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THE RULES LINKING STRUCTURES AND ELECTRONIC ABSORPTION SPECTRA OF ISOMERIC PYRROLOQUINOLINES

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Molecules of pyrroloquinolines with linear and angular structures have been studied by quantum-chemical methods. The different rules which govern the electronic absorption spectra of these isomers are determined by the different nature of the conjugated structures of the fragments in linear and angular pyrroloquinolines.

Keywords: pyrroloquinolines, chromophores, intensity of absorption bands, the MNDO method, the Hückel method, characteristic absorption bands, electronic absorption spectra.

During the synthesis of pyrroloquinolines based on benzaminoindoles it is possible to produce both linear and angular isomers [1, 2]. Further progress in the development of new methods for the preparation of pyrroloquinolines depends to a considerable extent on the methods of identification of the structure of the compounds produced. Naturally it is possible to use traditional methods for the determination of molecular structure – microwave spectroscopy, X-ray analysis, electron diffraction, ^{1}H NMR spectroscopy, and mass spectroscopy. However, the use of direct methods to determine the structures, in spite of technological progress, requires quite large amounts of material and consumption of time. Investigations of the electronic absorption spectra (visible and ultraviolet regions of the electronic spectrum) of a series of substituted pyrroloquinolines with linear and angular structures with various substituents, prepared by the authors [3], showed that there were definite rules which connected the spectroscopic characteristics with the structure of the molecules studied.

Both linear and angular pyrroloquinolines have basically 3 maxima in their spectra. Electronic absorption spectra of ethanol solutions of the pyrroloquinolines were measured on Cary-219 and Specord spectrophotometers in the wavelength range 200-400 nm. It should be noted that the intensity of the first short-wave absorption band is always less that for the second for linear pyrroloquinolines, whereas the reverse is true for the angular isomers. The intensity of the maxima in the long-wave region is always less for all isomers than the intensities of the bands described above. The demonstration of the of the objective nature of these rules may provide the basis for a sound rapid method to establish the structures of synthesised pyrroloquinolines with different structure by electronic spectroscopy.

The absorption bands in the spectra of pyrroloquinolines are explained by the presence of such strong chromophores as, pyrrole, pyridine, and benzene. In this connection in our work on the interpretation of the characteristic appearance of the spectra of linear and angular isomers of pyrroloquinolines we have studied the interaction of these chromophore fragments in the molecular system.

The rules which characterise the spectra of pyrrole, pyridine, benzene, and their aromatic derivatives have been thoroughly investigated [4-8].

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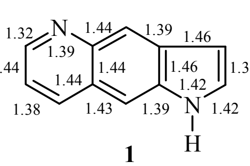
From an analysis of the literature data it can be confirmed that in the spectra of linear and angular isomers of pyrroloquinolines the characteristic absorptions in the 200-240 nm region are explained by the same chromophore as pyrrole, those in the 260-310 nm region as in pyridine, and in the 340-380 nm range as in the benzene ring. It is natural to suggest that the differences in the spectra of linear and angular pyrroloquinolines is determined by the different nature of the interactions of these chromophores.

Results of calculations on a series of derivatives of pyrroloquinolines with linear and angular structures with various substituents using the MNDO system with complete optimization of the geometry permitted the following conclusions to be drawn:

(1) all of the pyrroloquinoline molecules have planar structures;

(2) the HOMO and LUMO, and also a series of orbitals with energies below the LUMO and above the HOMO, are of π-type. Since just the characteristics of these orbitals which determine the spectral properties of the molecules studied, it can be confirmed that the basic role in the formation of the absorption spectra of pyrroloquinolines is played by the π-electron system of the skeleton. While substituents have only a corrective effect.

In connection with the above, the explanation of the characteristic behavior of the electronic spectra of the linear and angular isomers of pyrroloquinolines was discussed on the basis of the following model systems:



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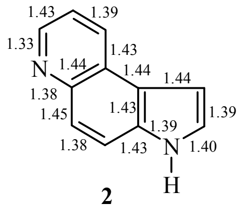

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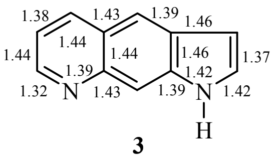

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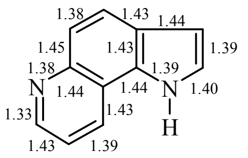

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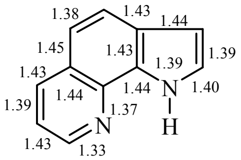

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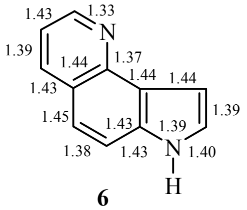

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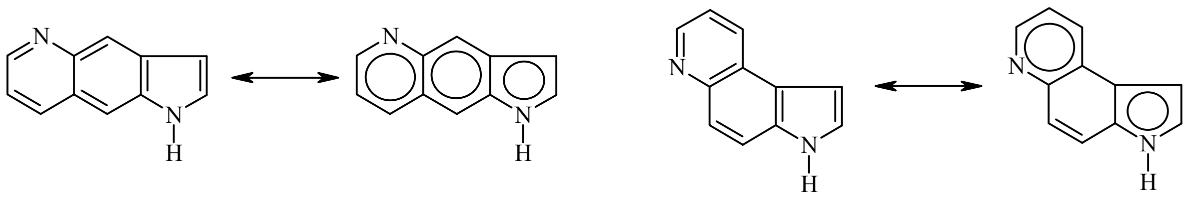
It is known from the literature (see [7] for example) that the degree of conjugation in a molecule frequently determines the structure of the electronic absorption spectra. The resonance energy, E_{res}, estimated from the interaction of isolated double bonds and lone electron pairs, can be used as a quantitative measure of the degree of conjugation. Values of E_{res} for the model systems **1-6**, calculated with the simple Hückel method [9, 10] with parameters for the heteroatoms from [11] showed that the values of the resonance energies of these models of pyrroloquinolines are very close (the differences do not exceed 2%). Hence the characteristics of the π-electronic systems of linear and angular models of pyrroloquinolines in the case of the most optimised conditions of electron interactions are practically no different from one another and do not explain the reasons for the observed rules in the structure of the measured spectra.

Let us turn to an analysis of the possible reasons for these results. The Hückel method is purely topological, It suggests implicitly the existence in aromatic systems of a negligible alternation of bond lengths in the resonance structures which in fact guarantees the optimal conditions for the interaction of the double bonds and the formation of the required π-electron systems. The structural deviation from this standard found in real linear and angular isomers of pyrroloquinolines is evidently the reason for the change in the character of the interaction of double bonds and non-bonded electron pairs. The MNDO-PM3 method was used to find the optimised geometry to explain the structural peculiarities of the chosen models of system **1-6**.

It follows from the schemes discussed above that the lengths of the C–C and C–N bonds in the pyridine and pyrrole units in linear and angular pyrroloquinolines are sufficiently close in the general case. But in the benzene ring of angular pyrroloquinolines the carbon bonds connecting the pyrrole and pyridine units are considerably longer than the analogous bonds in the linear systems (1.39 and 1.44 A respectively). It may be claimed that angular condensation of the pyridine ring disrupts the alternation of bond lengths in the benzene ring which impedes the formation of π-electron systems covering all of the atoms of the skeleton. Taking into account the real structures of the linear and angular isomers of pyrroloquinolines, the character of their conjugation may be shown by the following scheme:



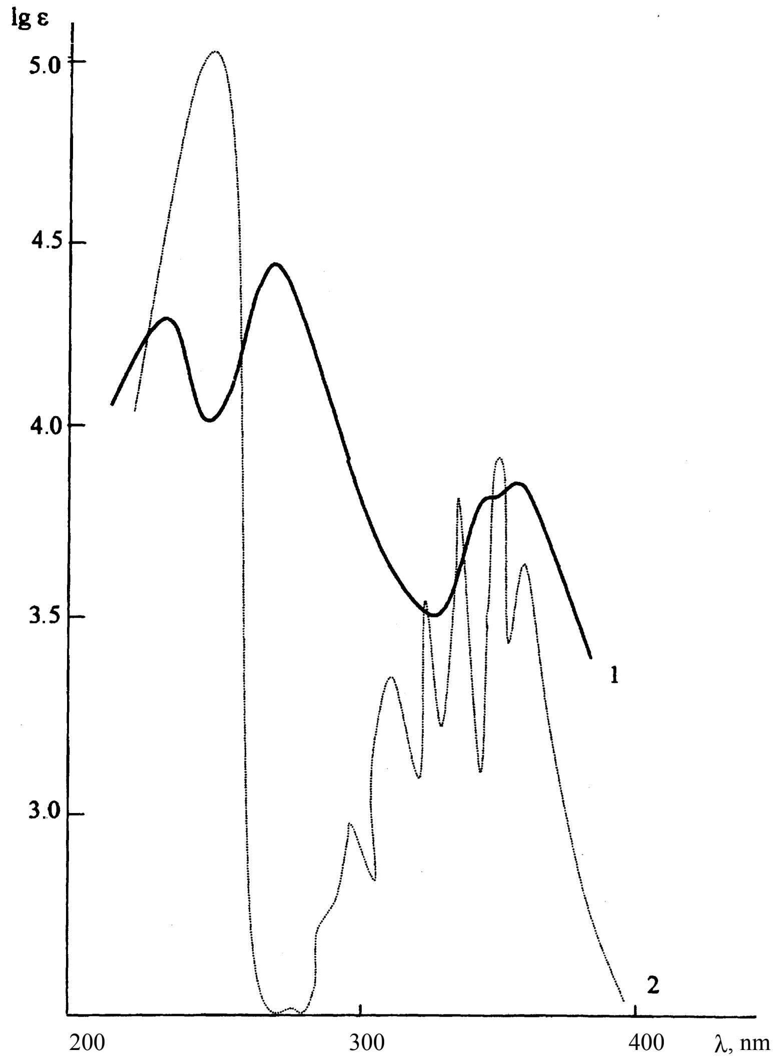


Fig. 1. Electronic absorption spectra; 1 – 2,3,6,8,9-pentamethylpyrrolo-1H-[2,3-*g*]-quinoline,
2 – anthracene.

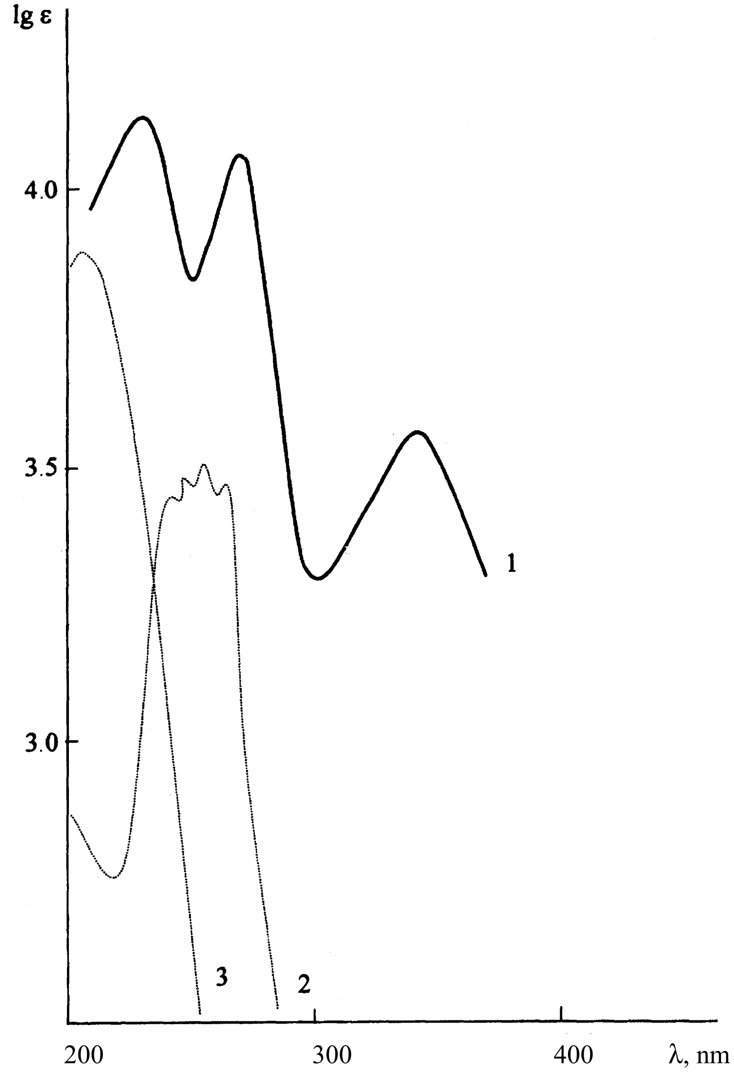


Fig. 2. Electronic absorption spectra: 1 – 1,2,4,7,9-pentamethylpyrrolo-3H-[3,2-*f*]-quinoline; 2 – pyridine; 3 – pyrrole.

For the angular pyrroloquinolines which shows structures with interacting pyrrole and pyridine, E_{res} ~1.52-1.53 β. The resonance energy for linear model systems falls within the interval 5.48-5.59 β. The structural differences between linear and angular model molecules produces important differences in the characteristics of the π-electron systems formed which should naturally show up in the spectral properties of pyrroloquinoline isomers.

Consequently it can be accepted that for pyrroloquinolines with linear fusion of the rings the UV spectra should show the properties of systems of conjugated chromophores, consequently anthracene can serve as a model for the interpretation of their spectra.

It is shown in Fig. 1 that the β-band, which is distinguished by its very high intensity in the spectra of condensed polycyclic aromatic hydrocarbons, appears at λ 260-310 nm in the spectra of linear pyrroloquinolines. This explains the high intensity of the second of the two shortwave bands in comparison with the first, which is due to electronic transitions in the pyridine part of the molecule.

For angular pyrroloquinolines the UV absorptions appear as the superposition of separate chromophores, pyrrole and pyridine (see Fig. 2) and the rules for the change in intensity of the first two bands in the absorption spectra are explained by the relative intensities of the characteristic bands in the spectra of pyridine and pyrrole.

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