to conclude with a high degree of probability that all of the compounds considered have a 4e-alkyl-4a-OH configuration. In fact, as we have previously shown [1, 2], regardless of the length of the alkyl substituent in the 4 position (C_2H_5 or n-C_4H_9), this ratio for the axial group lies within the limits of eight and is close to four for an equatorial group. The $I_{[M-C_2H_5]}+/I_{[M]}+$ ratios in the spectra of the alcohols (Ic, IIc, Vc, and VIc) are less than four, and this may constitute evidence for an equatorial orientation of the 4-alkyl group in all I-VI.

EXPERIMENTAL

The mass spectra were obtained with a commercial MKh-1303 spectrometer with direct introduction of the sample into the ion source at 40°; the ionization energy was 70 eV, and the ionization chamber temperature was 150°. The reproducibility of the mass spectra was verified by repeated recording on different days; the error in the measurement of the peak ratio did not exceed 5 rel. %.

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IONIZATION POTENTIALS OF DIPYRIDYLS AND DIQUINOLYLS

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The ionization potentials of a number of isomeric dipyridyls and diquinolyls were determined. The differences in their values make it possible to establish the site of fusion of the rings in the 2,2', 3,3', and 4,4' positions of the system. The absence of an appearance potential for the fragment ion, the existence of which is due to cleavage of the interannular bond in the doubled hetaryl compounds, constitutes evidence for its double-bond character.

According to the concepts of Szent-Györgyi [1], the physiological activity of many organic substances is due to their donor properties, which are manifested in an increased tendency to form charge-transfer complexes (CTC). In this connection, research to determine the ionization potentials (IP) of various dipyridyls and diquinolyls, the diverse physiological activities of which have been studied, seems to us extremely useful, inasmuch as the accumulation of such data opens up prospects for the prediction of the biological action of new substances from their IP. The present research may also be of interest for the evaluation of the correctness of quantum-chemical calculations of bisheteroaromatic systems, since the IP correspond at least approximately to the energy of the higher occupied molecular orbital (the Copman theorem) [2].

In a previous mass spectrometric study of dipyridyls [3] and diquinolyls [4], we were unable to unambiguously establish whether the bond between the hetaryl rings in their molecules is cleaved or whether the peaks of ions with masses equal to the mass of one ring of the system are represented exclusively by doubly charged ions.

In the present study we made an attempt to use the IP of the corresponding fragment ions for this purpose. The IP for a number of isomeric dipyridyls and diquinolyls are presented in Table 1.

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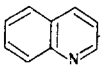
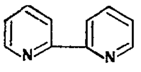
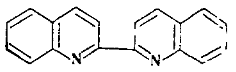
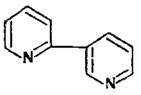
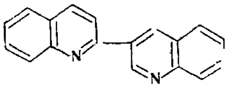
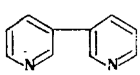
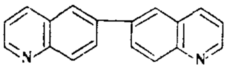
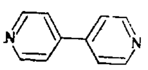
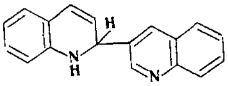
TABLE 1. Ionization Potentials (IP) of Isomeric Dipyridyls and Diquinolyls

Compound	Formula	IP, eV	Compound	Formula	IP, eV
		9.23[5]			8,30[6]
I		8,54	V		7,93
II		8,58	VI		7,97
III		8,46	VII		7,79
IV		9,18	VIII		6,81

It seemed of interest to ascertain the possibility of the use of the IP for the determination of the structures of the isomeric dipyridyls and diquinolyls, particularly for the establishment of the sites of fusion of the rings in their molecules. Attempts to use the IP for this purpose have already been made [7-9].

It follows from Table 1 that the assignment of the isomers can be made on the basis of a knowledge of the IP of dipyridyls and diquinolyls; however, the use of the IP for analytical purposes should, nevertheless, be approached with some degree of caution. Thus in the I-VII series the IP of molecules with ring fusion in the 2,2', 3,3', and 4,4' (or 6,6') positions differ sharply. However, the IP of the 2,2' and 2,3' isomers of both dipyridyl and diquinolyl were found to be practically equal (I and II and V and VI).

It has been established that there is a relationship between the degree of double bond character of the interannular bond (found from the results of quantum-chemical calculations), the reactivities [10], and the character of the change in the basicities [11] in a series of symmetrical bishetaryls; this relationship correlated fully with the stabilities of the molecular ions with respect to electron impact [3,4]. It was found that in the I-VII series under consideration here there is a correlation between these values and the IP. Moreover, the IP decreased in the order 4,4' > 2,2' > 3,3' isomers, following also the trend of the changes in the other above-indicated properties of the investigated dipyridyls and diquinolyls; this provides evidence for a decrease in the π-electron interaction of the rings in these bisheteroaromatic systems.

It is known that an increase in the number of conjugated π bonds and electron-donor substituents in a molecule promotes detachment of an electron [7]. The same principle is also observed when one compares the IP of pyridine and quinoline with the IP of dipyridyls and diquinolyls and with the IP found for 3-(1,2-dihydro-2-quinolyl)quinoline (VIII). It may be assumed that the general tendency toward a decrease in the IP for bishetaryls I-VII as compared with pyridine and quinoline serves as a confirmation of the presence of conjugation between the rings in the system, and the lowest IP, which was found for VIII, is a consequence of the donor character of the 1,2-dihydroquinolyl substituent.

It was stated above that one cannot, on the basis of an examination of the mass spectra of I-VII, determine, with a high degree of reliability, whether the C – C bond between the heteroaromatic rings is cleaved under the influence of electron impact. Our calculations of the intensities of the peaks for doubly charged molecular ions with the aid of the corresponding monoisotopic peaks were not, of course, highly accurate and were of an approximate nature [3, 4].

We attempted to determine the IP for the fragment ion with mass 78 (for dipyridyls I-IV) and with mass 128 (for diquinolyls V-VII). The hypothetical IP for the indicated ions should be found within the operational range of the apparatus and should be recorded in the 9-12-eV range [5-7]. In those cases in which the ion peak is doubly charged, the IP of the ion ranges from 25 to 30 eV [12]. The IP of the corresponding pyridyl and quinolyl fragment ions observed by us (over the entire range of operation of the apparatus) make it possible to assume that the interannular bond in such systems (of the diphenyl type) is not cleaved. The latter constitutes evidence that this bond has π-bond character. This was also confirmed during a study of the mass spectra of bisheteroaromatic compounds with nonequivalent rings [13]. At the same time, in an investigation of VIII we were able to record the peak of an ion with mass 130, which had the quinolinium cation structure, but, because of its low intensity and the low sensitivity of the apparatus, it was impossible to determine the precise IP of this ion. It may be asserted that the IP for it is 11.5 ± 0.5 eV. In the case of VIII, the interannular bond is known to be a simple δ bond and is cleaved under the influence of electron impact; this is responsible for the appearance of the indicated ion.

The results obtained in this study once again provide evidence that strong conjugation between the rings occurs in the investigated bishetaryl systems and that the double bond character of the interannular bond is a consequence of this strong conjugation; moreover, the possibility of the cleavage of this bond under the influence of electron impact is excluded under the conditions of the mass spectrometric study.

EXPERIMENTAL

The ionization potentials were measured with an MS-1302 mass spectrometer with a photoionization source prepared by the Special Design Office of Analytical Instrument Construction, Academy of Sciences of the USSR. A hydrogen lamp was used as the source of ionizing photons. The device was equipped with a vacuum monochromator with a system for differential evacuation. The resolution of the mass spectrometer was 1.5-2.0 Å at half the height of the lines in the spectrum. The studies were made over the 600-4000 A range. The spectral range of the light source was 850-2000 Å. Vaporization of the sample was effected with a system for direct introduction; the ampule temperature was 100-180°, and the ionization chamber temperature was 120-200°. The emission spectrum of the hydrogen lamp was recorded to determine the dispersion (D) of the monochromator. The calculations were made from the formula $D=\Delta\lambda/e$ (Å/mm), where $\Delta\lambda$ is the difference in the wavelengths of the reference lines at $\lambda_1=1610$ Å, $\lambda_2=1215$ Å, and $\lambda_3=1026$ Å; and e is the distance between the reference lines in millimeters. The mass spectrometer was tuned to the line corresponding to the molecular ion (or the fragment ion), and the effective ionization curve was recorded under stabilization conditions with an inverse relationship with respect to the light current. The IP were determined from the threshold value on the effective photoionization curve and calculated in the usual way. The accuracy in the determination of the IP was 0.03 eV.

The purity of the samples, which were obtained by the method developed in [13], was monitored by means of gas-liquid chromatography; the purity of the samples was 98-99%.

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