MASS-SPECTROMETRIC BEHAVIOR OF POLYNUCLEAR DERIVATIVES OF BENZO[f]QUINOLINE

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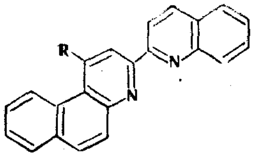
UDC 547.832:543.51

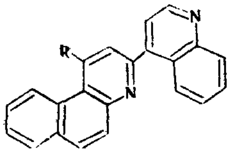
It was established on the basis of a study of the mass spectra of benzo[f]quinoline derivatives that contain a methyl group or an aromatic or heterocyclic ring in the 1 position and various quinolyl groups (2-, 4-, and 6-quinolyl) in the 3 position that the geometry of the molecule has a decisive effect on the strength of the chemical bond between the substituents and the benzoquinoline ring. The degree of coplanarity of the heterocyclic rings determines the strength of interannular conjugation and consequently the strength of the bond between the rings. For the investigated polyheterocyclic systems the coplanarity increases in the order 2-quinolyl < 6-quinolyl < 4-quinolyl. This fact in turn has a strong effect on the pathway of mass-spectrometric fragmentation for each series of derivatives, and this makes it possible to reliably distinguish the 2-, 4-, and 6-quinolyl derivatives from their mass spectra.

The present research was devoted to a study of the principal characteristic pathways of fragmentation of the molecular ions of polynuclear compounds of the benzo[f]quinoline series. The aim of the research was to establish a correlation between the structures of the benzoquinolines and their mass spectra and to ascertain the spatial orientation of the heterocyclic substituent in the 3 position.

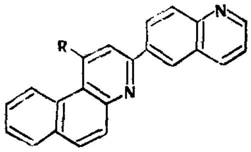
We studied the mass spectra of polynuclear benzo[f]quinoline derivatives with a methyl group or an aromatic or heterocyclic substituent R in the 1 position of the benzoquinoline ring and a quinolyl group (2-, 4-, and 6-quinolyl) in the 3 position. All of the investigated compounds were separated into three groups — A, B, and C — with respect to the type of quinolyl group present:



A



B



C

Within the limits of each of these groups the fragmentation of the benzo[f]quinoline derivatives under the influence of electron impact proceeds via a common scheme. The mass spectra of the investigated polynuclear compounds and the W_M values are presented in Table 1.

The studies showed that benzo[f]quinoline derivatives are stable with respect to electron impact.

The spectra of all of the compounds contain intense molecular-ion peaks (M^+), as well as peaks of doubly charged ions (M^{2+}). The most characteristic peaks in the spectra of compounds of the A and B type are the peaks of $[M - 130]^+$ ions (or $[M - 130, - R']^+$ ions, where R' is a fragment of substituent R, particularly m/e 251* for V, VI, XVII, and XIX-XXI). The peaks of the quinolyl ion at 128 are characteristic for compounds of the A type, while the

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*Here and subsequently, the numbers that characterize the ion are the mass-to-charge ratios.

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0009-3122/79/1504-0424$07.50

TABLE 1. Mass Spectra of Polynuclear Benzo[f]quinoline Derivatives

Compound No.	Compound	m/e values (relative intensities of the ion peaks in percent of the maximum)*
1	2	3
I	3-(2-Quinolyl)benzo[f]quinoline	128 (4), 151 (6), 153 (19), 305 (32), 306 (100), 307 (24). $W_M = 66$.
II	1-Methyl-3-(2-quinolyl)benzo[f]quinoline	128 (12), 159 (4), 160 (11), 165 (4), 190 (6), 191 (7), 305 (11), 317 (6), 318 (11), 319 (56), 320 (100), 321 (30). $W_M = 45$.
III	1-Phenyl-3-(2-quinolyl)benzo[f]quinoline	128 (42), 190 (15), 191 (64), 192 (8), 225 (4), 226 (7), 251 (12), 252 (22), 253 (10), 254 (6), 379 (20), 380 (8), 381 (99), 382 (100), 383 (61), 384 (5). $W_M = 22$.
IV	1-(p-Fluorophenyl)-3-(2-quinolyl)benzo[f]quinoline	88 (5), 128 (38), 129 (6), 199 (16), 200 (25), 269 (10), 270 (16), 397 (5), 399 (99), 400 (100), 401 (26). $W_M = 25$.
V	1-(p-Chlorophenyl)-3-(2-quinolyl)benzo[f]quinoline	128 (22), 180 (11), 181 (39), 208 (4), 251 (7), 379 (9), 380 (5), 381 (11), 382 (5), 415 (100), 416 (95), 417 (57), 418 (31), 419 (7). $W_M = 18$.
VI	1-(p-Bromophenyl)-3-(2-quinolyl)benzo[f]quinoline	128 (15), 189 (10), 190 (50), 191 (15), 251 (9), 377 (6), 378 (4), 379 (30), 380 (16), 381 (24), 382 (7), 459 (70), 460 (90), 461 (100), 462 (89), 463 (24). $W_M = 28$.
VII	1-(3-Pyridyl)-3-(2-quinolyl)benzo[f]quinoline	128 (10), 177 (5), 190 (9), 191 (18), 253 (6), 380 (5), 382 (100), 383 (70), 384 (10). $W_M = 30$.
VIII	1,3-Di(2-quinolyl)benzo[f]quinoline	128 (10), 215 (4), 216 (22), 217 (27), 303 (8), 396 (10), 430 (5), 432 (100), 433 (67), 434 (16). $W_M = 26$.
IX	1-(p-Fluorophenyl)-3-(4-quinolyl)benzo[f]quinoline	190 (6), 193 (8), 199 (16), 200 (18), 201 (4), 304 (5), 305 (98), 306 (23), 397 (19), 398 (6), 399 (80), 400 (100), 401 (30), 402 (4). $W_M = 28$.
X	1-(p-Chlorophenyl)-3-(4-quinolyl)benzo[f]quinoline	176 (4), 189 (10), 190 (43), 191 (4), 208 (4), 305 (100), 306 (28), 378 (4), 380 (7), 413 (6), 415 (50), 416 (74), 417 (37), 418 (25), 419 (7). $W_M = 23$.
XI	1-(p-Bromophenyl)-3-(4-quinolyl)benzo[f]quinoline	176 (7), 189 (8), 190 (40), 191 (14), 305 (100), 306 (26), 377 (6), 379 (11), 380 (6), 459 (32), 460 (35), 461 (50), 462 (45), 463 (10). $W_M = 28$.
XII	1-(p-Tolyl)-3-(4-quinolyl)benzo[f]quinoline	176 (10), 177 (6), 183 (8), 190 (19), 197 (8), 198 (10), 304 (8), 305 (100), 306 (30), 379 (8), 393 (13), 395 (69), 396 (78), 397 (29), 398 (5). $W_M = 25$.
XIII	1-(2-Quinolyl)-3-(4-quinolyl)benzo[f]quinoline	200 (4), 215 (24), 216 (17), 303 (6), 305 (16), 306 (4), 430 (10), 431 (6), 432 (100), 433 (76), 434 (18). $W_M = 28$.
XIV	3-(6-Quinolyl)benzo[f]quinoline	151 (4), 153 (16), 305 (32), 306 (100), 307 (27). $W_M = 70$.
XV	1-Methyl-3-(6-quinolyl)benzo[f]quinoline	149 (5), 151 (5), 153 (20), 159 (4), 160 (14), 190 (4), 303 (6), 304 (7), 305 (34), 306 (82), 307 (15), 318 (6), 319 (20), 320 (100), 321 (23). $W_M = 37$.
XVI	1-Phenyl-3-(6-quinolyl)benzo[f]quinoline	91 (7), 153 (6), 190 (10), 191 (23), 251 (8), 252 (15), 305 (13), 306 (27), 379 (8), 381 (48), 382 (100), 383 (31), 384 (5). $W_M = 43$.
XVII	1-(p-Tolyl)-3-(6-quinolyl)benzo[f]quinoline	189 (6), 190 (20), 191 (5), 197 (6), 198 (11), 242 (5), 251 (6), 266 (8), 381 (25), 395 (47), 396 (100), 397 (28). $W_M = 43$.
XVIII	1-(p-Fluorophenyl)-3-(6-quinolyl)benzo[f]quinoline	78 (5), 190 (4), 199 (16), 200 (17), 244 (4), 246 (4), 269 (4), 270 (15), 271 (4), 305 (4), 397 (6), 399 (50), 400 (100), 401 (34), 402 (4). $W_M = 44$.
XIX	1-(p-Chlorophenyl)-3-(6-quinolyl)benzo[f]quinoline	176 (4), 190 (15), 191 (20), 226 (4), 251 (12), 252 (8), 286 (6), 305 (4), 379 (11), 381 (17), 415 (47), 416 (100), 417 (44), 418 (34), 419 (10). $W_M = 28$.
XX	1-(p-Bromophenyl)-3-(6-quinolyl)benzo[f]quinoline	176 (13), 177 (6), 189 (12), 190 (40), 191 (60), 227 (7), 252 (19), 253 (21), 307 (4), 309 (4), 331 (5), 333 (5), 352 (4), 378 (6), 379 (7), 380 (27), 381 (21), 382 (43), 383 (12), 460 (35), 461 (100), 462 (62), 463 (99), 464 (30), 465 (4). $W_M = 43$.
XXI	1-(3-Pyridyl)-3-(6-quinolyl)benzo[f]quinoline	177 (6), 190 (18), 191 (10), 226 (6), 251 (6), 253 (12), 380 (7), 382 (100), 383 (76), 384 (25). $W_M = 33$.
XXII	1-(2-Quinolyl)-3-(6-quinolyl)benzo[f]quinoline	215 (9), 216 (19), 217 (4), 302 (4), 303 (8), 304 (5), 400 (4), 430 (6), 432 (100), 433 (72), 434 (22). $W_M = 31$.

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*The ion peaks with intensities 4% of the maximum peak in the spectrum are indicated.

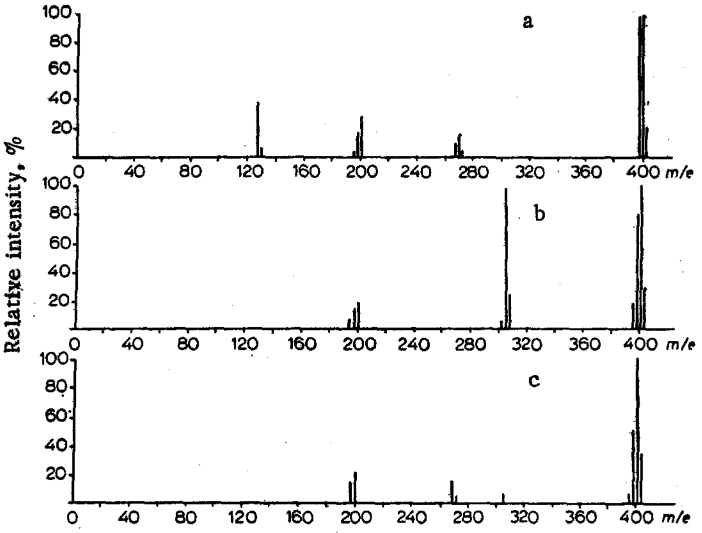


Fig. 1. Mass spectra: a) 1-(p-fluorophenyl)-3-(2-quinolyl)benzo[f]quinoline (IV); b) 1-(p-fluorophenyl)-3-(4-quinolyl)benzo[f]quinoline (IX); c) 1-(p-fluorophenyl)-3-(6-quinolyl)-benzo[f]quinoline (XVIII).

$[M - R]^+$ ion peak at 305 is characteristic for compounds of the B and C type. A common feature of the mass spectra of the compounds is the presence of $[M - H]^+$ ion peaks. However, it follows from their subsequent fragmentation that the structures of these ions are different for compounds of the A, B, and C type. It is apparent from an analysis of the spectra of the metastable ions (Table 2) that the fragmentation of the $[M - H]^+$ ions in the case of compounds A and B proceeds with detachment of a quinoline molecule and leads to the formation of the $[M - 130]^+$ ion, while the $[M - H, - R]^+$ ion at 304 is formed from the $[M - H]^+$ ions in the case of the 4-quinolyl isomers (B).

An analysis of the mass-spectrometric data showed that the fragmentation of 1-R-3(4-quinolyl)benzo[f]quinolines (B) under the influence of electron impact proceeds via a scheme similar to the scheme of the fragmentation of coplanar two-ring systems of the dipyridyl, diquinolyl, and 3-arylisoquinoline types [1, 2]. The detachment of a hydrogen atom from the molecular ion in compounds of the B type is evidently accompanied by the formation of an energetically favorable structure that is formed by the development of a five-membered ring through the nitrogen atom of the benzoquinoline ring. Only this cyclic $[M - H]^+$ ion can undergo subsequent fragmentation with the elimination of an R radical. The $[M - R]^+$ ion peak at 305 is most often the maximum peak in the mass spectra of compounds of this type, and $[M - 130]^+$ and 128 ion peaks, which, as we will show below, constitute evidence for the elimination of a quinolyl substituent, are always absent (Table 1).

The pathways of fragmentation of compounds of the B type constitute evidence for the considerable strength of the interannular bond between the benzoquinoline ring and the 4-quinolyl substituent.

It is known that a factor that determines the stability of an interannular bond with respect to electron impact is the coplanarity of the system. Under the condition of a close-to-coplanar orientation of the rings, the interannular C–C bond takes on the character of a π bond and becomes strong [3]. Consequently, from an analysis of the mass spectra one

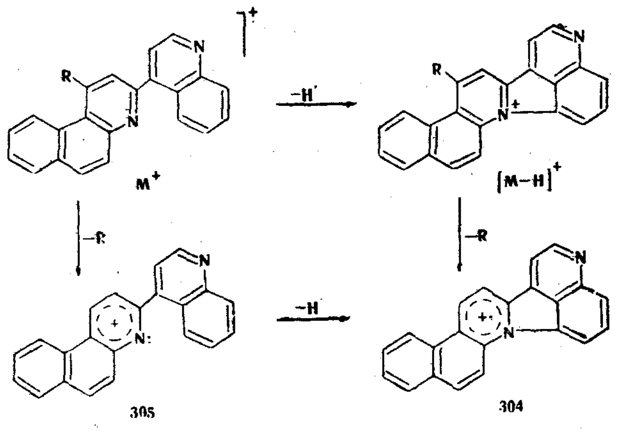


TABLE 2. Pathways of Fragmentation of the Ions of Some Benzo[f]quinolines Established from the Metastable transition by the DADI Method

Compound	Parent ion, m/e	Daughter ions, m/e	E/E_0
IV	400	128	0,3207
	399	270, 128	0,6774 0,3201
XII	396	381, 305	0,9632 0,7695
	395	380, 304	0,9608 0,7692
XVI	381	252	0,6606

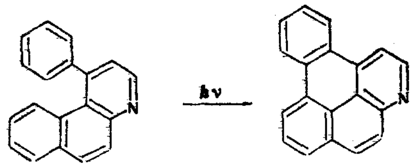
TABLE 3. Precise m/e Values of the Ions and Elementary Compositions of Some Benzo[f]quinolines

Compound	Measured m/e value	Elementary composition	Calc. m/e value
IV	400,1365	$C_{28}H_{17}N_2F$	400,1375
	397,1133	$C_{28}H_{14}N_2F$	397,1141
	270,0732	$C_{19}H_9NF$	270,0719
	128,0506	C_9H_6N	128,0500
XII	396,1623	$C_{29}H_{20}N_2$	396,1626
	395,1559	$C_{29}H_{19}N_2$	395,1548
	393,1403	$C_{29}H_{17}N_2$	393,1392
	305,1087	$C_{22}H_{13}N_2$	305,1079
XVI	382,1458	$C_{28}H_{18}N_2$	382,1470
	379,1229	$C_{28}H_{15}N_2$	379,1235
	305,1081	$C_{22}H_{13}N_2$	305,1079
	252,0828	$C_{19}H_{10}N$	252,0813

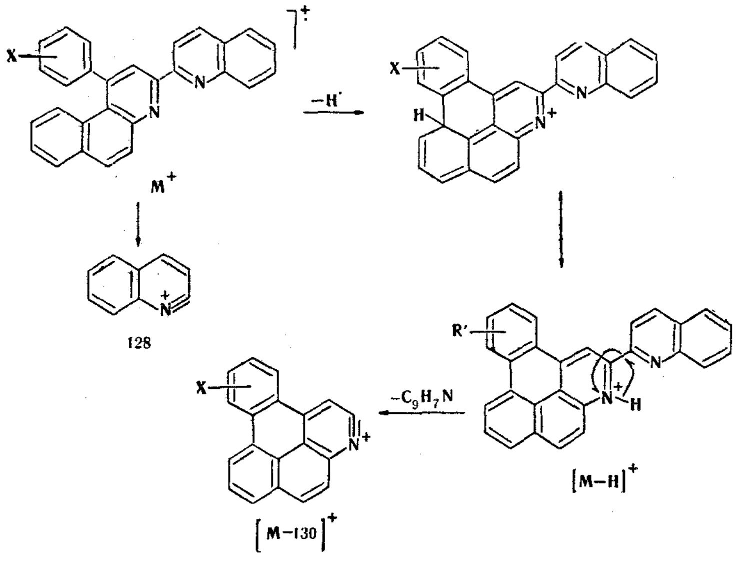
can draw a conclusion regarding the significant degree of coplanarity of the heterocyclic rings in compounds of the B type.

The dissociative ionization of compounds of the A and B type proceeds via a different scheme (Fig. 1 and Tables 1 and 2).

It is known [4] that under the influence of UV irradiation in an acidic medium 1-phenylbenzo[f]quinoline undergoes cyclodehydrogenation to give an energetically favorable system — the phenanthro[9,10,11-d,e,f]quinoline molecule:



Molecular ions of the A and B type that have an aromatic (heteroaromatic) substituent in the 1 position are evidently capable under electron impact of undergoing cyclization in a similar manner with the loss of a hydrogen atom and the formation of an $[M-H]^+$ even-electron ion:



The most likely process in the subsequent fragmentation of this cyclic $[M - H]^+$ ion is splitting out of a quinoline substituent in the form of a quinoline molecule and the formation of the $[M - 130]^+$ ion in accordance with the scheme presented above.

The peak of $[M - 130]^+$ ions is absent in the mass spectra of compounds of this series that do not have an aromatic substituent in the 1 position of the benzoquinoline ring (I, II, XIV, and XV), since the formation of a phenanthroquinoline system in this case is impossible.

Only the spectra of the 2-quinolyl isomers contain a peak at 128 corresponding to the quinolyl cation (Table 1). It is well known that localization of the charge on the quinolyl radical is possible only if the conjugation between the two heterocyclic rings is minimal. It follows from this that the 2-quinolyl derivatives (compounds of the A type), in contrast to the isomeric 4-quinolyl derivatives (B), are not coplanar.

This is in agreement with the conclusions that follow from allowance for the electrostatic forces that act between the fragments of a polynuclear molecule. In view of the electrostatic interactions between the electron-surplus nitrogen atom of the benzoquinoline ring and the quinolyl substituents, the 4-quinolyl group is in the most favorable stereochemical position, whereas the 2-quinolyl group, on the other hand, deviates from the plane of the molecule [5].

In addition to the $[M - 130]^+$ ion peaks typical for compounds of group A, the mass spectra of the 6-quinolyl derivatives (C) also contain low-intensity peaks of $[M - R]^+$ ions, which are most characteristic for compounds of the B type (Table 1 and Fig. 1). Consequently, both fragmentation pathways are possible for 1-aryl(hetaryl)-3-(6-quinolyl)benzo[f]-quinolines (C).

On the basis of the mass-spectrometric data obtained it may be concluded that the character of the fragmentation of the investigated polynuclear benzo[f]quinoline derivatives under the influence of electron impact is determined to a considerable extent by the geometry of the molecule and the spatial orientation of the substituents. The conjugation between the benzoquinoline ring and the quinoline substituent in the 3 position and, consequently, the coplanarity of the polyheterocyclic system in the investigated types of compounds, increase for the substituents under discussion in the order 2-quinolyl < 6-quinolyl < 4-quinolyl.

The calculation of the stabilities with respect to electron impact shows that compounds of the A type are the least stable. The W_M values for the 6-quinolyl derivatives (C) somewhat exceed the corresponding values for the 4-quinolyl isomers (B) (Table 1). This is explained by the fact that an electron deficit is created in the 1 position of the benzoquinoline ring under the influence of the electron-acceptor nitrogen atom of the 4-quinolyl substituent, as a consequence of which the bond with substituent R is weakened. At the same time, the 6-quinolyl group does not display an electron-acceptor effect, since the 6 position is formally the meta position with respect to the nitrogen atom [6].

As we have already noted, the fragmentation of polynuclear benzo[f]quinoline derivatives under the influence of electron impact proceeds via a common scheme within the limits of each of the examined groups (A, B, and C). Substituent R in the 1 position of the benzoquinoline ring does not have a substantial effect on the principal pathways of fragmentation of the investigated compounds, since this substituent is in a sterically hindered position [7], and its conjugation with the benzoquinoline ring is low.

The presence of a methyl group or substituents in the phenyl ring provides an additional fragmentation pathway (Tables 2 and 3). The detachment of these substituents is in agreement with the usual mass-spectral behavior of substituted aromatic compounds.

In addition to the ion peaks described above, $[M - 2]^+$ and $[M - 3]^+$ ion peaks that are often of high intensity and are associated with the successive elimination of two and three hydrogen atoms are observed in the mass spectra of the investigated compounds. It should be noted that peaks of doubly charged fragments that are formed from the doubly charged molecular ion are present in many mass spectra. It is interesting that the elimination of HCN that is characteristic for nitrogen-containing aromatic compounds takes place more intensively from the doubly charged ions.

Thus we have established that cleavage of the bonds between the benzoquinoline ring and the substituents (α cleavage) occurs under the influence of ionizing electrons on compounds of the 1-R-3-hetarylbenzo[f]quinoline series and that steric factors have a decisive effect on the strength of these bonds. The observed dependence of the intensity of the fragment ions on the spatial orientation of the substituents in the molecule can be used to establish the structures of new polynuclear benzo[f]quinoline derivatives.

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-311 spectrometer under the following conditions: the cathode emission current was 1.0 mA, and the ionizing-electron energy was 70 eV. The samples were introduced directly into the ion source of the mass spectrometer. The vaporization temperature of the samples was 150-200°C, and the ion-source temperature was 200°C. The benzo[f]quinolines were synthesized by the method in [8].

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CYCLOADDITION TO AMINOMETHYLENE DERIVATIVES OF 1-PHENYL-3-METHYLPYRAZOLE-5-THIONE AND 1-PHENYL-3-METHYLPYRAZOLE-5-SELENONE

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UDC 547.722.81

Addition products — anhydrides of 1-phenyl-3-methyl-4-alkylamino-4,5,6-tetrahydrothio(seleno)pyrano-3,2-pyrazole-5,6-dicarboxylic acids — were obtained by cycloaddition of maleic anhydride to aminomethylene derivatives of 1-phenyl-3-methylpyrazole-5-thione and 1-phenyl-3-methylpyrazole-5-selenone, while anhydrides of the corresponding dihydrothio(seleno)pyranopyrazoledicarboxylic acids were obtained by splitting out of an amine. The oxygen-containing analog does not undergo cycloaddition. An oxanol dye is formed from 1-phenyl-3-methyl-4-dimethylaminomethylene-5-pyrazolone, whereas the corresponding acyl derivative was isolated from the monomethyl derivatives.

In a continuation of our research on cycloaddition to aminomethylene derivatives of heterocyclic types [1, 2] we subjected maleic anhydride to reaction with monosubstituted derivatives of 1-phenyl-3-methyl-5-pyrazolone (Ia) and its sulfur (Ib) and selenium (Ic) analogs.

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 527-529, April, 1979. Original article submitted December 21, 1977; revision submitted October 30, 1978.

0009-3122/79/1504-0429$07.50