MASS-SPECTROMETRIC STUDY OF 4-AZAPHENANTHRENE DERIVATIVES

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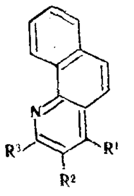
UDC 543.51:547.836.3

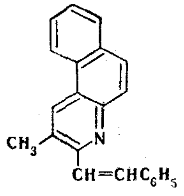
The mass spectra of 15 compounds of the 4-azaphenanthrene series and their deutero analogs with bulky R substituents (R = $-C{\equiv}CPh$, $-CH{=}CHPh$, $CHBr{-}CHBrPh$, $-CH{=}CHC_6H_4OCH_3$-p, $-COOH$, $-COOC_2H_5$, and $-CONHNH_2$) in the ortho position relative to the nitrogen atom were studied. An intense $[M - H]^+$ ion peak, the appearance of which is evidently due to a process involving cyclization of the carbon atom of the side chain with the nitrogen atom, is formed in the fragmentation of the styryl derivatives. The fragmentation of the compounds with a methyl group in the ortho position relative to the styryl grouping is accompanied by the formation of an intense $[M - Ph]^+$ ion peak. An "ortho effect" of the carboxyl and carbethoxy groups adjacent to the methyl substituent is observed in the mass spectra of the investigated compounds. The data obtained make it possible to establish the structures of bulky substituents in the ortho position relative to the ring nitrogen atom and the position of the methyl group in the pyridine ring of monomethylated azaphenanthrenes.

The mass-spectral behavior of 4-azaphenanthrenes containing methyl groups in the pyridine ring and their nitration products has been previously examined [1]. In the present research we studied the dissociative ionization of 4-azaphenanthrene derivatives I-VI and VII-XVI and 3-methyl-2-styryl-1-azaphenanthrene VI, a characteristic peculiarity of which is the presence of a bulky substituent in the ortho position relative to the nitrogen atom.

Except for dibromo derivative VIII, the mass spectra of the investigated compounds contain intense molecular-ion peaks (Table 1). The stability of the M^+ ions (W_M [2]) varies as a function of the character of the bulky substituent; the highest W_M values are observed for I and II, which contain a phenylethynyl group in the 3 position. The presence of styryl (III-VII), carboxy (IX-XII), carbethoxy (XIII), and hydrazido (XIV, XV) groupings lowers the W_M values by a factor of two to four, whereas in the case of VIII, which is the product of bromination of IV, the W_M value decreases by a factor of almost 15 as compared with the mass spectrum of IV. The W_M value in the mass spectrum of 1-azaphenanthrene derivative VI is higher by a factor of 1.3 as compared with the W_M value for the isomeric 4-azaphenanthrene V.



I-V, VII-XV



VI

I $R^1{=}CH_3$, $R^2{=}H$, $R^3{=}C{\equiv}CPh$; II $R^1{=}R^2{=}CH_3$, $R^3{=}C{\equiv}C{-}Ph$; III $R^1{=}CH_3$, $R^2{=}H$, $R^3{=}CH{=}CH{-}Ph$; IV $R^1{=}R^2{=}CH_3$, $R^3{=}CH{=}CHPh$; V $R^1{=}H$, $R^2{=}CH_3$, $R^3{=}CH{=}CHPh$; VII $R^1{=}CH_3$, $R^2{=}H$, $R^3{=}CH{=}CH{-}C_6H_4OCH_3$-p; VIII $R^1{=}R^2{=}CH_3$, $R^3{=}CHBr{-}CHBr{-}Ph$; IX $R^1{=}H$, $R^2{=}CH_3$, $R^3{=}COOH$; X $R^1{=}H$, $R^2{=}CH_3$, $R^3{=}COOD$; XI $R^1{=}CH_3$, $R^2{=}H$, $R^3{=}COOH$; XII $R^1{=}R^2{=}CH_3$, $R^3{=}COOH$; XIII $R^1{=}CH_3$, $R^2{=}H$, $R^3{=}COOC_2H_5$; XIV $R^1{=}CH_3$, $R^2{=}H$, $R^3{=}CONHNH_2$; XV $R^1{=}CH_3$, $R^2{=}H$, $R^3{=}CONDND_2$

The formation of the principal fragments in the high- and medium-mass regions in the dissociative ionization of the molecular ion of I can be represented by Scheme I. The appearance of $[M - nH]^+$ ions, where n = 1-5, and of the intense doubly charged M^{2+} ion (12%)

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TABLE 1. Mass Spectra of 4-Azaphenanthrenes I-XV and Stabilities (W_M) of Their Molecular Ions

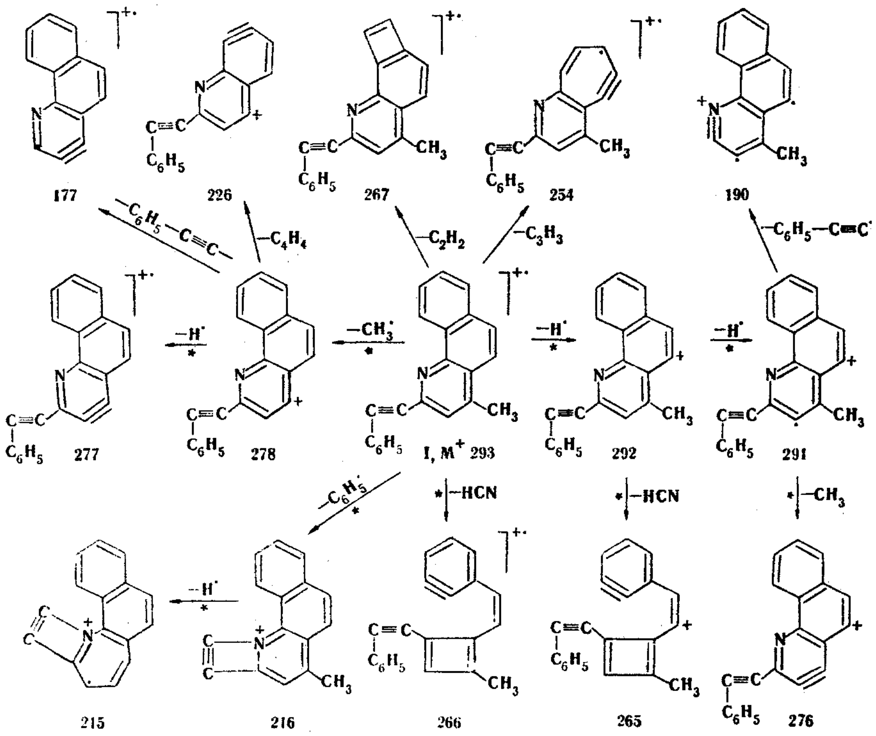
Compound	m/e values (relative intensities of the ion peaks, %)
1	2
I	295 (4,0), 294 (26), 293 (100), 292 (7,0), 291 (11), 290 (5,0), 289 (3,5), 288 (1,0), 279 (1,0), 278 (2,5), 277 (2,4), 276 (1,5), 275 (1,0), 267 (0,5), 266 (1,3), 265 (2,5), 264 (1,7), 263 (2,3), 252 (1,0), 240 (0,8), 239 (1,0), 238 (0,5), 226 (0,7), 216 (1,0), 215 (0,9), 214 (1,0), 191 (1,0), 190 (2,2), 189 (1,0), 177 (1,0), 166 (1,0), 165 (3,0), 164 (1,7), 163 (1,9), 152 (0,6), 151 (1,0), 150 (1,5), 140 (1,4), 139 (4,0), 138 (1,5), 127 (2,0), 126 (2,0), 125 (1,0), 115 (1,0), 77 (1,0), 76 (0,6), 63 (0,6), 51 (0,6), $W_M=57$
II	309 (5,0), 308 (28), 307 (100), 306 (22), 305 (9,0), 304 (9,5), 303 (2,2), 302 (2,0), 293 (2,7), 292 (11), 291 (9,5), 290 (4,0), 289 (1,6), 281 (1,7), 280 (1,0), 279 (1,0), 278 (2,0), 277 (1,8), 276 (1,0), 267 (0,8), 266 (1,0), 265 (1,4), 264 (1,0), 263 (1,2), 252 (0,5), 232 (1,5), 230 (1,8), 228 (1,7), 215 (0,7), 204 (0,5), 203 (0,6), 190 (1,7), 179 (1,0), 178 (2,5), 177 (1,0), 176 (1,8), 165 (1,5), 164 (0,8), 163 (1,7), 140 (2,0), 139 (4,0), 138 (1,5), 137 (1,8), 127 (1,8), 126 (2,0), 125 (1,0), 115 (1,9), 77 (1,8), 76 (1,0), 63 (1,0), 51 (1,0), $W_M=43$
III	297 (2,0), 296 (16), 295 (75), 294 (100), 293 (7,0), 292 (7,0), 291 (3,5), 290 (2,0), 282 (1,0), 281 (9,0), 280 (55), 279 (7,0), 278 (5,0), 277 (2,0), 276 (1,1), 268 (1,0), 267 (1,2), 266 (1,0), 265 (1,4), 253 (1,1), 252 (2,0), 218 (2,0), 217 (1,3), 216 (1,0), 193 (4,5), 192 (4,0), 191 (3,7), 190 (3,0), 189 (1,0), 178 (1,5), 177 (1,9), 166 (2,8), 165 (6,8), 164 (1,5), 163 (2,0), 153 (1,4), 152 (2,8), 151 (1,8), 140 (1,2), 139 (13), 127 (2,5), 126 (3,0), 125 (1,0), 115 (2,9), 91 (1,0), 77 (2,0), 63 (0,8), 51 (1,0), $W_M=15$
IV	311 (2,0), 310 (24), 309 (100), 308 (77), 307 (8,0), 306 (3,5), 305 (1,1), 304 (1,7), 296 (1,0), 295 (10), 294 (47), 293 (10), 292 (5,5), 291 (4,0), 290 (2,0), 282 (1,0), 281 (2,0), 280 (2,2), 279 (4,0), 278 (2,0), 277 (2,1), 276 (1,0), 267 (1,0), 266 (1,2), 265 (1,5), 254 (0,7), 253 (0,8), 252 (1,5), 251 (0,5), 234 (1,7), 233 (17), 232 (83), 231 (7,5), 230 (5,5), 229 (1,3), 228 (1,7), 218 (1,5), 217 (10), 216 (2,0), 215 (1,8), 207 (1,7), 206 (2,4), 205 (1,0), 204 (1,9), 203 (1,6), 202 (1,3), 191 (2,0), 190 (2,8), 189 (1,5), 179 (1,3), 178 (3,0), 177 (2,0), 176 (2,0), 166 (2,0), 165 (3,0), 164 (1,5), 163 (1,8), 152 (5,0), 151 (3,0), 150 (1,5), 147 (10), 146 (9,0), 145 (2,0), 140 (3,5), 139 (9,0), 138 (1,6), 133 (1,9), 128 (1,3), 127 (2,6), 126 (2,5), 115 (3,0), 114 (1,0), 102 (1,4), 78 (1,8), 77 (3,0), 76 (1,3), 63 (1,7), 51 (2,0), $W_M=20$
V	297 (2,0), 296 (23), 295 (100), 294 (77), 293 (12), 292 (9,0), 291 (5,0), 290 (3,0), 289 (1,8), 282 (2,5), 281 (12), 280 (46), 279 (8,0), 278 (5,5), 277 (3,5), 276 (2,5), 268 (2,6), 267 (3,6), 266 (3,5), 265 (3,5), 264 (1,7), 263 (1,8), 254 (2,0), 253 (2,5), 252 (4,0), 251 (1,6), 250 (2,0), 232 (1,3), 231 (1,7), 230 (1,8), 229 (2,5), 220 (2,5), 219 (13), 218 (64), 217 (16), 216 (8,0), 215 (2,0), 214 (1,8), 193 (3,4), 192 (3,6), 191 (3,1), 190 (5,0), 189 (2,8), 180 (1,5), 179 (1,8), 178 (2,5), 177 (2,7), 176 (1,8), 167 (1,7), 166 (3,0), 165 (7,5), 164 (3,8), 163 (5,0), 153 (2,0), 152 (3,5), 151 (2,5), 150 (2,0), 149 (1,8), 148 (3,8), 147 (9,0), 146 (5,0), 145 (2,8), 140 (17), 139 (17), 138 (3,0), 134 (2,8), 133 (4,0), 132 (2,5), 128 (2,8), 127 (3,6), 126 (5,5), 125 (2,8), 115 (5,5), 114 (2,5), 113 (4,0), 112 (1,8), 78 (3,5), 77 (4,8), 63 (4,4), 51 (5,0), $W_M=14$
VI	297 (2,0), 296 (23), 295 (100), 294 (85), 293 (10), 292 (7,6), 291 (5,5), 290 (1,8), 282 (2,5), 281 (13), 280 (65), 279 (9,0), 278 (7,0), 277 (4,0), 268 (2,0), 267 (3,8), 266 (2,0), 265 (2,0), 254 (1,0), 253 (1,3), 252 (2,8), 251 (1,0), 250 (1,0), 220 (2,0), 219 (11), 218 (80), 217 (20), 216 (6,5), 193 (2,5), 192 (3,5), 191 (4,4), 190 (6,5), 189 (3,0), 188 (1,0), 178 (1,4), 177 (3,0), 176 (1,4), 167 (1,4), 166 (2,3), 165 (9,0), 164 (5,5), 163 (7,0), 153 (2,0), 152 (2,3), 151 (3,0), 150 (2,3), 140 (27), 139 (26), 123 (1,3), 122 (3,0), 121 (4,0), 120 (2,4), 115 (5,0), 114 (1,6), 113 (2,0), 102 (2,0), 78 (2,3), 77 (6,0), 76 (2,7), 75 (2,3), 63 (3,9), 51 (5,0), $W_M=17$
VII	327 (2,0), 326 (16), 325 (98), 324 (100), 323 (1,5), 322 (0,7), 221 (0,5), 312 (1,5), 311 (8,0), 310 (37), 309 (2,0), 308 (2,2), 298 (0,9), 297 (0,5), 296 (0,6), 295 (2,0), 294 (1,8), 293 (1,0), 292 (2,0), 283 (0,7), 282 (5,0), 281 (9,5), 280 (6,0), 279 (3,6), 278 (2,5), 277 (0,7), 270 (0,6), 269 (0,6), 268 (2,2), 267 (8,5), 266 (3,5), 265 (3,6), 264 (0,8), 255 (1,4), 254 (2,2), 253 (1,0), 252 (1,0), 242 (1,3), 241 (1,2), 240 (0,9), 239 (1,0), 228 (1,0), 218 (0,9), 217 (0,6), 216 (0,5), 215 (0,7), 194 (2,0), 193 (2,5), 192 (3,5), 191 (3,5), 189 (0,9), 180 (0,7), 179 (0,8), 178 (1,7), 177 (2,2), 176 (1,4), 166 (2,5), 165 (7,0), 164 (2,0), 163 (4,0), 162 (1,2), 161 (1,6), 155 (3,0), 154 (1,2), 153 (1,3), 152 (2,2), 151 (1,2), 150 (1,2), 149 (1,0), 147 (3,0), 146 (4,0), 145 (1,2), 141 (2,5), 140 (5,0), 139 (10), 138 (1,3), 137 (0,5), 136 (2,0), 135 (5,0), 134 (2,5), 133 (6,0), 132 (1,5), 128 (2,2), 127 (4,0), 126 (4,2), 121 (1,5), 120 (1,0), 115 (1,5), 114 (1,7), 113 (1,5), 102 (0,8), 101 (2,0), 89 (1,5), 78 (3,5), 77 (2,5), 76 (1,0), 75 (1,0), 71 (1,0), 69 (1,0), 63 (1,2), 51 (1,1), $W_M=20$

TABLE 1. (cont.)

Compound	m/e values (relative intensities of the ion peaks, %)
1	2
VIII	472 (1,5), 471 (5,7), 470 (13,5), 469 (12), 468 (24), 467 (6,0), 466 (12), 392 (3,0), 391 (21), 390 (93), 389 (38), 388 (100), 387 (14), 386 (12), 376 (1,0), 375 (1,7), 374 (4,0), 373 (1,6), 372 (4,0), 313 (1,8), 312 (9,0), 311 (2,8), 310 (15), 309 (63), 308 (81), 307 (8,0), 306 (6,5), 305 (2,2), 304 (3,0), 296 (2,0), 295 (6,0), 294 (31), 293 (13), 292 (8,5), 291 (6,0), 290 (3,0), 282 (1,8), 281 (1,8), 280 (1,9), 279 (3,5), 278 (3,0), 277 (1,4), 276 (1,7), 267 (1,4), 266 (2,0), 265 (2,2), 264 (1,9), 263 (1,8), 254 (1,8), 253 (1,7), 252 (1,8), 234 (2,0), 233 (8,0), 232 (48), 231 (10), 230 (8,0), 229 (3,0), 228 (2,9), 227 (1,4), 220 (2,3), 219 (3,0), 218 (2,8), 217 (5,5), 216 (3,0), 215 (2,2), 207 (1,0), 206 (2,3), 205 (1,6), 204 (2,5), 203 (2,5), 202 (1,3), 201 (1,8), 195 (1,8), 194 (1,5), 193 (1,3), 192 (1,6), 191 (3,0), 190 (3,6), 189 (1,6), 180 (1,2), 179 (1,9), 178 (3,4), 177 (2,3), 176 (2,2), 167 (1,1), 166 (1,5), 165 (3,0), 164 (1,8), 163 (2,5), 156 (2,5), 155 (2,5), 154 (9,0), 153 (2,7), 152 (5,0), 151 (4,0), 150 (2,0), 147 (6,5), 146 (15), 145 (2,7), 141 (1,8), 140 (2,8), 139 (6,5), 138 (2,0), 137 (1,3), 133 (2,0), 132 (1,2), 128 (1,8), 127 (2,6), 126 (3,0), 125 (1,8), 124 (1,0), 123 (1,7), 115 (3,0), 114 (1,4), 113 (1,3). 111 (3,0), 110 (1,3), 109 (1,8), 103 (1,6), 102 (1,8), 101 (1,7), 97 (4,0), 96 (1,5), 95 (2,5), 86 (4,0), 83 (4,0), 82 (5,5), 81 (2,5), 80 (5,6), 79 (2,5), 78 (2,0), 77 (3,0), 76 (1,4), 71 (5,5), 70 (2,5), 69 (4,0), 63 (3,0), 51 (3,0), $W_M=1,2$
IX	239 (0,9), 238 (5,0), 237 (52), 220 (1,4), 219 (4,5), 195 (1,4), 194 (13), 193 (100), 192 (24), 191 (83), 190 (26), 189 (1,8), 188 (1,7), 180 (0,9), 179 (1,0), 178 (1,1), 177 (3,5), 176 (1,1), 175 (0,8), 167 (1,8), 166 (5,0), 165 (23), 164 (8,0), 163 (10), 162 (1,2), 154 (0,9), 153 (2,7), 152 (3,6), 151 (3,3), 150 (2,5), 149 (0,9), 141 (1,3), 140 (5,0), 139 (8,5), 138 (1,6), 137 (1,6), 128 (1,3), 127 (2,0), 126 (2,7), 125 (1,8), 124 (1,1), 123 (0,7), 115 (2,2), 114 (1,3), 113 (2,2), 112 (1,0), 111 (1,5), 110 (0,8), 90 (1,0), 89 (3,0), 88 (1,8), 87 (3,2), 86 (2,2), 77 (2,9), 76 (3,6), 75 (5,0), 74 (3,1), 63 (5,0), 62 (3,4), 51 (5,0), $W_M=12$
X	239 (8,0), 238 (32), 237 (31), 220 (3,0), 219 (11), 195 (13), 194 (80), 193 (100), 192 (40), 191 (96), 190 (40), 189 (5,0), 188 (3,0), 178 (5,0), 177 (8,0), 176 (1,5), 167 (6,0), 166 (16), 165 (30), 164 (18), 163 (19), 162 (5,0), 153 (5,0), 152 (8,0), 151 (7,0), 141 (3,0), 140 (10), 139 (12), 138 (3,0), 137 (3,0), 127 (3,0), 126 (5,0), 125 (1,5), 115 (5,0), 114 (1,5), 113 (4,0), 100 (1,5), 99 (3,0), 88 (4,0), 86 (5,0), 85 (3,0), 77 (3,0), 76 (4,0), 75 (6,0), 74 (4,0), 63 (7,0), 64 (3,0), 51 (1,5), $W_M=13$
XI	238 (5,0), 237 (40), 195 (2,0), 194 (16), 193 (100), 192 (15), 191 (12), 190 (12), 178 (4,0), 177 (6,0), 167 (2,0), 166 (6,0), 165 (17), 164 (5,0), 163 (5,0), 162 (2,0), 154 (2,0), 153 (3,0), 152 (4,0), 151 (3,5), 150 (3,0), 141 (1,2), 140 (3,0), 139 (4,3), 138 (1,0), 128 (4,0), 127 (2,2), 126 (2,0), 125 (1,0), 115 (2,0), 101 (1,0), 77 (1,7), 76 (1,0), 75 (1,8), 63 (2,8), $W_M=16$
XII	253 (1,7), 252 (12), 251 (70), 249 (1,2), 235 (0,7), 234 (0,8), 233 (3,0), 225 (1,7), 224 (0,8), 223 (2,5), 222 (1,5), 209 (2,0), 208 (18), 207 (100), 206 (30), 205 (40), 204 (26), 203 (6,0), 202 (2,5), 201 (1,4), 194 (1,2), 193 (2,5), 192 (8,0), 191 (10), 190 (25), 189 (2,5), 188 (2,0), 180 (4,0), 177 (7,0), 176 (5,0), 175 (2,0), 167 (3,0), 166 (5,0), 165 (9,0), 164 (5,0), 163 (3,0), 162 (1,8), 154 (2,0), 153 (3,0), 152 (8,0), 151 (7,0), 150 (4,0), 149 (2,0), 141 (2,0), 140 (3,5), 139 (4,0), 138 (2,0), 137 (2,0), 123 (2,5), 122 (4,0), 121 (4,5), 120 (2,0), 115 (3,0). 114 (1,5), 113 (3.0). 103 (5,0), 102 (15). 101 (3,0), 100 (2,0). 99 (1,5), 90 (3,0), 89 (10), 88 (7,0), 87 (3,0), 86 (2,0), 77 (3,5), 76 (10), 75 (5,0), 74 (3,0), 69 (2,5), 68 (2,0), 65 (2,0), 64 (2,0), 63 (6,0), 62 (2,0), 51 (4,0), $W_M=15$
XIII	266 (3,0), 265 (18), 237 (0,7), 221 (0,6), 220 (1,5), 195 (1,4), 194 (19), 193 (100), 192 (11), 191 (6,0), 190 (8,0), 189 (0,6), 178 (1,8), 177 (4,0), 167 (0,6), 166 (3,0), 165 (13), 164 (2,0), 163 (2,0), 153 (1,4), 152 (2,6), 151 (1,4), 150 (1,3), 140 (1,4), 139 (1,6), 128 (1,4), 127 (1,2), 126 (1,0), 115 (1,0), 101 (0,6), 86 (1,4), 82 (1,4), 81 (0,6), 77 (0,9), 76 (0,8), 75 (1,0), 74 (0,6), 63 (0,8), 51 (0,9), $W_M=11$
XIV	253 (3,0), 252 (16), 251 (86), 236 (3,6), 223 (2,2), 222 (2,0), 221 (1,2), 220 (6,0), 205 (2,0), 195 (2,0), 194 (12), 193 (76), 192 (100), 191 (18), 190 (20), 178 (4,0), 177 (12), 166 (11), 165 (34), 164 (8,0), 163 (8,0), 153 (5,0), 152 (10), 151 (4,0), 150 (4,0), 141 (2,0), 140 (4,0), 139 (5,0), 138 (2,0), 128 (4,0), 127 (3,0), 126 (2,0), 115 (4,0), 96 (4,0), 89 (2,0), 87 (2,0), 83 (3,2), 82 (3,0), 77 (3,0), 76 (2,5), 75 (2,2), 63 (5,0), 51 (3,0), $W_M=18$
XV	255 (5,0), 254 (26), 253 (36), 252 (22), 251 (5,0), 238 (2,0), 237 (5,0), 235 (2,0), 220 (4,0), 205 (3,0), 195 (12), 194 (50), 193 (46), 192 (100), 191 (18), 190 (20), 177 (12), 176 (2,5), 167 (3,0), 166 (8,0), 165 (36), 164 (8,0), 163 (7,0), 153 (7,0), 152 (9,0), 151 (4,0), 150 (4,0), 149 (4,0), 141 (5,0), 140 (4,0), 139 (4,0), 128 (3,0), 127 (4,0), 126 (3,0), 115 (4,0), 97 (4,0), 83 (4,0), 77 (2,0), 76 (2,0), 75 (3,0), 74 (4,0), $W_M=20$

is characteristic for polynuclear heteroaromatic compounds [3], and this confirms the condensed structure of I. In the first stage of the fragmentation of I, in addition to the splitting out of an H atom, CH_3, C_3H_3, and Ph radicals and HCN and C_2H_2 molecules are ejected. In the second stage one also observes the loss of neutral C_4H_4 and Ph—C≡C fragments. The appearance of the $[M - Ph]^+$ ion can be explained by the detachment of a phenyl radical from the side chain with subsequent connection of its β-carbon atom to the nitrogen atom; this is characteristic for the dissociative ionization of o-substituted pyridines [4-7]. The presence of a second methyl group in II leads to the development of new fragmentation pathways as compared with I, as a result of which $[M - 2CH_3]^+$ and $[M - CH_3, - Ph]^+$ fragments are formed.

Scheme 1



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*The numbers under the formulas are the ion mass-to-charge ratios (m/e).

The presence of a styryl substituent in III-VII and of a dibromophenyl grouping in VIII markedly increases the intensity of the $[M - H]^+$ ion. A similar fact was previously observed in the mass spectra of 2-styrylpyridine [8] and its derivatives [9]. Johnstone and Ward [8] and El Khadem and co-workers [9] explained this fact by the formation of a stable azaphenanthrene cation, which is formed as a result of cyclization of β-carbon atom of the phenyl group with the nitrogen atom. However, an intense $[M - H]^+$ ion peak is also observed in the fragmentation of VIII, in which a stable cation is not formed. The $[M - H]^+$ fragment in the mass spectra of III-VIII is probably formed as a result of the elimination of hydrogen from the β-carbon atom of the side chain with connection of the latter to the nitrogen atom of the azaphenanthrene ring (Scheme 2). This process, which leads to the development of a four-membered ring, also explains the appearance of the $[M - Ph]^+$ ion in the mass spectra of III-VII. The relative intensity of the $[M - Ph]^+$ ion peak is particularly high in the mass spectra of IV-VI, in which there is a methyl group in the ortho position relative to the styryl grouping. Steric interaction of the latter with the bulky substituent evidently leads to reorientation of the phenyl group from the trans to the cis position relative to the pyridine ring* with its subsequent detachment due to cyclization. A similar mechanism is evidently also responsible for the appearance of the maximally intense $[M - Br]^+$ fragment in the mass spectrum of VIII.

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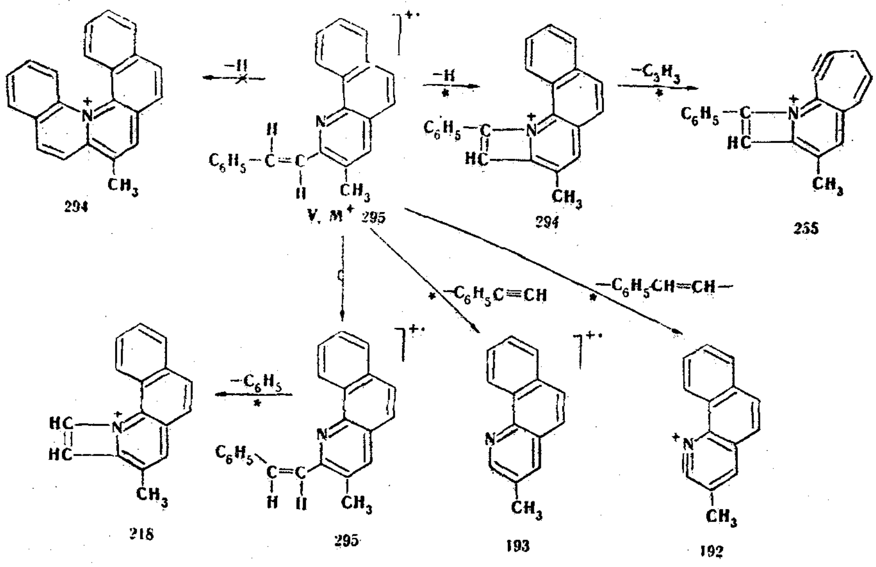
*According to the PMR spectral data, the pyridine ring in the III-VII molecules is trans-oriented with respect to the phenyl group.

Scheme 2



A characteristic feature of the dissociative ionization of styryl-substituted azaphenanthrenes III-VII is also the formation of an intense $[M - CH_3]^+$ ion and $[M - Ph - C\equiv CH]^+$ and $[M - Ph - CH = CH]^+$ fragments. The latter develop as a result of detachment of a bulky substituent directly from the molecular ions with and without transfer of one hydrogen atom to the principal part of the molecule. The high-resolution mass-spectral data for III and V-VII (with precise masses 193.0921 and 192.0827 and empirical formulas $C_{14}H_{11}N$ and $C_{14}H_{10}N$) and the presence of metastable ions ($m^* = 126.3$ and $m^* = 125$) confirm the pathway for the formation of the indicated fragments (Scheme 2). It is interesting to note that an $[M - Ph, - CH_3]^+$ ion, which is also formed in the mass spectrum of VIII from the $[M - 2Br, - Ph]^+$ fragment, is observed in the fragmentation of IV. Its appearance is due to steric interaction of the two adjacent methyl groups, since this fragment is not formed in the case of the dissociative ionization of III, V, and VI, which contain one methyl group in the pyridine ring of the azaphenanthrene ring.

The presence of a p-methoxy group in the phenyl ring in the side chain of VII increases the relative intensity of the $[M - CH_3]^+$ ion peak, and this constitutes evidence for partial elimination of a methyl group from the methoxy substituent. The appearance of an $[M - CH_3, - CO]^+$ fragment in the mass spectrum is a consequence of this process. The presence of a CH_3O group in VII is also responsible for the formation of the $[M - CH_2O]^+$ ion that is characteristic for the dissociative ionization of anisoles [10].

As in the case of o-substituted pyridine-2-carboxylic acids [11, 12], the principle pathway of fragmentation of 4-azaphenanthrenes IX-XIII, which contain a carboxy or carbethoxy substituent in the ortho position relative to the nitrogen atom, is splitting out of this substituent to give rearranged $[M - CO_2]^+$ and $[M - C_2H_4OCO]^+$ ions (for IX-XII and XIII, respectively), as well as $[M - COOH]^+$ and $[M - C_2H_5OCO]^+$ fragments. In addition, the indicated process is accompanied by the appearance of $[M - HCOOH]^+$ and $[M - C_2H_5COOH]^+$ ions, the intensities of the peaks of which increase significantly when there is a CH_3 group in the ortho position relative to the bulky substituent. Consequently, their formation is associated with the migration of a hydrogen atom from the methyl group to the carbonyl or carbethoxy radical at the instant of its detachment. This process is due to the "ortho effect" of substituents and makes it possible to establish the position of the methyl group in the pyridine ring of the 4-azaphenanthrene ring of IX, XI, and XIII. In the case of IX and XII, which also have a methyl group in the ortho position relative to the nitrogen atom, an $[M - H_2O]$ ion is also formed in their mass spectra. The fragmentation of deutero analog X confirms the pathways of the formation of the $[M - H_2O]^+$, $[M - CO_2]^+$, $[M - HCOO]^+$, and $[M - HCOOH]^+$ ions in the fragmentation of IX.

The principal pathway of dissociative ionization of hydrazide derivative XIV is the formation of rearranged $[M - NH_2{=}C{=}O]_{(A)}^+$ and fragment $[M - NH_2NHCO]_{(B)}^+$ ions. The relative intensity of the peak of the rearranged ion is lower than that of the fragment ion, in contrast to the corresponding ions in the mass spectra of IX-XIII. As in the case of the fragmentation of XI and XIII, which contain a methyl group in the meta position to a bulky substituent, the $[M - NH_2NHCHO]^+$ ion peak in the mass spectrum of XIV is of considerably lower intensity than the intensities of the peaks of the A and B fragments. A side pathway in the fragmentation of XIV consists in splitting out of CH_3 and $NHNH_2$ radicals by the M^+ ion to give fragments. The dissociative ionization of deutero derivative XV confirms the pathway for the formation of the A and B ions in the mass spectrum of XIV.

Thus the principal pathways in the fragmentation of substituted 4-azaphenanthrenes are determined by the nature of the bulky substituent in the ortho position relative to the nitrogen atom. This makes it possible to determine the structure of a given substituent and to establish the position of the methyl group in the pyridine ring of azaphenanthrenes containing a single methyl group.

EXPERIMENTAL

The mass spectra of I-XV were obtained with an MKh-1303 mass spectrometer with a system for direct introduction of the samples into the ion source at an ionizing voltage of 70 V and a temperature of 30°C. The high-resolution mass spectra of III and V-VII were measured with a JMS-01 SG-2 mass spectrometer with an automatic system for information processing. The compounds were synthesized and purified by the methods in [13, 14], while deutero analogs X and XV were obtained by refluxing 0.1 g of the substance in a tenfold excess of CH_3OD with subsequent recording of their mass spectra under conditions of deuterium exchange with CH_3OD vapors. The purity and individuality of the compounds were monitored by thin-layer chromatography and their IR, UV, and PMR spectra.

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