EFFECT OF ANNELATION ON THE REACTIVITIES OF BENZOQUINOLINES IN HETARYLATION*

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The π-electron charges, bond orders, dipole moments, and electronic spectra of benzoquinolines were calculated by the self-consistent-field (SCF) method with allowance for the coulombic repulsion of the electrons; the results of the calculations were in satisfactory agreement with the experimental data. The effect of the position of annelation of the benzene ring on the electronic characteristics of benzoquinolines and their basicities and behavior during hetarylation in the presence of acyl halides was evaluated.

In a preceding communication [1] we expressed the assumption that the principal parameters that determine the activity of N-heteroaromatic systems in hetarylation in the presence of acyl halides are the basicities of the heterorings, the order of the C–N ring bond, and the magnitude of the positive charge on the α- (or γ) carbon atom. To verify this assumption, we calculated the distribution of π-electron charge and the bond orders in the molecules of all of the possible benzoquinolines (Fig. 1) by the self-consistent-field (SCF) method with allowance for coulombic repulsion of the electrons. The dipole moments and the electronic and PMR spectra can be considered to be the most direct reflection of the electron distribution. These characteristics of the molecules were therefore also calculated on the basis of the electron distribution found. The same method for the calculation of the electron distribution and the spectra as was employed in the case of the hydrocarbon analogs of the compounds under consideration [2] was used. The parameters of the nitrogen atom (resonance integral $\beta_{CN} = -2.57$ eV, electronegativity $\delta_W = -1.68$ eV, and coulombic integral $\gamma_{NN} = +10.4$ eV) were selected from the electronic spectrum of pyridine, while the $\gamma(R)$ dependence was of the same type as that for carbon [3]. These same parameters proved to be acceptable for the calculation of the spectra of pyridine and 4,9-diazapyrene [1]. The goal that we set for ourselves included not only the interpretation of the spectra, but also quantitative reproduction of the lower bands. As seen from Table 1, not only are the three lower absorption bands, the assignment of which corresponds to the data in other studies [4, in satisfactory agreement with the experimental results, but, in addition, the lower triplet level is also in good agreement with the phosphorescence maximum [5].

The position of the lower absorption bands, particularly the first, in benzopyridines (quinoline and isoquinoline) is more satisfactory than in [6] and reproduces the experimental data. The lower levels, which differ little from one another, display a bathochromic shift with respect to pyridine. It is natural to compare the lower and weaker transition with the weak α band in naphthalene at 3.93 eV, and the second and more intense transition in both molecules can be related to the p band of naphthalene at 4.3 eV [3].

A further bathochromic shift of the lower band is observed in the spectra of benzoquinolines, and one's attention should be directed to the closeness of the symmetrical and asymmetrical bands in the spectrum of acridine; the lower band in the spectrum of benzo[g]quinoline is closer to the symmetrical band, while the next band is closer to the asymmetrical band. The lower transition, which is more intense, is close to 3.3-3.4 eV in the spectra of all of the benzoquinolines (Table 1) and corresponds to the p band of anthra-

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TABLE 1. Electron-Transition Energies (eV)

Compound	Sym-metry	Singlet			Triplet	
		calc.	†	exptl. [5]	calc.	exptl. [5]
Pyridine	A	6,2984	0,01	6,36	3,7854	3,68
		7,4686	0,91	7,04	4,4882	
	B	4,6484	0,03	4,96	4,2646	
		8,0456	0,12		5,2398	
Quinoline		3,8279	0,03	3,96	2,5794	2,69
		4,2184	0,12	4,43	3,7650	
				4,59		
Isoquinoline		3,8287	0,07	3,89	2,5500	2,63
		4,1944	0,21	4,59	3,8108	
				4,68		
Benzo[b]quinoline (acridine)	A	3,2967	0,195	3,18	1,6889	1,94
		6,1037	0,112	5,82	3,9812	
	B	3,3527	0,026	3,50	2,9802	
		4,1918	0,005		3,5404	
Benzo[c]quinoline (phenanthridine)		3,4075	0,016	3,53	2,6341	2,73
		4,0659	0,171		3,3364	
Benzo[*f*]quinoline		3,4025	0,018		2,5864	2,71
		4,8567	0,191		3,4254	3,35
Benzo[g]quinoline		3,2360	0,076		1,6725	
		4,4283	0,025		3,1995	
Benzo[h]quinoline		3,3966	0,022		2,5819	2,70
		4,0965	0,166		3,3028	3,32

†As in Russian original—Publisher.

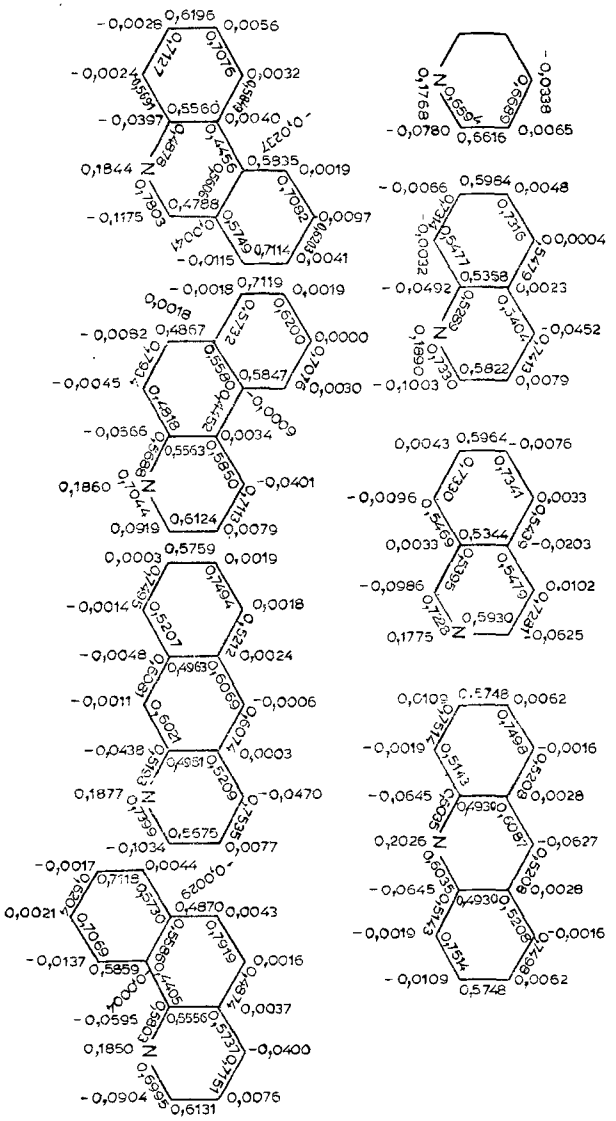


Fig. 1. Molecular diagrams of pyridine and benzo- and dibenzopyridines.

TABLE 2. Dipole Moments of Benzoquinolines

Compound	W_{100}	ε_{12}	α	V_{12}	β	P_{el}, cm^3	P_∞, cm^3	μ, D	μ_t, D calc.
Acridine	0,1966	2,2785	3,050	1,14403	−0,274	67,9	148,33	1,98	2,56
	0,2438	2,2799	3,036	1.14388	−0,283				
	0,3006	2.2816	3,027	1,14372	−0,283				
	0,3497	2,2831	3,032	1,14359	−0.280				
		α_{av}=3,036		β_{av}=−0,280					
Benzo[c]quinoline	0,1633	2,2788	3,857	1,14412	−0,275	70,3	176,60	2,28	2,38
	0,1995	2,2802	3,859	1,14402	−0,276				
	0,2473	2,2821	3,881	1,14389	−0,275				
	0,3775	2,2871	3,867	1,14354	−0,273				
		α_{av}=3,866		β_{av}=−0,275					
Benzo[*f*]quinoline	0,1978	2,2788	3,185	1,14394	−0,318	66,9	152,22	2,04	2,23
	0,2493	2,2805	3,209	1,14352	−0,301				
	0,3038	2,2822	3,193	1,14365	−0,303				
	0,3475	2,2836	3,194	1,14352	−0,302				
		α_{av}=3.195		β_{av}=−0,308					
Benzo[g]quinoline	0,01133	2.2730	4,325	1,14448	−0,794	62,0	146,70	2,03	2,24
	0,02272	2,2735	4,312	1,14439	−0,792				
	0,04575	2,2745	4,355	1,14419	−0,831				
	0,06347	2,2753	4,396	1,14405	−0,819				
		α_{av}=4,347		β_{av}=−0,809					
Benzo[h]quinoline	0,1972	2,2771	2,332	1,14396	−0,309	66,9	121,96	1,64	2,14
	0,2454	2,2781	2,282	1,14379	−0,318				
	0,3030	2,2795	2,310	1,14361	−0,317				
	0,3801	2,2813	2,315	1,14337	−0,317				
		α_{av}=2,313		β_{av}=−0,315					

TABLE 3. Diamagnetic Susceptibilities of Nitrogen Heterocycles (-10^{-6} cm^3/mole)

Molecule	π-Electron contributions			ΔX_{zz} calc.	X_{zz} calc.	X_m	
	dia	para	X_π			calc.	exptl. [15]
Pyridine	31,55	−0,30	31,25	57,46	86,75	48,41	48,4
Quinoline	93,29	−25,66	67,63	111,34	160,09	85,80	86,0
Isoquinoline	93,17	−26,07	67,10	110,81	159,56	85,63	83,9
Acridine	191,92	−77,08	114,85	176,06	244,27	126,81	114,9
Phenanthridine	194,22	−96,61	100,61	161,82	230,03	122,07	—
Benzo[f]quinoline	197,21	−96,60	100,61	161,82	230,03	122,07	—
Benzo[g]quinoline	191,81	−76,81	115,00	176,21	244,42	126,86	—

cene at 3.34 eV. The lower band in the spectra of the phenanthrene analogs is somewhat more of a short-wave band (3.4 eV) and corresponds to the weak α band of phenanthrene at 3.54 eV [3]. The longest-wave transition is the transition in the diazapyrene molecule [1], where, as in the case of acridine, two close and quite intense bands are observed, but in this case they have the same symmetry. It is natural to compare them with the α and p bands of pyrene, which are also close to one another (3.24 and 3.50 eV).

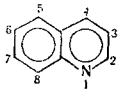
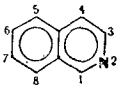
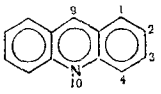
Thus, linear annelation leads to a somewhat greater bathochromic shift. This sort of effect is more clearly expressed in the case of phosphorescence terms, where the lower triplet (phosphorescence) level of phenanthrene analogs displays a small hypsochromic shift, while the anthracene analogs display a substantial bathochromic shift with respect to quinoline, such that phosphorescence in the visible region can be observed for the former, and phosphorescence in the IR region can be observed for the latter.

This is confirmed by the bands reported in [5, 7], which did not appear in the visible region of absorption of acridine, which, as shown by subsequent investigations [5], displays phosphorescence in the same region as anthracene (~2 eV). However, in the case of benzo[*f*]- and benzo[g]quinolines, the experimentally determined [5] positions of both the first and second triplet levels are in excellent agreement with the results of our calculations. Thus, the above description of the spectra, which is in agreement with the experimental data, confirms the results of calculations of the molecular diagrams of benzoquinolines.

Table 2, in which the calculated π-electron dipole moments, which, after introduction of a correction for the dipole moment of the σ bond (assumed to be 1.55 D and directed along the unshared pair of the nitrogen atom), proved to be in good agreement with the values that we found experimentally and with the literature data, may serve as a further confirmation of the adequacy of the electron distribution found.

The diamagnetic susceptibilities calculated by the method developed in [8], of the nitrogen heterocycles under investigation in the present paper are presented in Table 3. The presence of heteroatoms leads, within the framework of the π-electron variant of the SCF MO LCAO method, to additional additive parameters that characterize the diamagnetic properties of the C−N σ bonds, in addition to yielding the

TABLE 4. Proton Chemical Shifts of a Series of Nitrogen Heterocycles (relative to tetramethylsilane in ppm)

Molecule		Calc.	Exptl.
Pyridine 	2	1,56	1,71[11]
	3	2,95	3,23
	4	2,91	2,85
Isoquinoline 	1	0,93	0,86[12]
	3	1,33	1,55
	4	2,38	2,50
	5	2,37	2,30
	6	2,69	2,44
	7	2,70	2,52
	8	2,34	2,15
Quinoline 	2	1,25	1,10[13]
	3	2,65	2,66
	4	2,27	2,04
	5	2,34	2,24
	6	2,70	2,50
	7	2,69	2,31
	8	1,92	1,91
Acridine 	1	1,96	2,06[14]
	2	2,44	2,50
	3	2,42	2,18
	4	1,55	1,65
	9	1,49	1,35

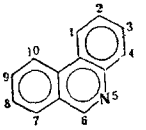
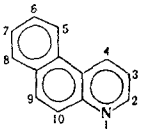
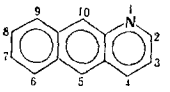
Molecule		Calc.
Phenanthridine 	1	1,89
	2	2,58
	3	2,54
	4	1,84
	6	0,78
	7	2,20
	8	2,49
	9	2,53
	10	1,86
Benzo[*f*]quinoline 	2	1,08
	3	2,52
	4	1,81
	5	1,86
	6	2,56
	7	2,52
	8	2,26
	9	2,26
	10	1,82
Benzo[g]quinoline 	2	1,04
	3	2,44
	4	1,94
	5	1,49
	6	1,96
	7	2,44
	8	2,43
	9	1,99
	10	1,09

TABLE 5. 6-Substituted 5-Acyl-5,6,7,8,9,10-hexahydrophenanthridines (IVa-g) and 2-Substituted 1-Acyl-1,2-dihydrobenzo[*f*]quinolines (Va-g)

Compound	R	R'	mp, °C (crystallization solvent)	M* found	M* calc	Empirical formula	Found, % C	Found, % H	Found, % N	Calc., % C	Calc., % H	Calc., % N	Yield, %
IVa	C_6H_5	3-Indolyl	223—224 (ethanol)	404	404	$C_{28}H_{24}N_2O$	83,3	6,1	6,8	83,1	5,9	6,9	51
IVb	CH_3	3-Indolyl	252—254 (ethanol)	342	342	$C_{23}H_{22}N_2O$	80,4	6,8	8,1	80,7	6,4	8,2	46
IVc	C_6H_5	1-Methyl-3-indolyl	241—242 (ethanol)	418	418	$C_{29}H_{26}N_2O$	83,4	6,3	6,5	83,2	6,2	6,7	37
IVd	C_6H_5	2-Methyl-3-indolyl	272—273 (benzene)	418	418	$C_{29}H_{26}N_2O$	83,9	6,5	6,7	83,2	6,2	6,7	55
IVe	C_6H_5	1-Methyl-2-pyrrolyl	289—291 (ethanol)	368	368	$C_{25}H_{24}N_2O$	81,3	6,6	7,8	81,9	6,5	7,6	13
IVf	C_6H_5	2-Methyl-5-furyl	285—286 (propanol)	369	369	$C_{25}H_{23}NO_2$	79,6	6,4	3,9	81,3	6,2	3,7	21
IVg	C_6H_5	1-Methyl-1,2,3,4-tetrahydro-6-quinolinyl	208—210 (heptane)	441†	434	$C_{30}H_{30}N_2O$	82,7	7,1	6,7	82,9	6,9	6,5	17
Va	CH_3	3-Indolyl	171—172 (ethanol)	338	338	$C_{23}H_{18}N_2O$	79,8	6,1	8,8	81,6	5,4	8,3	64
Vb	*m*-$CH_3C_6H_4$	3-Indolyl	241—242 (hexane)	414	414	$C_{29}H_{22}N_2O$	83,3	6,0	7,1	84,0	5,3	6,7	58
Vc	CH_3	1-Methyl-3-indolyl	140—141 (heptane)	352	352	$C_{24}H_{20}N_2O$	79,8	5,0	8,0	81,8	5,7	8,0	62
Vd	C_6H_5	1-Methyl-3-indolyl	159—160 (heptane)	414	414	$C_{29}H_{22}N_2O$	84,1	5,4	6,7	84,0	5,3	6,7	50
Ve	C_6H_5	2-Methyl-3-indolyl	244—245 (heptane)	414	414	$C_{29}H_{22}N_2O$	83,7	5,5	6,5	84,0	6,3	6,7	58
Vf	C_6H_5	1-Methyl-2-pyrrolyl	140—142 (heptane)	364	364	$C_{25}H_{20}N_2O$	82,5	5,5	7,1	82,4	5,5	7,7	42
Vg	C_6H_5	2-Pyrrolyl	230—231 (pentanol)	350	350	$C_{24}H_{18}N_2O$	82,5	5,2	8,1	82,2	5,2	8,0	11

*Mass spectrometrically.

†By the Rast method.

π-electron parameters of the Hamiltonian that are described above. In this case, all of the σ bonds were assumed to be magnetically equivalent, and the tensor of the diamagnetic susceptibility with components $X_{XX}^N = X_{ZZ}^N = -2.58 \cdot 10^{-6}$ cm^3/mole and $X_{YY}^N = 0$, where X is the axis along which the unshared pair is directed, and Z is the axis perpendicular to the plane of the molecule, was formally ascribed to the unshared pair of nitrogen. These parameters were selected in such a way as to reproduce the experimental data for pyridine [9].

We note that $X_m = 48.4 \pm 0.1$ (48.41), $\Delta X_{ZZ} = 57.45 \pm 0.8$ (57.46), $X_{ZZ} = 86.8 \pm 0.8$ (86.75), $X_{XX} = 30.4 \pm 0.5$ (30.45), and $X_{YY} = 28.3 \pm 0.5$ (28.02). The results of our calculations are given in parentheses; all of the quantities are given in units of -10^{-6} cm^3/mole.

A comparison of the data in Table 3 with the calculations of the hydrocarbon analogs of the heteroaromatic systems under consideration [8] shows that the presence of a nitrogen atom leads to a slight increase (with respect to the modulus) of the π-electron contributions to the diamagnetic susceptibility and demonstrates the weak sensitivity of the diamagnetic susceptibility to the position of the heteroatom in the molecule. At the same time, the chemical shifts of related compounds (for example, quinoline and isoquinoline, acridine and phenanthridine, and benzo[*f*]quinoline and benzo[g]quinoline) that we examined differ appreciably (Table 4).

In our comparison of some of the calculated chemical shifts with the experimental data available in the literature [10-13], the effect of the unshared pair of the nitrogen atom was taken into account by means of the additive parameter -1.37 ppm for the protons noted in Table 4 by means of asterisks [sic] and -0.48 ppm for the protons adjacent to the heteroatom. As seen from Table 4, the calculation satisfactorily reproduces the peculiarities of the PMR spectra, and this constitutes evidence in favor of the electron-density distributions found and the external magnetic field induced π-electron currents, which form the basis of the calculation of the molecular magnetic properties.

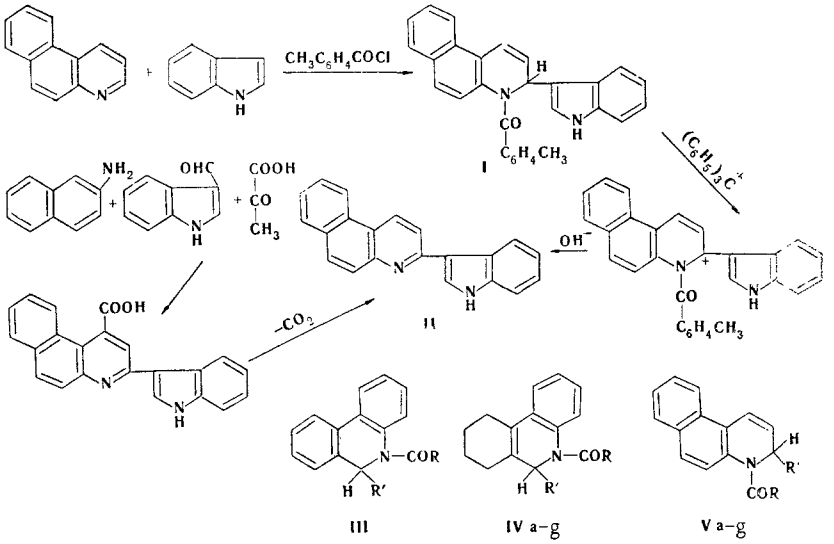
Judging from the molecular diagrams (Fig. 1) and our previous experimental data, correlation between the activity of the heterocycle in hetarylation and the calculated C–N bond orders and the charge on the α-carbon atom is not observed in the benzopyridine series. If such a correlation did exist, we would have observed higher activity of quinoline rather than of isoquinoline, which contradicts our data. In addition, this sort of relationship, nevertheless, does exist in the benzoquinoline series, although correlation with the basicities of the heterocycles is absent. In fact, if the reactivities of compounds of the benzoquinoline series in hetarylation are compared (by estimating the minimum temperature and the reaction time, as well as the yield of hetarylated compound and the possibility of hetarylation of weak nucleophiles), it turns out that phenanthridine is less active in hetarylation than acridine, isoquinoline, and quinoline [15]. Benzo[*f*]quinoline proved to be even less active: the reaction could be carried out only with the most nucleophilic π-surplus heterocycles – pyrrole and indole (Table 5) – and dialkylanilines and similar activated aromatic compounds were not hetarylated even under severe conditions.

We did not study the activity of benzo[g]quinoline in hetarylation, but, judging from the calculated values, this heterocycle should be more active than benzo[*f*]quinoline and somewhat less active than phenanthridine. Benzo[h]quinoline does not undergo hetarylation even under severe conditions, probably as a consequence of shielding of the ring-nitrogen atom in it and the impossibility of the formation of N-acyl salts.

In order to differentiate between the effects of structural and electronic factors on the activity of the heterocycles, we investigated the behavior in this reaction of 7,8,9,10-tetrahydrophenanthridine. It was found that this heterocycle resembles its electronic analog – quinoline – more with respect to its activity than phenanthridine. Various 7,8,9,10-tetrahydrophenanthridine derivatives of indoles, pyrroles, α-methylfuran, and 1-methyl-1,2,3,4-tetrahydroquinoline were relatively easily obtained. However, the yields in a number of cases were low because of considerable resinification.

The structures of all of the synthesized compounds were proved by comparison of the IR and UV spectra with the spectra of compounds of known structure, which were synthesized via the scheme on the following page.

The mass spectra of the synthesized compounds also confirmed their structure. We have previously [16, 17] established the principles of the dissociative ionization (during a mass-spectra study) of partially hydrogenated N-acyl derivatives of quinoline and isoquinoline. It was legitimate to assume that the disintegration of III-V under electron impact would proceed via a similar scheme.



However, the mass spectra of III-V contain substantial differences in the trend of the disintegration: there are no peaks of ions corresponding to dehydrogenation of the molecular ion, and elimination of a hetaryl residue from the phenanthridine or 5,6-benzoquinoline portion of the molecule in the first stage of disintegration of the molecular ion is not observed. Consequently, N-benzoyl- or N-acetylphenanthridine cations or 5,6-benzoquinolinium cations are not formed. The maximum peaks are those of the ions formed by elimination of acetyl or benzoyl residues from the molecular ion (this was confirmed by the corresponding metastable processes), i.e., these compounds disintegrate in a manner similar to the dissociative ionization of aromatic amines.

The high intensity of the $(M-RCO)^+$ ion peak, where $R=CH_3$ and C_6H_5, is evidently due to a rearrangement process associated with migration of a hydrogen atom from the tetrahedral carbon atom to the nitrogen atom of the phenanthridine or 5,6-benzoquinoline ring. The rearrangement process promotes aromatization of the $(M-RCO)^+$ ion. The dehydrogenation that follows this process leads to the formation of ions with the structures of polycyclic-heterocyclic compounds with a bridge-nitrogen atom [18-20], as attested to by the appearance of the corresponding group of doubly charged ions with masses $(M-RCO)^{2+}$, $[(M-RCO)-H]^{2+}$, and $[(M-RCO)-2H]^{2+}$.

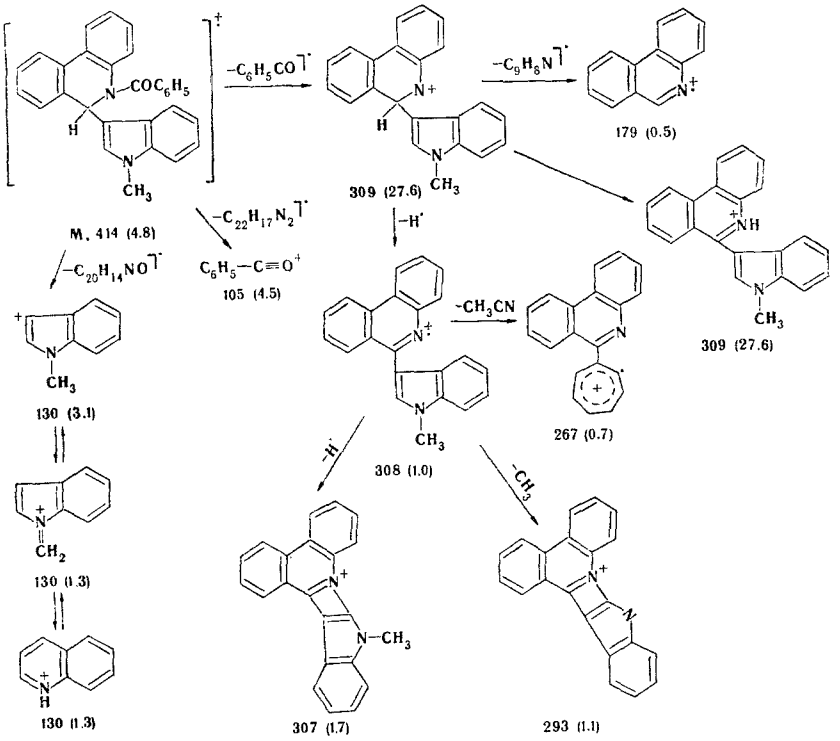
Elimination of a neutral HCN or CH_3CN particle from the pyrrole ring of indole from the $[(M-RCO)-H]^{+\cdot}$ ion radical shows that the α-position of the indole ring is not blocked, and the latter makes it possible to form a judgment regarding the site of fusion of the phenanthridine or 5,6-benzoquinoline ring with the indole ring in II-V.

The position of the methyl group in the indole fragment of the molecule is also readily established by comparison of the intensities of the $\{[(M-RCO)-H]-CH_3\}^+$-ion peaks. It is known [21] that the intensity of the $(M-CH_3)^+$ peak in the spectrum of N-methylindole is considerably higher than in the spectra of its homologs with a methyl substituent in any other position of the ring.

Thus, the disintegration of III-V can be represented by the scheme* on the following page (in the case of a compound of the III type, the preparation of which we have previously described).

In synthesized bisheterocyclic systems of the III-V type, in which conjugation between the rings is absent because of the partial hydrogenation of one of them, the C–C bond between the heterorings is cleaved during electron impact. This sort of process is not observed in those cases where both heterorings in the system are completely aromatic [18]. The detachment of one of the heterorings in III-V is confirmed by the presence of a rather intense peak of an ion with the structure of the corresponding heterocyclic substitutent (the N-methylindole fragment of the molecule, which rearranges to the more stable quinolinium cation – see the following disintegration scheme – is recorded in the mass spectrum).

*The numbers under the formulas denote the mass numbers, while the numbers in parentheses are the intensities in percent of the total ion current.



It should be noted that additional disintegrative channels associated with aromatization of the hydrogenated ring are not observed in the spectra of IVa-g, which have a hydrogenated phenanthridine ring. According to the mass spectra, the presence of a hydrogenated ring in benzoquinoline is easily detected, inasmuch as intense ion peaks with m/e 184 and 183 appear in the mass spectrum as a result of cleavage of the C–C bond.

EXPERIMENTAL

The mass spectra were recorded with an SN-6 spectrometer with a system for direct introduction of samples into the ion source at a cathode emission current of 1.5 mA, a trap current of 15-20 mA, and an ionization chamber temperature of 180°.

The dipole moments were calculated from the formula $\mu = 0.221\sqrt{P_\infty - P_{el}}$, where P_∞ is the polarization at infinite dilution, and P_{el} is the molecular refraction, which is equal to the electronic polarization and is calculated from the refractive indices and the densities. The refractive indices of the solutions were measured with an IRF-23 refractometer with the cuvette described in [22]. The densities were determined pycnometrically. The P_∞ value was calculated by the method in [23], and all of the measurements were made at 25 ± 0.005°. The "cryoscopically" pure-grade benzene was purified by the method in [24] and had bp 79.8° (740 mm), d_4^{29} 0.87369, n^{29} 49,793, and ε^{29} 2.2725.

Chromatography in a loose thin layer of aluminum oxide was realized in benzene–hexane–chloroform (6 : 1 : 30). 7,8,9,10-Tetrahydrophenanthridine was obtained by the method in [25] and had mp 61-62° and R_f 0.65.

Typical Hetarylation Method. A 0.01-mole sample of acetyl chloride and 0.01 mole of the compound to be hetarylated were added to a solution of 0.02 mole of benzoquinoline in 25 ml of anhydrous benzene or dimethylformamide (DMFA), after which the reaction mixture was held at room temperature or heated to 100° for 2 to 10 h. At the end of the reaction (monitoring by TLC), the solvent was removed by distillation, and the residue was neutralized with ammonium hydroxide, washed with hot water, dried, and crystallized from a suitable solvent. The yields and characteristics of the compounds obtained are presented in Table 5. The IR spectra of all IV and V contained characteristic bands at 1650-1700 cm^{-1} (ν_{CO}), while bands at 3450 cm^{-1} (ν_{NH}) were additionally observed in the spectra of IVa, b, d, e, and Va, b, e, g.

2,5-Di(1-benzoyl-1,2-dihydrobenzo[*f*]-2-quinolinyl)pyrrole. This compound was obtained along with Vg as described above by hetarylation of pyrrole with benzo[*f*]quinoline in the presence of benzoyl chloride. The yield of product with mp 161-162° (from pentanol) was 16%; R_f 0.23. IR spectrum: 1680 (CO) and

3430 cm^{-1} (NH). Found: C 83.1; H 5.1; N 6.5%; M 642 (Rast method). $C_{44}H_{31}N_3O_2$. Calculated: C 83.4; H 4.9; N 6.6%; M 633.

2-(3-Indolyl)benzo[*f*]quinoline. A) A solution of 0.7 g (91.7 mmole) of Vb and 0.58 g (1.7 mmole) of triphenylmethyl perchlorate in 10 ml of acetonitrile was refluxed for 14 h, after which the mixture was decomposed with ammonium hydroxide and extracted with chloroform. The extract yielded 0.4 g (85%) of greenish crystalline 2-(3-indolyl)benzo[*f*]-quinoline with mp 304-305° (from ethanol) and R_f 0.88. Found: C 85.6; H 5.0; N 9.4%. $C_{21}H_{14}N_2$. Calculated: C 85.7; H 4.8; N 9.5%. The picrate had mp 222-223° (from ethanol). Found: N 13.3%. $C_{21}H_{14}N_2 \cdot C_6H_3N_3O_7$. Calculated: N 13.4%.

B) A solution of 1.88 g (13 mmole) of 3-formylindole, 2 g (13 mmole) of β-naphthylamine, and 1 ml of H_2SO_4 in 20 ml of absolute ethanol was refluxed for 1 h, after which it was cooled to 60°, a solution of 1.2 g (13 mmole) of pyruvic acid in 10 ml of ethanol was added dropwise, and the mixture was refluxed for another 3 h. It was then cooled, and the precipitated 2-(3-indolyl)benzo[*f*]quinoline-4-carboxylic acid was separated to give 0.9 g (90%) of a product with mp 321-322° (dec., from ethanol). Found: C 78.1; H 4.1; N 8.2%. $C_{22}H_{14}N_2O_2$. Calculated: C 78.1; H 4.2; N 8.3%.

Decarboxylation of the acid at 200° gave 2-(3-indolyl)benzo[*f*]quinoline; no melting-point depression was observed for a mixture of this product with a sample obtained by method A.

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