MASS SPECTRA OF PYRROLO [1,2-a]BENZIMIDAZOLE AND IMIDAZO[1,2-a]BENZIMIDAZOLE DERIVATIVES

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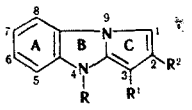
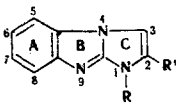
The closeness of the electronic structures of the ions formed in the first act of disintegration of the ions is responsible for the monotypic character of the subsequent fragmentation of pyrrolo[1,2-a]benzimidazole and imidazo[1,2-a]benzimidazole derivatives. The mass-spectrometric disintegration of the investigated systems has something in common with the fragmentation of thiazolo[3,2-a]benzimidazole derivatives.

We have previously studied the principles of fragmentation of thiazolo[3,2-a]benzimidazole derivatives [1] and established that the fragmentation of the molecular ions for these compounds is realized primarily through cleavage of the bonds in the thiazole ring with subsequent localization of the charge either on the common nitrogen atom or on the sulfur atom.

In order to study the peculiarities that replacement of the heteroatom in one of the rings introduces in the fragmentation of the systems above, we investigated the mass spectra of a number of pyrrolo[1,2-a] benzimidazole (I-IV) and imidazo[1,2-a]benzimidazole (V-VIII) derivatives, the synthesis of which was described in [2-4]. The spectral data obtained are presented in Table 1.



I-IV



V-VIII

I $R=CH_3$, $R^1=H$, $R^2=C_6H_5$, II $R=R^1=CH_3$, $R^2=C_6H_5$; III $R=CH_3$, $R^1=H$, $R^2=C_6H_5$; IV $R=CH_2C_6H_5$, $R^1=H$, $R^2=C_6H_5$; V $R=H$, $R^1=C_6H_5$; VI $R=CH_3$, $R^1=C_6H_5$; VII $R=C_6H_5$, $R^1=CH_3$; VIII $R=R^1=C_6H_5$

Just as in the case of the previously studied triazolobenzimidazoles, compounds of both classes have high stabilities with respect to electron impact (W_M values higher than 30%), and this is explained by their high aromaticity.

A characteristic feature of the fragmentation of the investigated substances is the case of elimination of an R radical from the molecular ion. The advantageousness of this process is evidently explained by the stabilities of the resulting structures A and B, the charge in which is localized on the common nitrogen atom. The great similarity in the electronic structures of A and B is responsible for the monotypic character of their subsequent fragmentation. As a result of this, identical characteristic ions appear in the spectra of both groups of compounds.

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TABLE 1. Mass-Spectral Data for the Compounds Obtained*

I 40 (5,1), 41 (6,7), 42 (3,6), 43 (7,6), 51 (1,4), 55 (2,2), 56 (8,1), 57 (2,1), 71 (1), 77 (4,5), 78 (3,4), 81 (1), 91 (1,3), 102 (6,6), 103 (2,7), 115 (2,1), 118 (1,2), 122 (1,2), 127 (1,2), 128 (1,7), 129 (7,3), 149 (1,1), 200 (1), 202 (1,5), 203 (1,3), 204 (1,3), 229 (3,6), 230 (3,7), 231 (14,9), 232 (5,5), 244 (2,4), 245 (7,5), 246 (100), 247 (20,9), 248 (2,1).

II 49 (1), 50 (1,2), 62 (1), 64 (1), 74 (1), 75 (1,1), 76 (2,4), 77 (3,5), 89 (1), 91(1), 92 (1), 102 (2,3), 103 (1), 109 (1), 115 (3,2), 116 (2), 117 (2,4), 140 (1), 149 (1,3), 157 (1,1), 168 (1,3), 169 (1,2), 183 (2,4), 218 (1,2), 242 (3), 243 (8,9), 244 (6,8), 245 (15,6), 246 (3,3), 257 (2,5), 258 (5,8), 259 (49,4), 260 (100), 261 (20), 262 (2,2).

III 41 (1), 58 (2,5), 65 (1), 71 (1), 77 (1), 91 (14,5), 92 (1,5), 102 (2,5), 103 (1), 115 (1,5), 129 (2), 142 (1), 167 (1), 168 (7), 169 (100), 170 (15,5), 171 (1), 245 (1), 257 (1), 258 (1), 259 (3,5), 260 (69), 261 (15,5), 262 (2,5).

IV 65 (1,4), 77 (1,4), 91 (19), 92 (2), 102 (2,8), 103 (1,9), 115 (1), 128 (1,2), 129 (6,3), 204 (1,0), 231 (100), 232 (28,8), 233 (3,4), 321 (18,2), 322 (76,3), 323 (21,2), 324 (3,2).

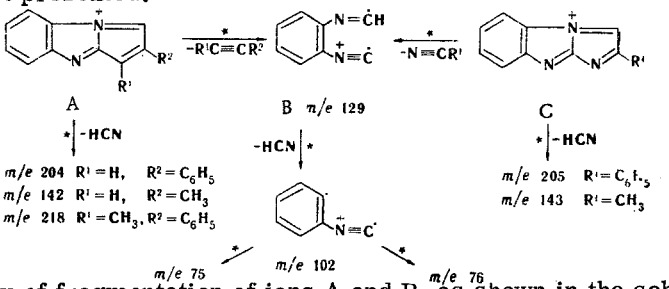
V 43 (1,1), 45 (1), 53 (1), 76 (2,1), 77 (3,2), 89 (2,3), 90 (2,8), 91 (1,2), 102 (5,1), 103 (10,4), 104 (3,8), 129 (5,1), 130 (1,3), 179 (1,7), 205 (4,7), 206 (2,3), 207 (1,3), 230 (1,1), 231 (3,6), 232 (12,3), 233 (100), 234 (25,5), 235 (3).

VI 45 (1), 77 (1,9), 102 (4,8), 103 (1,2), 104 (1,8), 117 (1,7), 118 (2,7), 129 (9,2), 130 (1,2), 170 (1), 205 (2), 206 (1), 231 (1,5), 232 (12,5), 233 (2,5), 245 (1,7), 246 (6,3), 247 (100), 248 (19), 249 (1,9).

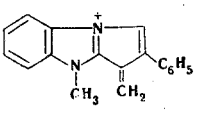
VII 51 (1,2), 76 (2), 77 (9,1), 78 (1,2), 90 (2,3), 91 (1,1), 92 (1,1), 102 (4,8), 103 (4,3), 104 (2,2), 115 (2,5), 116 (2), 117 (3,1), 118 (5,3), 128 (1,4), 129 (5), 130 (2), 132 (1,1), 142 (1,0), 143 (5,2), 144 (6,4), 170 (9,1), 171 (1,4), 178 (1,1), 179 (1,5), 205 (1,8), 206 (2,1), 207 (2,7), 208 (1,2), 219 (2,7), 220 (1,4), 232 (1,1), 245 (9,1), 246 (63,6), 247 (100), 248 (8,9), 249 (1,8).

VIII 72 (1,8), 102 (1,3), 103 (2,3), 129 (1,8), 165 (1,3), 178 (1,5), 179 (1,3), 180 (2,6), 205 (4,1), 206 (1,8), 207 (1), 232 (1,5), 281 (1), 307 (18,4), 308 (66,3), 309 (100), 310 (24,2), 311 (3,1).

*The relative intensities of the ion peaks with m/e values higher than 39 are indicated. The peaks with intensities lower than 1% are not presented.



The principal pathway of fragmentation of ions A and B, as shown in the scheme above, is cleavage of the bonds in the pyrrole and imidazole rings with elimination of $R^1C = CR^2$ and $N \equiv CR^1$, respectively. The composition of ion C formed in this case and of the other ions observed was established on the basis of data from the high-resolution spectra of I and V. Ion C and the products of its fragmentation were characterized for the spectra of the previously investigated thiazolo[3,2-a]benzimidazole derivatives [1], and cleavage of the bonds in the thiazole ring, which leads to the formation of ion C, was the most advantageous fragmentation process for thiazolobenzimidazoles. Thus the spectra of the investigated imidazobenzimidazoles and pyrrolobenzimidazoles are characterized by a common fragmentation pathway. In addition to the formation of ion C, elimination of HCN is peculiar to the fragmentation of A and B.



Elimination of a hydrogen atom from the molecular ion to give stable structure D is observed when a methyl group is introduced in the 3 position of II.

Splitting out of H evidently occurs from the CH_3 group in the 3 position rather than in the 4 position, inasmuch as the $[M-H^{\cdot}]^+$ ion peak is absent in the spectrum of I. This pathway of fragmentation of the molecular ion of II is predominant and appreciably suppresses fragmentation to give ions A and C . The ion peak of structure A is observed in the spectrum of II, but its intensity is considerably lower than the intensity of ion D.

The presence of a nitrogen atom in the C ring in imidazobenzimidazole derivatives V-VIII creates the possibility of charge localization on this atom. Relatively intense peaks of $RN^+ \equiv CR^1$ (m/e 118, R = CH_3, R^1 = C_6H_5, R = C_6H_5, R^1 = CH_3; m/e 180 R = R^1 = C_6H_5) and $N \equiv C-C_6H_5^+$ fragments therefore appear in addition to ions B and C and the products of their fragmentation in the spectra of V–VIII. When a phenyl

group is introduced, considerable formation of the phenyl cation is observed only for N-phenyl-substituted compounds, while cleavage of the 2-3 and 1-10 bonds to give the $C_6H_5C \equiv \overset{+}{N}R$ ion is preferable for the C-phenyl derivatives (V, VI) by virtue of conjugation of the phenyl group with the imidazole ring.

In the case of 1,2-diphenylimidazobenzimidazole (VIII) both fragmentation pathways are realized, and both $[M-C_6H_5^{\cdot}]^+$ and $C_6H_5^{+\cdot}$ and $C_6H_5C \equiv \overset{+}{N}C_6H_5$ ions are observed in the spectrum. In addition, the ion peak with m/e 165 characteristic for diphenyl-substituted imidazoles is present. The most intense peak among the fragment ions in the spectrum of VIII is affiliated with $[M-H\cdot]^+$. The mechanism of detachment of hydrogen from the molecular ion was not investigated, but an examination of the literature data on the spectra of diphenyl-substituted imidazoles [5] provides a basis to suppose that H· is eliminated from the phenyl groups, and the high intensity of the $[M-H\cdot]^+$ ion peak compels one to assume that the resulting ion has an extremely stable structure.

Thus the fragmentations of pyrrolo- and imidazobenzimidazoles have something in common because of the advantageouness of the sort of fragmentation of the molecular ions in which fragments of similar electronic structures with charge localization on the common nitrogen atom are formed. The subsequent fragmentation of these ions proceeds primarily with cleavage of the bonds in the pyrrole and, correspondingly, imidazole rings. The fragments formed in this case are analogous to the ion observed in the spectra of the previously investigated thiazolo[3,2-a]benzimidazoles. The presence of a nitrogen atom in the C ring in the imidazobenzimidazoles leads to the appearance in the spectra of ions with charge localization on this atom, similar to the sulfur-containing fragments in the spectra of thiazolobenzimidazoles. Thus, all of the investigated three-ring systems with a common nitrogen atom – pyrrolo[1,2-a]benzimidazoles, imidazo[1,2-a]benzimidazoles, and thiazolo[3,2-a]benzimidazoles – have mass-spectrometric fragmentations with something in common as a consequence of primary cleavage of the bond in the C ring.

EXPERIMENTAL METHOD

The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the source. The ionizing-electron energy was 50 eV, the emission current was 75 mA, and the temperature of the ionization chamber was 125°. The high-resolution spectra were recorded with a JMC-01 (SG-2) spectrometer, for which the authors thank Zh. K. Torosyan and V. A. Zamureenko.

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