HETEROCYCLIC ANALOGS OF PLEIADIENE

II. A General Consideration of Systems Containing an N-Atom of the Pyrrole Type. The Problem of the Participation of a Pyrrole Nitrogen Atom in a Six-Membered Ring*

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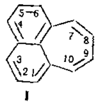
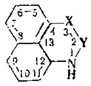
The problem of the participation of a N-atom of the pyrrole type in six-membered heteroaromatic systems has been considered within the framework of Hückel's molecular orbital method. The π-electronic characteristics of heterocyclic analogs of pleiadiene and a number of heteroaromatic compounds related to them have been considered from the point of view of reactivity, structure, and physical properties.

The chemistry of pleiadiene (I) a nonalternant-nonbenzenoid hydrocarbon has scarcely been studied because of its poor availability [2]. Heterocyclic analogs of pleiadiene are more readily accessible—in the first place, perimidine (II) and naphtho[1, 8-d, e]triazine (III). Because chemistry of heteroaromatic compounds resembles the chemistry of their carbocyclic precursors in many respects, we have undertaken a study of these analogs of pleiadiene. In this work the results of quantum-mechanical calculations by the MOH method of heteroanalogs of pleiadiene containing a pyrrole nitrogen atom are subjected to analysis.



I



II–V

II X = N, Y = CH;
III X = Y = N;
IV X = Y = CH;
V X = CH, Y = N

This family includes, besides compounds II and III, the hitherto unknown 1H-benzo[d, e]quinoline (IV) and 3H-benzo[d, e]cinnoline (V).

Calculations and results. All the calculations were carried out in Hückel's approximation with all the overlap integrals neglected. The parameters recommended by Streitweiser [3] were used for the heteroatoms:

$$\alpha_{\dot{N}}=\alpha^0+0.5\beta^0;\ \alpha_{\ddot{N}}=\alpha^0+1.5\beta^0;\ \alpha_{N^+}=\alpha^0+2.0\beta^0;$$
$$\alpha_{\dot{O}}=\alpha^0+1.0\beta^0;\ \alpha_{\ddot{O}}=\alpha^0+2.0\beta^0;\ \alpha_{O^-}=\alpha^0-0.5\beta^0;$$
$$\alpha_S=\alpha^0;$$
$$\beta_{(C \overset{\dots}{=} C)}=\beta_{(C=N)}=\beta_{(C=O)}=\beta_{(C-S)}=\beta_{(C-N^+)}=\beta^0;$$
$$\beta_{(C-N)}=\beta_{(C-O)}=0.8\beta^0,$$

where α^0 and β^0 are the standard Coulomb and resonance integrals, respectively.

The resolution of the secular determinants was obtained on a "Minsk-12" electronic computer.

The calculations of the π-electronic charges and the orders of the mobile bonds for the heteroanalogs of pleiadiene and the naphthazoles isomeric with them are given in Tables 1 and 2. The values of the total π-electronic energy E^{π} and the energy of the first electronic transition $E^{\pi-\pi^*}$ (in β^0 units) calculated by a known proceduce [3] are given in Table 3. The electronic parameters of the other substances are given in the form of molecular diagrams and, in part, in the summarizing Table 3.

DISCUSSION OF THE RESULTS

For systems II–V to satisfy the 4n + 2 rule, one of the nitrogen heteroatoms in each of them must supply two π-electrons to the aromatic ensemble, as is the case in pyrrole. However, the participation of a N-atom of the pyrrole type in a six-membered system is an unusual phenomenon and we must dwell especially upon this problem, which has not hitherto been subjected to special consideration.

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*For part I, see [1].

Table 1. π-Electron Charges of the Atoms of the Heterocyclic Analogs of Pleiadiene and of the Naphthazoles

Compound	Atom No.												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Perimidine (II)	+0.244	+0.256	−0.301	+0.048	−0.084	+0.006	−0.068	0.000	−0.073	+0.007	−0.093	+0.063	−0.008
Naphtho[1,8-de]triazine (III)	+0.254	+0.018	−0.146	+0.036	−0.050	+0.005	−0.038	0.000	−0.072	+0.007	−0.092	+0.064	+0.013
H-Benzo[de]quinoline (IV)	+0.227	+0.104	−0.099	+0.027	−0.080	+0.005	−0.069	0.000	−0.080	+0.007	−0.099	+0.061	−0.004
3H-Benzo[de]cinnoline (V)	+0.221	−0.155	+0.073	+0.013	−0.036	+0.004	−0.030	0.000	−0.076	+0.006	−0.096	+0.061	+0.015
3H-Benzo[e]indole (XVIa)	+0.247	+0.016	−0.113	−0.052	−0.006	−0.008	−0.007	−0.009	−0.005	−0.012	−0.027	−0.016	−0.007
3H-Naphtho[2,1]pyrazole (XVIb)	+0.258	−0.230	+0.031	−0.060	+0.005	−0.009	+0.001	−0.009	+0.002	−0.012	+0.006	−0.019	+0.035
3H-Naphtho[1,2]imidazole (XVIc)	+0.266	+0.152	−0.302	−0.023	−0.010	−0.004	−0.007	−0.007	−0.004	−0.010	−0.026	−0.016	−0.007
3H-Naphtho[1,2]triazole (XVId)	+0.293	−0.095	−0.172	−0.025	−0.001	−0.005	0.000	−0.006	+0.002	−0.009	+0.004	−0.018	+0.032

Table 2. Mobile Bond Orders of the Heterocyclic Analogs of Pleiadiene and the Naphthazoles*

Compound	Bond														
	1—2	2—3	3—4	4—5	5—6	6—7	7—8	8—9	9—10	10—11	11—12	12—13	1—12**	4—13	8—13
Perimidine (II)	0.437	0.788	0.437	0.641	0.629	0.707	0.551	0.554	0.712	0.621	0.671	0.547	0.381	0.552	0.600
Naphtho[1,8-de]triazine (III)	0.406	0.826	0.444	0.641	0.628	0.708	0.550	0.553	0.713	0.620	0.671	0.544	0.322	0.509	0.527
H-Benzo[de]quinoline (IV)	0.382	0.828	0.460	0.630	0.633	0.704	0.551	0.554	0.710	0.624	0.664	0.550	0.329	0.514	0.581
3H-Benzo[de]cinnoline (V)	0.327	0.839	0.450	0.638	0.629	0.707	0.551	0.553	0.711	0.622	0.667	0.545	0.330	0.514	0.525
3H-Benzo[e]indole (XVIa)	0.417	0.807	0.504	0.482	0.580	0.710	0.614	0.716	0.564	0.530	0.741	0.566	0.534	0.372	0.612
3H-Naphtho[2,1]pyrazole (XVIb)	0.373	0.793	0.520	0.477	0.582	0.709	0.616	0.714	0.566	0.526	0.748	0.557	0.536	0.402	0.605
3H-Naphtho[1,2]imidazole (XVIc)	0.469	0.771	0.482	0.488	0.577	0.712	0.613	0.717	0.563	0.532	0.741	0.566	0.502	0.369	0.617
3H-Naphtho[1,2]triazole (XVId)	0.442	0.774	0.516	0.477	0.582	0.709	0.616	0.714	0.566	0.526	0.749	0.556	0.536	0.399	0.593

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*All the compounds in the text and in the tables are named in accordance with the "Chemical Abstracts" and "Ring Index" rules. The noncanonical numbering of the atoms in formulas II-V and XVI is for convenience in giving the information in the tables.

**The 1—12, 4—13, and 8—13 bonds in compounds II-V correspond to the 5—10, 1—13, and 4—13 bonds in compounds XVI.

Table 3. Energies of the Highest Occupied Molecular Orbitals, $E_{h.o.}$, Total π-Electronic Energies, E^{π}, Energies of the First Electronic Transitions, $E^{\pi\to\pi^*}$, and Position of the Long-Wave Absorption Maxima of the Compounds Studied*

Compound	$E_{h.o.}$	E^{π}	$E^{\pi\to\pi^*}$	λ_{max}, nm
Pleiadiene (I)	−0.241	19.145	−0.698	560
Anthracene	−0.414	19.314	−0.828	375
Phenanthrene	−0.605	19.448	−1.210	342
Perimidine (II)	−0.328	20.283	−1.002	400
Naphtho[1,8-de]triazine (III)	−0.352	20.723	−0.835	451
1H-Benzo[de]quinoline (IV)	−0.273	19.692	−0.955	—
3H-Benzo[de]cinnoline (V)	−0.321	20.204	−0.870	—
3H-Benzo[e]indole (XVIa)	−0.486	19.808	−1.123	—
3H-Naphtho[2,1]pyrazole (XVIb)	−0.581	20.362	−1.148	—
3H-Naphtho[1,2]imidazole (XVIc)	−0.520	20.412	−1.155	324
Naptho[2,3]imidazole	−0.482	20.346	−1.037	342
3H-Naphtho[1,2]triazole (XVId)	−0.589	20.898	−1.124	324
Bipyridylidene (VIII)	+0.149	19.036	−0.562	—
Pyrid-4-one (IXa)	−0.776	12.058	−1.387	260
Pyrid-4-one (IXb)	+0.085	10.793	−0.835	—
2H-2-Pyrindine (Xa)	−0.376	13.768	−0.943	—
2H-2-Pyrindine (Xaa)	−0.374	14.981	−1.010	—
3-Vinylpyridine (Xb)	−0.668	10.973	−1.318	278
4-Vinylpyridine (Xc)	−0.734	10.975	−1.315	—
1-Vinylfulvene (XI)	−0.441	9.929	−0.668	—
1H-1-Pyrindine (XII)	−0.466	13.792	−0.901	—
Phenoxazine (XIII)	−0.440	23.826	−1.440	317
Phenothiazine (XIV)	+0.146	20.686	−0.854	317
Diphenylamine (XV)	−0.607	19.465	−1.607	285

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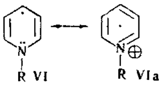
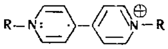
*We measured the UV spectra on an SF-4A instrument in methanolic solution. The spectral data for pleiadiene and 3-vinylpyridine were taken from the literature [3,15]. For the MOH data for pleiadiene, anthracene, and phenanthrene, see [16].

Problem of the participation of a pyrrole nitrogen atom in a six-membered ring. The simplest conceivable six-membered system with a N-atom of the pyrrole type (VI) is unstable because of its radical nature (seven π-electrons). Such compounds, consisting essentially of cation radicals (VIa), are formed as intermediates in the reduction of pyridinium salts [4].

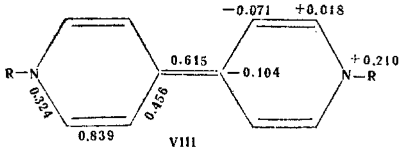


VI VIa



VII

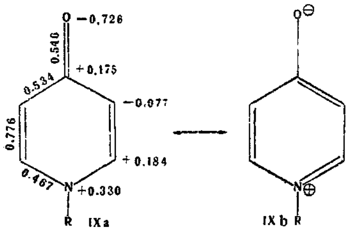
In more complex systems including a six-membered ring of type VI as a fragment conditions may arise for the stabilization of a structure with a pyrrole nitrogen atom. Thus, the violet cation radicals VII are completely stable [4]. The reduction of the cation radicals VII leads to the diamagnetic bipyridylidenes VIII. In spite of the presence of 14 π-electrons, the participation of the pyrrole nitrogen atoms in such quinoid structures does not promote the stabilization of the molecule.



VIII

A quantum-mechanical calculation shows that in the ground state of the molecule VIII two π-electrons are present in the antibonding level with an energy x = +0.149.* This must lead to very ready oxidizability. The low value of the energy of the first electronic transition (−0.562 β^0) satisfactorily explains the deep color of these compounds.

The α- and γ-pyridones, the thioxopyridones, and compounds related to them belong to another possible class of structures containing a pyrrole-like N-atom.



IXa IXb

Since in these compounds (for example IX) seven π-electrons are formally present in the hetero ring, a tendency to eject the "superfluous" electron favors an increase in the contribution of bipolar structures of type IXb. This is shown in all the physical and chemical properties of the pyridones [5] and also in the results of quantum-mechanical calculations: the high values of the charges on the N- and O-atoms, the low order of the C=O bond, etc. From the energy point of view, taking into consideration the value of the total π-electronic energy (Table 3), the limiting structure IXa is considerably more stable than IXb. This means that the real state of the valence bonds in the molecule of pyrid-4-one is intermediate between the quinoid and benzoid configurations.

A related problem is encountered in the pyrindines — nitrogen analogs of azulene. Calculations by the MOH method show that participation of the pair of electrons of the N atom in the formation of an aromatic ten π-electronic structure is energetically favorable for the pyrindines, since the π-electronic energy of the model XI (1-vinylfulvene) with the nitrogen atom excluded from conjugation is considerably lower than that for the conjugated 2H-2-pyrindine (Xa, Table 3).

2-Pyrindine (II) and 1-pyrindine (XII) can each exist theoretically in the form of three tautomeric forms (for example, Xa–Xc) of which the most interesting is the tautomer with the hydrogen atom on the nitrogen (Xa, R = H, and XII, R = H). However, in an equilibrium mixture the concentration of the latter is negligible. At first sight, this appears strange since the π-electronic energy of the more stable tautomers Xb and Xc, which are the π-electronic analogs of the vinylpyridines, are considerably lower. The explanation must be sought in the high polarization of the molecules of the pyrindines as a result of which the basicity of the C-atoms of the five-membered ring become greater than the basicity of the nitrogen atom in pyridine itself or in the vinylpyridines. Thus, for example, the

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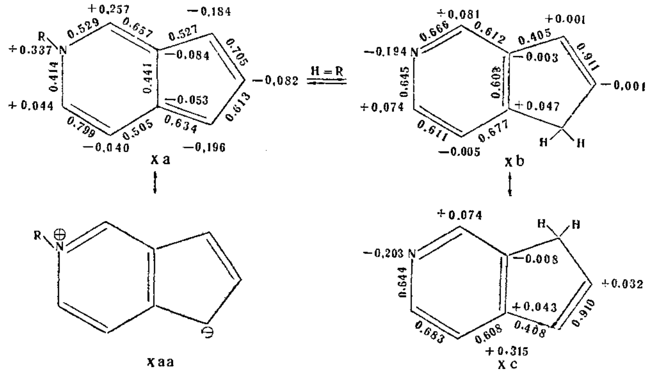
* Here and below, the values of the energies of the orbitals are given in the units $x = (\alpha^0 - e)/\beta^0$.

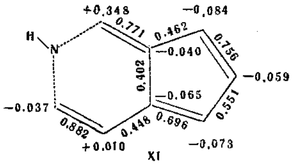


Xa

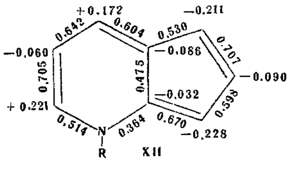
Xb

Xaa

Xc



XI

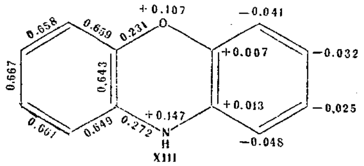


XII

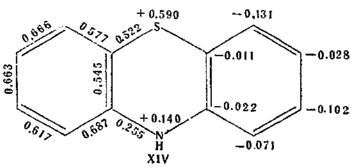
pK_a values of compounds XII with R = CH_3 and H are, respectively, 8.7 and 5.7 [7]. In agreement with this, the unsubstituted pyrindine XII protonates and alkylates at the nitrogen atom while the heteroanalogs of azulene with a fixed structure Xa or XII (R = CH_3, C_6H_5) protonate in accordance with our calculations at the C-atoms of the five-membered ring. The marked polarization of the molecules of the pyrindines is also reflected in the anomalously high positive charge on the nitrogen atoms and in the high order of the C—N bonds as compared with five-membered pyrrole-like structures [9]. It is significant that the magnitude of the π-electronic energy also indicates a greater stability of the bipolar benzoid structure Xaa as compared with the quinoid structure Xa.

In addition to the bipyridylidenes, pyridones, and pyrindines, many other six-membered heterocyclic structures in which the nitrogen atom provides two π-electrons for cyclic conjugation are known. The majority of them also have the quinoid type of structure and form only more complicated copies of the compounds considered (for example, the anhydrobases of the carbolines and of the azaindoles, etc.).

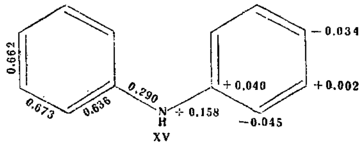
Examples of nonquinoid six-membered structures with N-atoms of the pyrrole type are phenoxazine (XIII) and phenothiazine (XIV). If it is assumed that in these compounds each of the two heteroatoms contributes two electrons to the conjugated cyclic system, they do not obey Hückel's rule as a whole since they contain 16 π-electrons. In accordance with this, phenoxazine and, particularly, phenothiazine, tend to give up the "superfluous" electrons, being oxidized to a cation radical or a dication [10,11]. The ease of oxidation of compounds XIII and XIV is in harmony with the results of molecular-orbital calculations, according to which their highest occupied molecular orbital is characterized by an extremely high energy: x = −0.440 and +0.146, respectively.* Nevertheless, the degree of



XIII



XIV



XV

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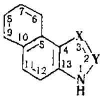
*For a quantum mechanical calculation of the molecule of phenothiazine using other parameters, see [12]. Taking the d-orbital of sulfur into account, the highest occupied orbital of the molecule XIV becomes bonding, and in this case it is characterized by a fairly high energy [13].

participation of the oxygen and sulfur atoms in cyclic conjugation is apparently very small. Thus, for example, in their reactivities phenoxazine and phenothiazine closely resemble diphenylamine (XIV), and the absence of coloration sharply distinguishes them from the majority of other six-membered heteroaromatic structures with a N atom of the pyrrole type. This can be explained both by the unsuitability of the 16 π-electronic cyclic structure and by the acoplanarity of compounds XIII and XIV [14].

In our calculations we did not take into account the latter factor or the participation of the d-orbitals of sulfur. This is probably the reason why the values of the electronic density that we obtained for phenothiazine, unlike those for compounds XIII and XV, do not satisfactorily reflect its real reactivity.

Heterocyclic analogs of pleiadiene. In contrast to the compounds considered above, the heterocyclic analogs of pleiadiene II–V do not possess a quinoid system of bonds and moreover satisfy the $4n + 2$ rule. Consequently the absence from them of parasitic phenomena connected with tautomerism, acoplanarity, and the lability of the quinoid structure is to be expected.

The features of these compounds appear very clearly against the background of the properties of the naphthazoles (XVI) isomeric with them.* In this connection we have also carried out quantum-mechanical calculations of the angular heterocyclic systems XVI. In the naphthoimidazole series, the linear isomer and the 1H tautomer of compound XVIc were also subjected to analysis.



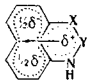
XVIa-d

a X = Y = CH; 3H-benz[e]indole;
b X = CH, Y = N; 3H-naphtho[2, 1]pyrazole;
c X = N, Y = CH; 3H-naphtho[1, 2]imidazole;
d X = Y = N; 3H-naphtho[1, 2]triazole.

The most prominent property of pyrimidine and naphtho[1, 8-d, e]triazine, as of pleiadiene, is their deep coloration (green and red, respectively), which sharply distinguishes them from the colorless compounds XVI. This color is well explained by the calculations. As in the pleiadiene–anthracene–phenanthrene series, they show that the energy of the first electronic transition $E^{\pi \rightarrow \pi^*}$, responsible for the long-wave absorption band, is considerably lower for the heterocyclic analogs of pleiadiene than for the isomers XVI corresponding to them (Table 3). In general there is a very good qualitative relationship between the positions of the long-wave absorption bands and the values of $E^{\pi \rightarrow \pi^*}$ for all the compounds that we have studied. Thus, the results obtained explain the deeper coloration of naphtho[1, 8-d, e]triazine as compared with pyrimidine. On the basis of the calculated values of $E^{\pi \rightarrow \pi^*}$ it may be predicted that the color of compounds II–V will become deeper in the sequence II < IV < V < III.

The color of the heterocyclic analogs of pleiadiene also witnesses their relatively low aromaticity. Experimental results confirm this: 2, 3-dihydropyrimidines are aromatized to pyrimidines [17] with considerably more difficulty than dihydro derivatives of other heteroaromatic systems [18]. Correspondingly, the total π-electronic energies of compounds II–V are 0.11–0.17 β^0 lower than for their benzoid analogs XVI (Table 3).

The calculations also show that in compounds II–V, as in pleiadiene itself, there is a clear tendency to the expulsion of the "superfluous" π-electron from the peri ring into the naphthalene system with a resulting distribution of charges corresponding to the structure XVII:



XVII

For a quantitative evaluation of this effect, it is convenient to compare the magnitudes of the total π-electronic charges on the atoms not included in the naphthalene part of the molecule. For pleiadiene, anthracene, and phenanthrene these are atoms 7–10 and 1–4, respectively, and for compounds II–V and XVI they are atoms 1–3. As can be seen from Table 4, a shift in the electron density in the naphthalene ring also takes place in the analogs of pleiadiene and in the naphthazoles. However, in absolute magnitude it is far higher in the former. On this basis we must expect a greater readiness for their participation in reactions of nucleophilic substitution at the atoms of the hetero ring. Pyrimidine in fact very readily undergoes amination at position 2 with sodium amide [1] and, according to our results, naphtho[1, 8-d, e]triazine is readily hydrolyzed by dilute hydrochloric acid to 1-amino-8-naphthol.

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*Similarly, it is desirable to compare the properties of pleiadiene with those of anthracene and phenanthrene.

Table 4. Total π-Electronic Charges on the Atoms Not Participating in the Naphthalene Nucleus

Group of atoms	Peri system (pleiadiene analogs)	1,2-system (angular)	2,3-system (linear)
—CH=CH—CH=CH—	+0.154	0.000*	0.000*
—CH=CH—N̈H—	+0.232	+0.150	—
—CH=N—N̈H—	+0.139	+0.059	—
—N=CH—N̈H—	+0.199	+0.116**	+0.118
—N=N—N̈H—	+0.126	+0.026	—

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*The zero values of the π-electronic charges for anthracene and phenanthrene follow from the alternant nature of these hydrocarbons.

**For the $N_{(3)}$–H tautomer of naphtho[1,2]imidazole' the analogous value for the $N_{(1)}$–H tautomer is +0.115.

It is interesting, however, that the difference in the values of the π-charges in the hetero systems II–V and XVI is due almost exclusively to the atom in position 2. Furthermore, the positive charge on the pyrrole N-atom and the multiplicity of the $N_{(1)}$—$C_{(2)}$ bond in the naphthazole series are considerably higher. In agreement with the higher aromaticity of compounds XVI as compared with II–V, this shows the greater participation of the electron pair of the pyrrole nitrogen atom of the naphthazoles in the formation of a 14 π-electron aromatic system. It becomes clear from this why the acidic properties of the NH group of pyrimidine are weakened in comparison with those of naphtho-[1,2] imidazole.

In respect of electrophilic substitution reactions, molecular-orbital calculations give approximately the same pattern for pleiadiene itself and for its heteroanalogs. The charge densities show the preferential attack by an electrophilic reagent of the $C_{(11)}$ atom of compounds II–V. An exception is 1H-benzo[de]quinoline in which, as in indole and benzoindole, the greatest electron density is concentrated on the $C_{(3)}$ atom. Compound IV will probably take part in an electrophilic substitution reaction with somewhat greater difficulty than its isomer from the XVI series in which the electronic density in position 3 is higher; for the other pleiadiene analogs the pattern will be the opposite. Unfortunately, until now not only quantitative but also reliable qualitative information on its electrophilic substitution in the series of pleiadiene and its analogs has been lacking. Compounds II–V may also react with electrophilic reagents in the protonated form. However, as calculation has shown, in the pyrimidine cation, as compared with the neutral molecule, the distribution of electron density is qualitatively unchanged.

Thus, the investigation carried out has shown that the participation of a N atom of the pyrrole type in six-membered aromatic structures is achieved in the majority of cases by the formation of unstable quinoid structures, the nonobservance of the 4n + 2 rule, or a disturbance of the coplanarity of the molecule. Exceptions are the more stable heterocyclic analogs of pleiadiene II–V which can be considered at the present time as the most typical representatives of heteroaromatic systems with a pyrrole-like nitrogen atom. In addition, as we shall show subsequently, in view of the presence in the hetero ring of seven π-electrons these compounds possess, in addition to their color, a whole series of other extremely unusual properties.

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