MASS SPECTROMETRIC STUDY OF LINEAR AND ANGULAR PYRROLODIBENZOFURANS, PYRROLODIBENZOTHIOPHENES, AND PYRROLOCARBAZOLES

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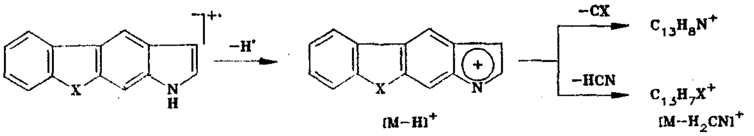
The analysis of the mass spectra of unsubstituted pyrrolodibenzofurans and α-carboxy- and α-carbethoxypyrrolodibenzofurans, α-carboxy- and α-carbethoxypyrrolodibenzothiophenes, and α-carbethoxypyrrolocarbazoles, in which the pyrrole ring is fused to faces a, b, or c, permits finding the differences in the relative intensities of the peaks of their fragmentary ions due to the presence of additional free reactions in these structures or different internal stabilization of the fragmentary ions. The mass spectral characteristics which make it possible to identify the type of fusion of the pyrrole ring by comparison of the mass spectra of pairs of isomers are reported.

We recently reported that the comparative analysis of the mass spectra of unsubstituted linear and angular pyrrolodibenzothiophenes permits determining the type of linkage of a pair of isomers in the presence of mass spectra [1]. In particular, it was found that the successive cleavage of a hydrogen atom and the HCN molecule is slightly more probable for molecular ions (M^+) of compounds with an angular structure than for M^+ of isomers with a linear type of linkage of the heterocyclic rings. It was interesting to determine whether this rule extends to the mass spectrometric behavior of analogous derivatives of benzofuran and indole and to establish the character of the mass spectral differences of their carboxy and carbethoxy derivatives which we recently synthesized [2-5].

The analysis of the values of the stability of M^+ (values of W_M,* Table 1) obtained from the mass spectra of isomeric linear and angular unsubstituted pyrrolodibenzofurans I-V (Table 2) shows that the type of linkage of the rings has almost no effect on the value of W_M, as in many sulfur compounds. Under the effect of electron impact, the M^+ of all compounds lose the hydrogen atom (primarily from the nitrogen atom†) with subsequent elimination of the HCN molecule, confirmed by the high-resolution mass spectrum (scheme 1). This permits stating that the positive charge is localized in the indole part of the molecule in the M^+ of compounds I-V.



The analysis of the relative intensities of the fragmentary ions permits noting that as in the series of sulfur analogs [1], loss of the hydrogen atom and subsequently the HCN molecule is slightly less probable for the angular isomers (the values of $I_{M^+}/I_{[M-H]^+}$ are higher, and $I_{[M-H]^+}/I_{[M-H_2CN]^+}$ are lower) than in the case of linearly constructed molecules.

The data from the mass spectra of carboxy- (a) and carbethoxy-substituted (b) isomeric pyrrolodibenzofurans I-V, pyrrolodibenzothiophenes VI-X, and pyrrolocarbazoles XI-XIV show

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*$W_M = \Sigma/M^+/\Sigma I\Phi_i \cdot 100$, i.e., it corresponds to the percentage fraction of the current of M^+ in the total ionic current [6].
†Confirmed by the mass spectra of N–D analogs.

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TABLE 1. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of Pyrrolodibenzofurans I-V (% Σ_{50})

Compound	Dibenzofuran	Type of linkage*	W_M	$I_M/I_{[M-H]^+}$	$I_{[M-H]^+}/I_{[M-H_2CN]^+}$
I	Pyrrolo[3,2-*a*]	<A	34,3	5,7	2,9
II	Pyrrolo[2,3-*b*]	‖A	34,0	6,2	2,3
III	Pyrrolo[2,3-*c*]	<B	35,5	5,7	3,8
IV	Pyrrolo[3,2-*c*]	≪B	34,7	5,2	3,4
V	Pyrrolo[3,2-*b*]	‖B	35,4	6,2	2,6

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*Here and below, the sign < indicates angular linkage, and the sign ‖ indicates a linear type of linkage. The sign ≪ indicates angular linkage with the pyrrole nitrogen atom in position 4 of the dibenzofuran fragment.

TABLE 2. Mass Spectra of Unsubstituted Pyrrolodibenzofurans I-V

Compound	Values of m/z* (relative intensity, %)
I	207 (100), 206 (15), 180 (7), 179 (5), 178 (4), 152 (10), 151 (10), 150 (6), 104 (25), 102 (3), 89 (16)
II	207 (100), 206 (16), 180 (12), 179 (5), 178 (5), 152 (14), 151 (12), 150 (8), 104 (24), 102 (2), 89 (14)
III	207 (100), 206 (16), 180 (6), 179 (5), 178 (4), 152 (12), 151 (10), 150 (8), 104 (30), 89 (10)
IV	207 (100), 206 (16), 180 (8), 179 (4), 178 (5), 152 (14), 151 (14), 151 (12), 150 (8), 149 (4), 104 (30), 89 (10)
V	207 (100), 206 (13), 180 (6), 179 (4), 178 (4), 152 (12), 151 (11), 150 (8), 126 (2), 104 (30), 89 (12)

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*The molecular ion and the ten most intense peaks are reported.

TABLE 3. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of Compounds I-III, V-IXa, and I-III, V-XIVb (% Σ_{50})

Compound	Name of basic heterocyclic nucleus	Heteroatom X	W_M	I_{Φ_1}/I_M	I_{Φ_1}/I_{Φ_2}	Type of linkage
Ia	Pyrrolo[3,2-a]dibenzofuran	O	11.1	1.45	0.56	< A
IIa	Pyrrolo[2,3-b]dibenzofuran	O	9.8	1.09	0.95	‖ A
Ib	Pyrrolo[3,2-a]dibenzofuran	O	11.0	2.26	0.34	< A
IIb	Pyrrolo[2,3-b]dibenzofuran	O	11.3	1.90	0.57	‖ A
IIIa	Pyrrolo[2,3-c]dibenzofuran	O	11.5	1.50	0.47	< B
Va	Pyrrolo[3,2-b]dibenzofuran	O	10.5	1.30	0.74	‖ B
IIIb	Pyrrolo[2,3-c]dibenzofuran	O	11.6	2.52	0.27	< B
Vb	Pyrrolo[3,2-b]dibenzofuran	O	12.2	1.97	0.45	‖ B
VIa	Pyrrolo[3,2-a]dibenzothiophene	S	11.6	1.32	0.35	< A
VIIa	Pyrrolo[2,3-b]dibenzothiophene	S	10.6	1.23	0.48	‖ A
Xb	Pyrrolo[2,3-a]dibenzothiophene	S	7.5	2.14	0.50	≪ A
VIb	Pyrrolo[3,2-a]dibenzothiophene	S	13.4	1.78	0.24	< A
VIIb	Pyrrolo[2,3-b]dibenzothiophene	S	13.6	1.58	0.31	‖ A
IXa	Pyrrolo[2,3-c]dibenzothiophene	S	12.2	1.30	0.39	< B
VIIIa	Pyrrolo[3,2-b]dibenzothiophene	S	11.3	1.10	0.50	‖ B
XIVb	Pyrrolo[3,2-c]dibenzothiophene	S	8.1	2.09	0.10	≪ B
IXb	Pyrrolo[2,3-c]dibenzothiophene	S	12.7	1.97	0.27	< B
VIIIb	Pyrrolo[3,2-b]dibenzothiophene	S	13.3	1.58	0.39	‖ B
XIb	Pyrrolo[2,3-a]carbazole	NH	6.8	2.00	0.72	≪ A
XIIIb	Pyrrolo[2,3-c]carbazole	NH	12.2	2.20	0.48	< B
XIIb	Pyrrolo[3,2-b]carbazole	NH	12.6	1.83	0.71	‖ B

that the heteroatom of the second heterocycle, the type of linkage of the heterocycles, and the character of the substituent in most cases have no significant effect on W_M, whose values range from 10 to 13% (Table 3). The values of W_M are significantly lower than the average values only in the case of angularly linked structures with the nitrogen atom in position 1 (compounds Xb and XIb) or 4 (compound XIVb) of the dibenzo heterocycle, and as in a series of

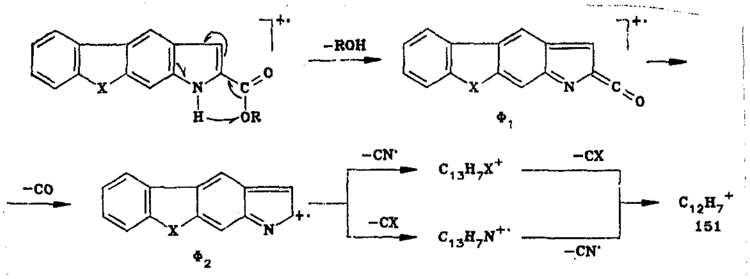
TABLE 4. Mass Spectra of Compounds Ia,b-IXa,b and Ib-XIVb

Compound	Values of m/z* (relative intensity, %)
Ia	251 (68), 233 (100), 207 (9), 205 (57), 204 (12), 179 (16), 177 (30), 150 (20), 117 (34), 103 (28), 75 (44)
IIa	251 (92), 233 (100), 207 (7), 205 (94), 204 (34), 179 (24), 177 (40), 176 (12), 150 (30), 117 (33), 75 (38)
IIIa	251 (68), 233 (100), 207 (6), 206 (12), 205 (48), 204 (10), 179 (18), 177 (32), 150 (24), 117 (40), 103 (14)
Va	251 (76), 233 (100), 207 (25), 204 (12), 179 (20), 177 (27), 176 (30), 150 (22), 117 (26), 103 (20), 75 (32)
VIa	267 (76), 249 (100), 223 (10), 222 (12), 221 (35), 220 (29), 195 (22), 177 (56), 150 (10), 125 (52), 111 (36)
VIIa	267 (78), 249 (100), 223 (10), 222 (14), 221 (48), 220 (28), 195 (22), 177 (50), 150 (10), 125 (34), 111 (54)
VIIIa	267 (86), 249 (100), 221 (50), 220 (35), 195 (29), 177 (82), 176 (21), 151 (13), 150 (22), 125 (25), 111 (43)
IXa	267 (76), 249 (100), 223 (11), 222 (10), 221 (40), 220 (26), 195 (21), 177 (52), 150 (10), 125 (54), 111 (52)
Ib	279 (84), 261 (8), 233 (100), 205 (33), 179 (20), 177 (17), 150 (13), 117 (8), 103 (8), 90 (24), 89 (17)
IIb	279 (52), 233 (100), 205 (56), 179 (34), 177 (21), 150 (20), 117 (8), 103 (10), 90 (28), 89 (12), 75 (5)
IIIb	279 (40), 233 (100), 205 (28), 179 (18), 177 (16), 150 (12), 117 (12), 103 (4), 90 (20), 89 (15), 75 (9)
Vb	279 (50), 267 (2), 261 (3), 233 (100), 205 (45), 179 (28), 177 (18), 150 (14), 117 (12), 90 (30), 89 (6)
VIb	295 (48), 249 (100), 223 (3), 222 (10), 221 (24), 220 (18), 195 (28), 177 (38), 150 (8), 125 (14), 111 (16)
VIIb	295 (46), 249 (100), 223 (3), 222 (12), 221 (32), 220 (20), 195 (32), 150 (8), 125 (6), 117 (40), 111 (6)
VIIIb	295 (65), 249 (100), 223 (3), 222 (12), 221 (40), 220 (20), 195 (34), 177 (38), 150 (8), 125 (13), 111 (12)
IXb	295 (54), 249 (100), 223 (4), 222 (10), 221 (25), 220 (16), 195 (26), 177 (36), 150 (8), 125 (16), 111 (12)
Xb	295 (46), 266 (8), 249 (100), 221 (50), 220 (16), 195 (28), 194 (3), 177 (41), 176 (4), 151 (7), 150 (8)
XIb	278 (50), 232 (100), 204 (72), 203 (22), 178 (31), 177 (37), 176 (14), 151 (9), 150 (11), 149 (13), 80 (47)
XIIb	278 (54), 232 (100), 204 (71), 203 (17), 178 (40), 177 (44), 176 (17), 151 (10), 150 (17), 149 (42), 80 (100)
XIIIb	278 (46), 232 (100), 204 (49), 203 (15), 178 (20), 177 (33), 176 (12), 151 (7), 150 (9), 149 (12), 80 (15)
XIVb	295 (47), 249 (100), 221 (40), 220 (19), 195 (28), 194 (6), 177 (66), 176 (15), 151 (11), 150 (17), 125 (10)

*The molecular ion and the ten most intense peaks are reported.

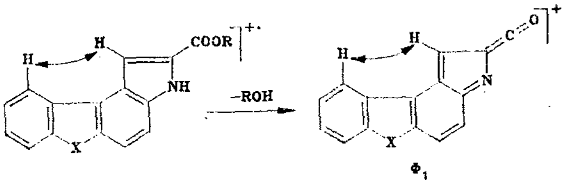
uncondensed five-member heterocycles [7], sulfur-containing compounds (Xb, XIVb) are slightly more resistant to electron impact than nitrogen-containing derivatives (XIb).

The processes of dissociative ionization of all of the carbonyl-containing compounds studied are of the same type and are characterized by loss of M^+ of the water molecule (in the case of acids Ia-IXa) or ethyl alcohol (for carbethoxy-substituted Ib-XIVb) with the formation of an ion of type Φ_1 (scheme 2), characteristic of 2-carboxy(carbethoxy)pyrroles and indoles [8-10]. The acyl cation Φ_1 formed in this way eliminates the CO molecule (ion Φ_2) which subsequently successively loses the CN and CX particles with the formation of a hydrocarbon ion with m/z of 151 ($C_{12}H_7^+$).



The analysis of the relative intensities of the fragmentary ions (Table 3) of the isomeric structures with a different mutual position of the heterocyclic rings permits concluding that the establishment of the type of linkage with the mass spectrum of only one of the isomers is not possible. At the same time, a comparixon of the values of I_{Φ_1}/I_{M^+} and I_{Φ_1}/I_{Φ_2} for the pairs of compounds which can be formed (and are actually formed) in the process of

Fischer cyclization of the corresponding hydrazones (cf. [1-5]) shows that in all cases, the values of I_{Φ_1}/I_{M^+} are higher and I_{Φ_1}/I_{Φ_2} are lower for "angular" (<) compounds than for linearly constructed compounds. This is probably due to the fact that in the case of angular structures, the additional free interactions which arise between the hydrogen atoms in positions 1 and 10 (scheme 3) in structures I and VI results in an increase in the internal energy of M^+, which facilitates the process of its decomposition and increases the probability of subsequent elimination of the CO molecule by ion Φ_1.



We note that in the case of compound Xb, which contains a NH group in position 1, the value of I_{Φ_1}/I_{Φ_2} is two times higher than in angular compound VIb, but with the NH group in position 3. A similar effect is also observed in the case of isomeric angular structures XIVb and IXb. In both cases, the elimination of the pyrrole nitrogen atom in the composition of the hydrogen atom ROH molecule apparently decreases the internal energy of the ion, which results in its stabilization.

The analysis of the relative intensities of the peaks of the fragmentary ions in the mass spectra of pairs of isomeric structures thus permits establishing the type of linkage of the heterocyclic nuclei in condensed heterocycles of the type investigated with sufficient confidence.

EXPERIMENTAL

The synthesis of all of the compounds studied is described in [2-5]. The mass spectra were made on a Finnigan-4200 instrument with an ionization energy of 70 eV. The metastable ions were recorded on a MX-1303 with an energy of 50 eV. The N-deuterium labeled compounds were prepared by three successive dissolutions and evaporations of the samples in CH_3OD.

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