (Table 2), the pyrrole > thiophene > furan order of π-surplus character remains qualitatively unchanged and is determined only by the electronegativity of the heteroatom.

The results of quantum-mechanical calculations, even when the simple Hunckel method is used (Table 3), quite adequately reflect the successive decrease in the π-surplus character on passing from pyrrole to azoles and then to pyridine. It is interesting that imidazole and pyrazole still display π-surplus character, while pyridine is a typical π-deficient heterosystem.

In condensed systems the π-surplus character is also extended to the annelated benzene rings. If the heteroring contains six π electrons, migration of the π-electron density from it is relatively low. Thus, according to the results of MO calculations, 50% of the surplus π charge in the indole and carbazole molecules remains in the pyrrole ring (Diagram 1). The situation changes markedly when "hyper-Hückel" electrons appear in the heteroring. For example, the six-membered ring with seven π electrons in pyridines X is formally a π-surplus system. However, according to the laws of aromatic character, repulsion of the "surplus" π electron from this ring is so great that it acquires an overall positive charge, and the five-membered ring condensed with it becomes a π-surplus system (Diagram 2 and Table 4). The π-electron density distribution in indolizine XIII is more uniform, since, because of the bridged position of the pyrrole nitrogen atom, both the five-membered ring and the six-membered ring are π-surplus systems here. Nevertheless, the results of the calculations and the reactivities show that a large part of the negative charge is concentrated in the five-membered ring.

Azaindenes are arranged in the following order with respect to the total or average π-electron density on the carbon atoms: indolizine > 2-pyridine > 1-pyridine. This order reflects the π-donor strength of the heteroatom in these compounds. However, if the five-membered ring is singled out as a π-surplus fragment, the order of π-surplus character is reversed.

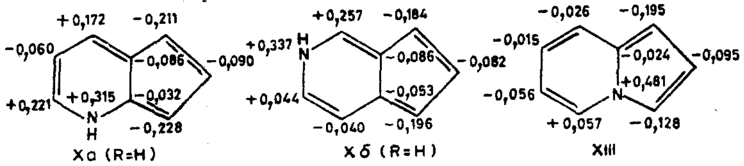


Diagram 2. π Changes in the Azaindenes (Hückel MO) [24, 25]

Similar regularities have also been observed by means of calculations by the CNDO-2 (complete neglect of differential overlap) method for compounds consisting of several condensed

TABLE 2. Effective π Charges in the molecules of Five-Membered Heterocycles

Compound	PPP [18]			CNDO-2 [19]			Hückel MO [20]		
	C-2	C-3	Average	C-2	C-3	Average	C-2	C-3	Average
Pyrrole	−0,080	−0,041	−0,060	−0,085	−0,085	−0,085	−0,049	−0,136	−0,092
Furan	−0,059	−0,012	−0,035	−0,067	−0,080	−0,074	−0,024	−0,120	−0,072
Thiophene	−0,069	−0,029	−0,049	−0,085	−0,071	−0,078	—	—	—

TABLE 3. Effective π Charges on the Carbon Atoms of Pyrrole, Diazoles, and Pyridine

Compound	Total charge		Av. charge	
	CNDO-2	Hückel MO [22]	CNDO-2	Hückel MO [22]
Pyrrole	−0,386[21]	−0,280	−0,097[21]	−0,070
Imidazole	−0,224[21]	−0,011	−0,075[21]	−0,004
Pyrazole	−0,130[21]	−0,031	−0,043[21]	−0,010
Pyridine	+0,181*[23]	+0,196	+0,036*[23]	+ 0,039

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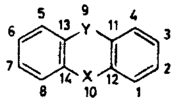
*(σ + π) charge.

TABLE 4. Average π Charges on the Carbon Atoms of Azaindene Molecules [24, 25]

Compound	Entire molecule	Six-membered ring	Five-membered ring
1-Pyridine	−0,039	+0,043	−0,129
2-Pyridine	−0,042	+0,025	−0,120
Indolizine	−0,061	−0,013	−0,111

TABLE 5. Effective π Charges in Phenoxazine, Phenothiazine, and Phenoxanthiin Molecules (by the SCF MO method) [27]



Compound	Position						Av. charge	
	1(8)	2(7)	3(6)	4(5)	11(13)	12(14)	entire molecule	hetero-ring
Phenoxazine X=NH, Y=O	−0,062	−0,012	−0,025	−0,039	−0,028	−0,030	−0,033	−0,028
Phenothiazine X=NH, Y=S	−0,063	−0,007	−0,027	−0,024	−0,047	−0,021	−0,032	−0,034
Phenoxathiin X=O, Y=S	−0,041	−0,009	−0,016	−0,025	−0,035	−0,060	−0,022	−0,021

TABLE 6. σ_R^o Constants of Some Heteroaromatic Radicals

Radical	IR spectral data [30]		NMR data [31]
1-Methyl-2-pyrrolyl	−0,23	—	—
2-Thienyl	−0,17	−0,14	−0,06
2-Furyl	−0,20	−0,13	−0,05
2-Selenyl	−0,18	—	—

heterorings, particularly for purine tautomers [26].

In the perimidine (IV) molecule and in azaindenes, the naphthalene ring, in which a large part of the surplus π-electron density is concentrated [10-12], rather than the heteroring is the π-surplus fragment. In the phenoxazine, phenothiazine, and phenoxathiin molecules both heteroatoms are donors of two π electrons, and there are therefore formally eight π electrons in the heteroring. As a result, these compounds are highly π-surplus systems, and the migration of π-electron density to the benzene rings is very high (Table 5). Phenoxazine and phenothiazine are close to one another with respect to their degree of π-surplus character and considerably surpass phenoxathiin.

Unfortunately, semiempirical computational methods do not make it possible to construct a unified scale of π-surplus character of heterocyclic compounds. Their results depend to a great degree on the parameters used and are evidently reliable only when data for closely related compounds are compared. The *ab initio* method of calculation may offer a certain amount of hope in this regard, but up until now only an extremely limited number of heterocycles have been calculated with it, and the results obtained for the same compound by different authors do not always coincide (for example, see the data for pyridine [6, 28]).

There are also no reliable methods for the experimental evaluation of the π-electron density. Hopes for a possible correlation between the π-electron density and the chemical shifts of protons or ^{13}C nuclei have also been found to be unjustified, and the approximate correlation found more likely corresponds to the total (σ + π)-electron densities [29]. The use of the σ_R^o constants of the corresponding radicals is promising as a measure of the π-surplus character of the individual positions of the ring. The data in Table 6 give an extremely plausible picture for the π position of five-membered heterocycles, although there is a certain vagueness with respect to the relative π-surplus character of furan and thiophene.

Criteria of π-Donor Character

It might be expected that π-surplus character is associated with the presence of a high-lying upper occupied molecular orbital (UOMO) that is readily accessible to an electron ac-

TABLE 7. Ionization Potentials (IP_1, eV) of π-Surplus Heterocycles

Compound	Exptl.		Calc. [17]
	PES, PI [34,35]	EI [36]	
Pyrrole	8,21	8,40	8,90
1-Methylpyrrole	8,09	—	—
Furan	8,90	8,99	9,02
Thiophene	8,86	9,12	—
Selenophene	—	9,01	—
Indole	7,75	—	8,36
Benzofuran	8,29	—	8,60
Benzothiophene	8,17	—	—
Carbazole	7,57	—	8,25
Dibenzofuran	7,90	—	8,37
Isoindole	—	—	7,81
Phenothiazine	7,62	—	—

ceptor (a Lewis acid) and determines the π-donor character of the compound. The quantitative evaluation of π-donor character can then be based on measurement of the energy of this orbital.

Ionization Potential. The most rigorous method for the evaluation of the UOMO energy is the determination of the ionization potential (IP_I) of the compound. For most heteroaromatic systems it is due to detachment of an electron from the π orbital, i.e., it characterizes the π-donor character directly. However, for some heterocycles (pyridazine, pyrimidine, cinnoline, and phthalazine) IP_1 is determined by detachment of an electron from the nonbonding sp^2 orbital of the heteroatom [32]. The π-donor character is then usually characterized by the second ionization potential, and the chief experimental difficulty then consists in determining which of the ionization potentials should be ascribed to the π orbital and which should be ascribed to the p orbital.

Experimentally, the ionization potentials are determined for the rarefied gas phase by photoelectronic spectroscopy (PES), photoionization (PI), or electron impact (EI). The first two methods make it possible to obtain more accurate adiabatic potentials, whereas the EI method leads to the so-called vertical ionization potentials, which are somewhat elevated as compared with the adiabatic values [33].

The calculated IP_1 values obtained by quantum-mechanical methods differ appreciably from the experimental values (Table 7) but, as a rule, accurately reflect the tendency in the changes in the IP_1 of various compounds and consequently lead to the same fundamental conclusions. Good correlation between the experimental IP_1 of various compounds (including heterocyclic compounds) and the calculated UOMO energies, including the results of calculation by the simple Hückel MO method [33, 34], has been noted.

The data in Tables 7 and 8 make it possible to draw the following conclusions.

1) As in the furan, benzofuran, dibenzofuran and thiophene, benzo/b/thiophene, dibenzothiophene series, the ionization potential decreases successively in the pyrrole, indole, carbazole series, i.e., an increase in the size of the aromatic π system leads to an increase in the UOMO energy. This sequence is not in agreement with the relative π-surplus character of the same heterocycles (see above). Thus, the π-surplus character and the π-donor character do not necessarily change in the same direction.

2) The π-donor properties of pyrrole considerably exceed those of other five-membered heterocycles. The IP_1 of furan and thiophene are close, and the PES and PI methods lead to somewhat larger IP_1 for furan, whereas the EI method gives the opposite result. The results of the first two methods, which are in agreement with the relative π-surplus character of these rings and the electronegativities of the corresponding heteroatoms, are more plausible. Evidence in favor of this is also provided by the order of the change in the IP in a series of benzo analogs of five-membered heterocycles:indole > benzothiophene > benzofuran. The IP_1 for selenophene is close to that of furan.

3) There is evidently no relationship between the aromatic character and the π-donor character of heterocycles. Thus in the indole–isoindole pair, the less aromatic [judging from the resonance energy per π electron (REPE) [38]] isoindole is a greater π donor, while in the pyrrole–furan pair and in the pyrrole–indole–carbazole series one observes the opposite order (Table 9). A more distinct correlation between the π-donor character and the resonance

TABLE 8. First π-Electron Ionization Potentials of Azines and Azoles

Compound	IP_1 (eV)	Compound	IP_1 (eV)
Pyridine [6, 32]	9,31	Acridan [32]	7.24
Pyridazine [6]	10,5	sym-Triazine [6]	11.4
Pyrimidine [6]	10,6	sym-Tetrazine [6]	12.1
Pyrazine [6]	10,5	Imidazole [37]	8.78
Quinoline [32]	8,62	Pyrazole [37]	9.15
Isoquinoline [32]	8,55	1,2,4-Triazole [37]	10,0
Acridine [32]	7,78	1,2,3-Triazole [37]	10,06
Acridone [32]	7,60	Tetrazole [37]	11,3

TABLE 9. Indexes of Aromatic Character (REPE [38]) and Calculated Ionization Potentials [17] of Some π-Surplus Heterocycles

Compound	REPE (β)	IP_1(eV)	Compound	REPE (β)	IP_1 (eV)
Pyrrole	0,039	8,90	Furan	0,007	9,02
Indole	0,047	8,36	Cyclo[3.2.2]azine	0.040	8,28[39]
Carbazole	0,051	8,25	Cyclo[3.3.3]azine	0.001	7,49[39]
Isoindole	0,029	7,81			

energy should exist for aromatic and antiaromatic compounds. Thus, the aromatic cyclo[3.2.2]-azine (XIV, 10 peripheral π electrons) has an UOMO with lower energy than that of the antiaromatic cyclo[3.3.3]azine (XV, 12 peripheral π electrons).

4) In conformity with our expectations, monocyclic π-deficient heterocycles are characterized by high ionization potentials, and the energy of detachment of a π electron from the UOMO increases as the number of aza groups in the molecule increases (Table 8). However, the ionization potential decreases on passing to the benzo analogs of π-deficient heterocycles, and acridine, for example, has extremely appreciable π-donor character in that it forms π complexes with electron acceptors such as chloranil [40]. This phenomenon is associated with the decrease in the total number of π electrons in the molecule and is similar to that which is observed in the pyrrole—indole—carbazole series.

5) With respect to their π-donor properties, azoles lie between π-surplus and π-deficient systems with the same number of identical heteroatoms (for example, compare imidazole with pyrrole and pyridine). The π-donor character of azoles decreases as the number of "pyridine" nitrogen atoms increases.

Ease of Formation of Charge-Transfer Complexes (CTC). The method of evaluation of the electron-donor properties of compounds based on their ability to form charge-transfer complexes (CTC) on reaction with tetracyanoethylene (TCE), chloranil (CA), trinitrobenzene (TNB), iodine, and some other electron acceptors [41] has been widely extended in the last 15 years. There is a definite relationship between the position of the charge-transfer band of a complex and the ionization potential of the donor [42]; although it is generally parabolic in nature, it has been established that it is close to linear for donors with IP_1 ranging from 7 to 11 eV [43]:

$$h\nu_{CT} = m\ IP_1 + b,$$

where $h\nu_{CT}$ is the energy of electron transfer corresponding to the charge-transfer band, IP_1 is the ionization potential of the donor, and m and b are empirical constants. The overwhelming majority of aromatic compounds, including π-surplus heterocycles, have first ionization potentials in this ring. This fact makes it possible, by measurement of the position of the charge-transfer band, to estimate the ionization potential and, consequently, the relative π-donor character in solution, which is of particular value to the organic chemist.

Many empirical equations that interrelate the IP_1 of π donors and the energy of the electron transition corresponding to the charge-transfer band for a certain acceptor have been derived by means of the method of least squares:

for complexes with TNB [44], $IP_1 = 4.25 + 1.39 \cdot 10^{-4}\nu_{max}$;
for complexes with TCE [45], $IP_1 = 1.704h\nu_{CT} + 4.20 \pm 0.1$;
for complexes with CA [45], $IP_1 = 3.906h\nu_{CT} - 0.112 \pm 0.1$.

TABLE 10. Position of the Charge-Transfer Bands (nm) of the CTC of Five-Membered Heterocycles with Various Acceptors

Donor	Acceptor			
	TCE		chloranil [46]	iodine [48]
	In $CHCl_3$ [46]	In CCl_4 [47]		
Pyrrole	530	540; 400	505; 390	360; 285
1-Methylpyrrole	—	540; 425	510; 425	360; 310
Furan	450	445; 295	390	317
Thiophene	399	445; 390	348	295

TABLE 11. Position of the Charge-Transfer Bands (nm) of the CTC of the Benzo Analogs of Five-Membered Heterocycles

Donor	Acceptor		
	TCE [46]	chloranil	TNB [52, 53]
Indole	543	496[49]	380
Carbazole	605	535[50]	410
Benzofuran	465	—	—
Dibenzofuran	498	—	—
Benzo[b]thiophene	528; 477	448[51]	—
Dibenzothiophene	550	488[51]	—

During charge transfer, an electron passes from the UOMO of the donor to the lower vacant orbital of the acceptor [33]. Thus, the higher the UOMO, i.e., the lower the IP_1 of the donor, the higher the wavelength at which the maximum of the charge-transfer band is found in the electronic spectrum. Two charge transfer bands are sometimes observed in the spectrum of a CTC. It is assumed that the higher-frequency band is associated with transfer of a π electron lying in the next occupied orbital of the donor [41]. The longer-wavelength charge-transfer band is usually assumed to be the "true" band, i.e., the one that directly determines the strength of the donor. There is no need to calculate the ionization potentials of compounds to obtain a qualitative comparison of their donor strength — it is sufficient to compare the maxima of the charge-transfer bands.

It must be noted that the formation of a CTC takes place practically instantaneously. The change in the free energy during the formation of a CTC and the enthalpy of the process usually do not exceed 2-4 kcal/mole [41]. In addition, in the case of neutral donors and acceptors the position of the charge-transfer band is only slightly sensitive to the nature of the solvent [41].

It follows from the data in Table 10 that the π-donor character of five-membered heterocycles regardless of the nature of the acceptor, changes in the order pyrrole > furan ≥ thiophene. The ease of formation of a CTC is almost the same for 1-methylpyrrole and pyrrole. These data in general correspond to the gas-phase ionization potentials, although the degree of difference in π-donor character between furan and thiophene remains unclear. It is evidently small, since Yoshida and Kobayashi [47] present practically identical values for the long-wave charge-transfer band of furan and thiophene. In this connection, one should recall the disparity in the estimate of the relative ionization potential of furan and thiophene by the PES and EI methods.

On passing from five-membered heterocycles to their benzologs (Table 11), the charge-transfer band is shifted to the long-wave region of the spectrum as the number of condensed benzene rings increases, i.e., the π-donor character changes in the following order: pyrrole < indole < carbazole; furan < benzofuran < dibenzofuran; thiophene < benzothiophene < dibenzothiophene. These orders are in complete agreement with the change in the gas-phase ionization potentials; the CTC method and the ionization potentials are in agreement with one another in that in the benzofuran–benzothiophene pair, the sulfur-containing heteroring is the greater π-donor system.

A great deal of research has been devoted to CTC of compounds of the phenothiazine group (Table 12). Like the results of other methods, the results indicate a similarity between the π-donor properties of phenothiazine and phenoxazine (phenothiazine evidently only slightly surpasses phenoxazine in this respect). A study of CTC with tetracyanoquinodimethane has shown that both of these heterocycles surpass phenoxanthiin with respect to their π-donor character [56].

TABLE 12. Position of the Charge-Transfer Bands (nm) of the CTC of Compounds of the Phenothiazine and Perimidine Group (in acetonitrile) [54]

Donor	Acceptor		
	TCE	CA	TNB
Phenothiaizne	855	787	495
10-Methylphenothiazine	827	694	441
Phenoxazine	847	730	512
Perimidine	—	—	545*
1-Methylperimidine	—	—	556*

*In chloroform [55].

Perimidines have exceptionally high π-donor character, judging from the position of the charge-transfer band for complexes with TNB (Table 12). Considerable π-donor character is retained in the 1,3-dimethylperimidinium cation, which forms a CTC with dichlorodicyanobenzoquinone [55] and readily undergoes the same electrophilic substitution reactions as perimidine itself [57]. Unfortunately, the literature contains practically no data on the CTC of the cations of other π-surplus heterosystems. The data on the CTC of bridged heterocycles are just as scanty.

One of the disadvantages of the CTC method for the evaluation of π-donor character is the appreciable sensitivity of the position of the charge-transfer band to steric hindrance. Thus, the charge-transfer band in the spectra of π complexes of 10-alkylphenothiazines is shifted to the short-wave region as compared with phenothiazine; this does not reflect the actual change in the ionization potential with allowance for the +I effect of the alkyl groups. This is explained by the fact that the π-donor and π-acceptor molecules usually strive to orient themselves parallel to one another, which creates the best conditions for complexing. According to x-ray diffraction data, this sort of parallel character is observed in the phenothiazine-TNB complex [58] but is evidently disrupted on passing to 10-alkylphenothiazines.

The identical positions of the charge-transfer bands in pyrrole and 1-methylpyrrole complexes is most likely a consequence of steric hindrance. If steric hindrance is absent, one should expect absorption in the longer-wave region for the CTC of 1-methylpyrrole. Of significance in this respect is 1-methylperimidine, in the spectrum of the charge-transfer band of the complex with TNB is shifted to the long-wave region as compared with perimidine. The reason for this apparently consists in the fact that the π-donor fragment in perimidines is the naphthalene ring, and the N-methyl group, because of its remoteness from it, does not have an appreciable effect on the orientation of the components in the CTC. However, when there are a large number of bulky substituents in the molecule, they may have an unfavorable effect on complexing, even when they are far away from the donor center. Most investigators assume that in indoles the π-donor center near which the acceptor molecule is oriented is the C_2-C_3 bond [59, 60]. On passing from indole to mono- and dimethoxyindoles that contain a CH_3O group in the benzene ring, the charge-transfer band undergoes a substantial bathochromic shift; this is completely understandable when one takes into account the +M effect of the methoxy group. However, in the spectra of the CTC of trimethoxyindoles this band is somewhat unexpectedly shifted to the short-wave side as compared with the band of dimethoxyindoles [61]. Proceeding from these observations, it may be concluded that the position of the charge-transfer band for compounds that contain bulky donor groups is a reflection of the compromise between the true π-donor character of the compound and steric factors that hinder electron transfer.

Another disadvantage of the method is the sometimes-observed dependence of the position of the absorption bands of the complexes on the nature of the acceptor. Thus, the λ values for phenothiazine and phenoxazine complexes with TNB provide evidence for the somewhat greater donor character of phenoxazine, while the same data for complexes with TCE and CA lead to the opposite conclusion (Table 12). The complexes of 5- and 6-methoxyindoles with TNB and TCE constitute another example [61].

In principle, these anomalies are not surprising, since different acceptors should differ from one another with respect to their geometric and electrostatic requirements for the formation of CTC; the fine structure of one donor may be in greater conformity with the requirements of a given acceptor, while the same acceptor may prove to be less suitable for

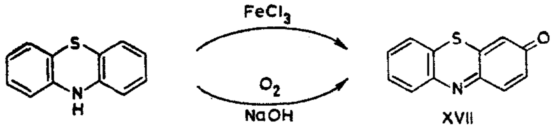
TABLE 13. Formation Constants of Some Complexes (liter·mole^{-1}) [47]

Donor	Acceptors			IP_1 (eV)
	TCE	CA	iodine	
1-Methylpyrrole	—	1,04	6,50	8,09
Furan	0,35	0,13	0,20	8,90
Thiophene	0,53	0,22	0,59	8,86
Benzene	1,03	0,33	0,16	9,25

charge transfer for a second donor. In this connection, in order to avoid incorrect conclusions in the evaluation of the actual π-donor character of compounds it is necessary to use, as far as possible, a sufficiently extensive set of acceptors.

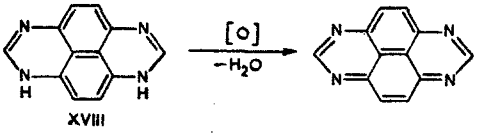
The formation constants of CTC have extremely limited value in the evaluation of π-donor character. Thus, the K_S values of complexes of benzene with TCE and CA considerably surpass those of thiophene and furan (Table 13). However, if one judges from the ionization potentials and position of the charge-transfer bands, the π-donor properties of benzene are considerably weaker than for any of the examined five-membered heterocycles. Many such examples can be found among indole complexes [59, 61]. The inapplicability of stability constants as a criterion of π-donor character is explained by the fact that they are determined not only by the UOMO energy of the donor but to an even greater degree by electrostatic interaction and van der Waals forces [61].

Ease of Oxidation Reactions. Inasmuch as they have high-lying UOMO, π-surplus heterocycles are distinguished by a considerable tendency to undergo oxidation. Thus phenothiazine is converted by the action of $FeCl_3$ to deeply colored phenothiazone (XVII), which in alkaline media is formed by simple aeration of a suspension of phenothiazine [62]; this is evidently due to the prior formation of the anion:



The introduction of electron-donor substituents in the phenothiazine molecule increases the tendency to undergo oxidation; for example, 3,6-bis(dimethylamino)phenothiazine (leucomethylene blue) readily undergoes autoxidation [63]. Similarly, perimidine itself is stable in air but its N-anion is almost immediately converted to a black slightly soluble oxidation product, which evidently has a dimeric quinoid structure [64]. Both 6(7)- and 4(9)-aminoperimidines are oxidized in air in the form of the bases [65]. It is curious that perimidines with an amino group in the electron-deficient 2 position are resistant to autoxidation [66]. Instances of autoxidation in alkaline media have been described for indole [67] and pyrrole (68, 69] derivatives.

The diperimidine molecule (XVIII) has exceptionally high π-donor character. Its UOMO energy is $\alpha + 0.104\beta$, which is considerably higher than that of perimidine ($E_{UOMO} = \alpha + 0.328\beta$). It is not surprising that red diperimidine is oxidized very rapidly in air to give the colorless and stable tetraazapyrene [65, 70]:



Many π-surplus heterocycles form cation radicals under controllable oxidation conditions [anodic oxidation [71, 72], oxidation with $Pb(OAc)_4$–CF_3COOH [73] and CH_3NO_2–CF_3COOH [74] systems, etc.]. Thus the electrochemical oxidation of phenothiazine leads to the formation of the completely stable (in the absence of moisture and air) orange cation radical XIX, which on further oxidation is converted to red dication XX [71]:

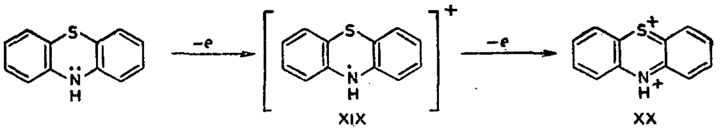


TABLE 14. Polarographic Oxidation Potential (with respect to a saturated calomel electrode with acetonitrile as a solvent)

Compound	$E_{1/2}^{ox}$, V	Compound	$E_{1/2}^{ox}$, V
Carbazole [72]	1,16	Phenothiazine [76]	0.59
9-Methylcarbazole [72]	1,10	10-Methylphenothiazine [76]	0,73
9-Ethylcarbazole [72]	1,12	Phenoxazine [77]	0,59
9-Isopropylcarbazole [72]	1,14	Phenoxathiin [77]	1.25
9-Phenylcarbazole [72]	1,21		

TABLE 15. Rate of Electron Transfer between Cation Radicals and Neutral Molecules and UOMO Energies of the Latter [77]

Compound	k	E_{UOMO} (β)
Phenothiazine	$6{,}7 \cdot 10^9$	0,129
Phenoxazine	$4{,}5 \cdot 10^9$	0,270
10-Methylphenothiazine	$2{,}2 \cdot 10^9$	0,312
Phenoxathiin	$0{,}36 \cdot 10^9$	0,412

Another unusual reaction of cation radicals is their dimerization. The cation radical of carbazole is converted to 3,3'-dicarbazolyl and a small amount of N,N'-dicarbazolyl [72].

In principle, the tendency of π-surplus heterosystems to undergo oxidation can be used for the quantitative evaluation of their π-donor character by means of oxidative polarography. In fact, the polarographic oxidation potential is directly related to the ionization potentials, the spectra of the CTC, and the UOMO energy [41, 75]. A necessary condition of correlation of the polarographic potentials with any other parameter is reversibility of the electrode process.

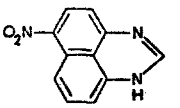
The literature contains little information regarding the polarograpnic oxidation of heterocycles, although it characterizes the π-donor character of a compound in solution. It follows from the data in Table 14 that phenothiazine and phenoxazine are oxidized with equal ease, while phenoxathiin is oxidized with considerably greater difficulty. This is in agreement with the evaluation of the relative π-donor character and π-surplus character of these heterocycles according to the data from the spectra of the CTC and the results of MO calculations.

Carbazole is oxidized with greater difficulty than phenoxazine and phenothiazine; this is not in agreement with the experimentally found ionization potentials (Table 7) but is in agreement with the relative ease of formation of CTC (Tables 11 and 12). The fact that the ionization potential of phenothiazine, determined by electron spectroscopy [35, 78], is too high is not excluded. One should also take into account the fact that irreversible waves were obtained in the polarographic oxidation of carbazole and 9-alkylcarbazole. 9-Alkyl groups in carbazole lower the oxidation potential, evidently owing to the +I effect. The small increase in the $E_{1/2}$ value for 9-phenylcarbazole also seems completely logical, since the N-phenyl group in a number of five-membered heterocycles usually displays weak electron-acceptor properties [22]. However, 10-methylphenothiazine is oxidized with greater difficulty than phenothiazine, evidently, as in the formation of a CTC (Table 12), because of steric factors (see [79] for steric effects in polarography).

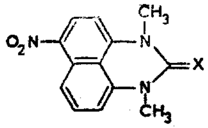
The polarographic oxidation of phenylpyrroles and triarylimidazoles was studied in extremely great detail in [80, 81].

Other Methods for the Evaluation of π-Donor Character. Studies of the kinetics of electron transfer between cation radicals and neutral molecules in compounds of the phenothiazine group (Table 15) have shown that the higher the π-donor character of neutral molecules, the higher the rate of the process [77]. In this case there is agreement with other methods in the evaluation of the relative π-donor character of these heterocycles, as well as correlation with the UOMO energies.

Good correlation between the ionization potentials, spectra of the CTC, and the energy of the first electron transition ($E^{\pi \rightarrow \pi^*}$) of the donor, which is easily measured [82], has previously been observed for alternate condensed hydrocarbons. No such studies have been made for heteroaromatic compounds. However, a satisfactory relationship between the position of the charge-transfer band in the spectra of CTC of perimidine and dihydroperimidine structures and the position of the long-wave absorption band in the spectra of their 6-nitro derivatives (XXI-XXIV) has been found in the author's laboratory:



XXI



XXII-XXIV

XXII X = CH_2; XXIII X = O ; XXIV X = S

The existence of this sort of conformity is evidently explained by the similar character of the interaction of the nitro group and the electron acceptor (in the case of CTC) with the π system of perimidines and dihydroperimidines. In both cases the interaction takes place through the π-donor centers of the naphthalene ring; this reflects the relative π-donor character of the compounds: XXI > XXII > XXIII, XXIV.

Electrophilic Substitution Reactions of π-Surplus Heterocycles

Inasmuch as π-surplus character, like π-donor character, is a reflection of the π-electron distribution in the molecule, it should be related primarily to the ground state of the molecule. Nevertheless, the usual practice is to identify the π-surplus character with the concrete reactivity: with the ease of electrophilic substitution and oxidation reactions and, to some extent, with the ease of the formation of CTC and π complexes with metal carbonyls (the latter are known for pyrrole [83], indole [84], and thiophene [85]). Although the reactivity is determined by the difference in the energies of the ground state of the reagents and the transition state of a reaction, there are probably situations in which the kinetic data or data on the position of an equilibrium may prove to be useful for the evaluation of the relative π-surplus character of compounds. For this it is necessary that the reactions in all cases proceed via an identical mechanism and that the energies of the transition complexes for the various substrates be close.

Despite the wealth of kinetic information on electrophilic substitution reactions in a series of π-surplus heterocycles, only a small part of this information is suitable for the comparison of reactivities. This is explained mainly by the diversity of the investigated reactions and the differences in the conditions of the kinetic measurements. Nevertheless, a number of studies in which the authors specially set out to make a quantitative comparison of the reactivities of π-surplus heterosystems on the basis of data from kinetic experiments are known. Thus it has been found that the rates of acylation of five-membered heterocycles with trifluoroacetic anhydride (in dichloroethane at 75°) in the 2 position are related to one another as follows [86, 87]: thiophene:selenophene:furan:pyrrole = $1:6.5:1.4 \cdot 10^2:5.3 \cdot 10^7$. Correspondingly, the ratio of the rates of protodesilylation of α-trimethylsilyl derivatives of benzene, thiophene, and furan is 1:4810:17,200 [88]:

$$\mathrm{HetSi(CH_3)_3} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{HClO_4}} \mathrm{Het{-}H + (CH_3)_3SiOCH_3}$$

Acidic deuterium exchange and mercuration take place six to 10 times more rapidly in selenophene than in thiophene [89, 90]. The reactivity of tellurophene lies between the reactivities of selenophene and furan [91]. The relative reactivities of the heterocycles in these reactions change in the same order as the π-donor character: the lower the first ionization potential of the substrate, the higher the reactivity. It has been proposed [92] that this conformity is determined by the similarity of the structure of the molecular ions formed during detachment of an electron from the molecules and the intermediate σ complex in the reaction.

However, in our opinion, the indicated coincidence is accidental. There is hardly a theoretical basis to expect a strict correlation between the π-donor character of the substrate and the ease of its entry into electrophilic substitution reactions in the case of the usual bimolecular addition-elimination mechanism. For this to occur, the step involving the formation of the σ complex should be the rate-determining step, whereas, insofar as we know, there are no reliably established cases of reactions of this sort in the heterocyclic series, and the rate-determining step is, as a rule, the step involving the formation of a σ complex. As a result, the relative ease of reactions in a series of monotypic substrates or the reactivities of the various positions of the same substrate are determined by the

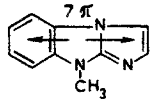
TABLE 16. Rate Constants of Acidic Deuterium Exchange, Effective Atomic Charges (q), and Electrophilic Localization Energies (L^+) of Azaindenes [97]

Compound	Position	k, sec^{-1}	q (PPP)	L^+, eV
Indole	3	$2{,}0 \cdot 10^{-7}$	$-0{,}072$	23,34
1-Methylindole	3	$2{,}5 \cdot 10^{-7}$	$-0{,}073$	23,30
Indolizine	1	$7{,}0 \cdot 10^{-5}$	$-0{,}090$	22,27
Indolizine	3	$3{,}6 \cdot 10^{-4}$	$-0{,}105$	21,82
2-Methylisoindole	1,3	$2{,}4 \cdot 10^{-3}$	$-0{,}082$	21,63

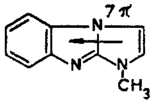
stability of the corresponding σ complex or, if one draws the reactivity indexes into this examination, by the electrophilic localization energy [93].

The validity of the above is confirmed by a comparison of the reactivities of five-membered heterocycles with their benzologs. If π-donor character played the decisive role, one should have expected an increase in the reactivities on passing from monocyclic compounds to condensed compounds, in conformity with the change in their ionization potentials and the ease of formation of CTC. In fact, this is not observed. Pyrrole is twice as reactive as indole in the Vilsmeier reaction [94], while furan is more reactive than dibenzofuran by a factor of 1000 in protodesilyation [88]. The reactivities decrease in the order thiophene > benzothiophene > dibenzothiophene in the same reaction and in acidic deuterium exchange [95], i.e., an order that is the reverse of the order of decreasing IP_1. Moreover, it is unimportant whether one compares the partial rate factors of the individual positions or the overall reactivities [88]. The ratio of the activities of the most reactive 3 position in dibenzothiophene, dibenzofuran, and 9-ethylcarbazole is 6.25:19.2:50,100 (data for protodesilylation; the reaction rate for trimethylsilylbenzene was taken as 1.00) [88].

The isomeric 9H- (XXV) and 1H-imidazo[1,2-a]benzimidazole (XXVI) provide another example of the nonconformity between π-donor character and the reactivities [96]. According to the LCAO MO data, the 1H isomer is a greater π-donor system, but it is considerably less active in electrophilic substitution reactions. The reason for this may consist in the different π-surplus character of the imidazole ring on the right in which these reactions take place. Whereas the π-electron density in the 9H isomer is shifted from the central ring (which contains seven π electrons) to the extreme imidazole ring (and to the benzene ring to a lesser extent), in the 1H isomer, on the other hand, the π electrons are shifted in the opposite direction. In the case of XXVI, some electrophilic substitution reactions therefore take place even in the benzene ring [96].



XXV



XXVI

The considerable decrease in the reactivities on passing from five-membered heterocycles to their benzologs can also be linked to a decrease in the π-surplus character of condensed systems. Thus π-surplus character to a greater extent than π-donor character determines the reactivities of compounds with respect to electrophiles. In addition, there is no universal correlation between the π-surplus character and the reactivities. Thus, for example, furan, benzofuran, and dibenzofuran undergo electrophilic substitution reactions more readily than their more π-surplus sulfur analogs. Similarly, the rate of deuterium exchange in the azaindene series [97] does not completely correlate with the charge densities but is in good agreement with the electrophilic localization energies (Table 16).

The above discussion shows that the concept of π-surplus character, despite its qualitative lucidity, is extremely difficult to characterize in quantitative terms. Nevertheless, it has valuable classificational as well as theoretical and practical significance. The establishment of the π-surplus character of a compound makes it possible to predict its high π-donor character and activity in reactions with electrophiles and makes its study with respect to a number of practically valuable properties promising.

It should be emphasized that there is no quantitative relationship between π-surplus character and π-donor character. These two concepts must be clearly distinguished. In contrast to π-surplus character, π-donor character is readily amenable to quantitative determination. The most accurate method for its evaluation is determination of the ionization potential. The CTC method gives good results, although it does have some limitations, and oxidative polarography is a promising method. It is obvious that systematic studies of all of the problems touched upon above encompassing, insofar as possible, a large number of heterocyclic compounds, particularly bridged compounds, are needed.

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SYNTHESIS OF NITROPHENYL DERIVATIVES OF 1,3,4-OXADIAZOLE

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Acylation of nitrobenzhydrazides with nitrobenzoyl chlorides and ethyl chlorocarbonate yielded a number of corresponding 1,2-diacylhydrazines, which were converted by the action of phosphorus oxychloride to nitro-substituted 2,5-diphenyl- and 2-phenyl-5-ethoxy-1,3,4-oxidazoles.

2,5-Diphenyl-1,3,4-oxadiazole derivatives containing various substituents (Cl, Br, Alk, OAlk) in the phenyl rings are finding extensive application in scintillation technology and in other fields of science and technology [1-3].

The present paper is devoted to the synthesis of the little-studied nitro-substituted 2,5-diphenyl- and 2-phenyl-5-ethoxy-1,3,4-oxidiazoles via the scheme

I-VI VII-XI XII-XXI XXII-XXIX

We obtained starting 1,2-diacylhydrazines XII-XXI by acylation of the hydrazides of benzoic (I), 2-nitro- (II), 3-nitro- (III), 4-nitro- (IV), 3,5-dinitro- (V), and 2,4,6-trinitrobenzoic (VI) acids with the appropriate benzoyl chlorides, as well as ethyl chlorocarbonate. They were subsequently cyclized to oxidiazoles by the action of $POCl_3$.

The formation of nitro derivatives of 2-phenyl-5-ethoxy-1,3,4-oxadiazole is possible when there is only one nitro group in the benzene residue of the starting hydrazone (oxidiazoles XXVIII and XXIX). Di- and trinitro-substituted 1-benzoyl-2-carbethoxyhydrazines (XX

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